HIGHER ETHERS AS REPLACEMENT OXYGENATES FOR METHYL TERTIARY BUTYL ETHER IN GASOLINE: SYNTHETIC AND ENVIRONMENTAL ASPECTS

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Jeff Snelling

Certificate of Approval:

Christopher R. Roberts
Professor
Chemical Engineering

Mark O. Barnett, Chair
Associate Professor
Civil Engineering

Joe M. Morgan
Associate Professor
Civil Engineering

Clifford R. Lange
Associate Professor
Civil Engineering

Dongye Zhao
Associate Professor
Civil Engineering

George T. Flowers
Interim Dean
Graduate School

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Jeff Snelling

A Dissertation

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Requirements for the

Degree of

Doctor of Philosophy

Auburn, Alabama
May 10, 2007

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Jeff Snelling

Signature of Author

Date of Graduation

DISSERTATION ABSTRACT

HIGHER ETHERS AS REPLACEMENT OXYGENATES FOR METHYL TERTIARY BUTYL ETHER IN GASOLINE: SYNTHETIC AND ENVIRONMENTAL ASPECTS

Jeff Snelling

Doctor of Philosophy, May 10, 2007
(M.S., Auburn University, 1998)
(B.Ch.E., Auburn University, 1995)
(M.S., University of Houston-Clear Lake, 1988)
(B.S., University of Houston-University Park, 1980)

290 Typed Pages

Directed by Mark O. Barnett

The use of oxygenates, particularly methyl tertiary butyl ether (MtBE), in reformulated gasoline has reduced the levels of carbon monoxide and unburned hydrocarbons in ambient air. However, the widespread contamination associated with MtBE use has prompted a search for replacement oxygenates. Among the alternatives are higher carbon ethers. Two ethers are of particular importance because they can be prepared from readily available petroleum refinery feedstocks. These two ethers are methyl tertiary hexyl ether (MtHxE) and methyl tertiary octyl ether (MtOcE). In order for the higher ethers to compete in the fuel oxygenates market, an economically feasible process for their production must be developed. It would be desirable to produce these ethers via the etherification of olefins with methanol derived from synthesis gas, with the synthesis gas in turn being derived from coal or biomass. An economic advantage would be provided if the olefins could be etherified directly with synthesis gas, without the isolation of the intermediate methanol. Chapter III reports a parametric study of the preparation of MtHxE and MtOcE from olefins and methanol, and identifies the optimum initial conditions for the development of a continuous process to produce these ethers from olefins and synthesis gas in a single-step etherification reactor.

The introduction of these ethers into fuel supplies guarantees their introduction into the environment as well. There are two main sources of these contaminants; direct emissions into the atmosphere from automobiles and releases from leaking underground fuel tanks. Therefore, two different models were employed to assess the associated risks. Chapter IV presents the results of atmospheric contaminant transport modeling studies, which indicate that these ethers are likely to contaminate air at about the same concentration as MtBE. Multimedia fate modeling studies suggest that atmospheric dispersion and deposition of these ethers is not likely to be ecotoxicologically relevant. On the other hand, these ethers are likely to be carcinogens, and humans could be exposed to unacceptable concentrations of these ethers in urban air. Groundwater contaminant transport modeling studies indicate that these ethers may contaminate community water supply wells at concentrations similar to those that are known to cause widespread public health concern for MtBE. The screening-level risk assessment presented in Chapter V suggests the need for a more rigorous risk assessment before these compounds are widely used to replace MtBE in gasoline.

ACKNOWLEDGEMENTS

First and foremost, the author wishes to thank Dr. Christine W. Curtis for her patience and guidance, and for co-authoring Chapter III along with Dr. YoonKook Park. The material in Chapter III was previously published by the author in *Fuel Processing Technology*, 2003, *83*, 219-234. The work in Chapter III was supported by a DOE grant, DE-FC26-99FT40540. Thanks is also due to Dr. Mark O. Barnett for co-authoring Chapters IV and V, and for serving as committee chair. Thanks is due to Dr. Dongye Zhao for co-authoring Chapters IV and V, and for serving as a committee member. Dr. J. Samuel Arey also co-authored Chapters IV and V. The material in Chapter IV was previously published by the author in the *Journal of the Air and Waste Management Association*, 2006, *56*, 1484-1492. The material in Chapter V has been accepted for publication by the journal *Environmental Toxicology and Chemistry*.

Thanks is also due to Drs. Joe M. Morgan, Clifford R. Lange and Christopher R. Roberts for serving as committee members, and to Dr. Robert B. Cook for serving as the outside reader. The author thanks Rebecca Moseley and Drs. Russell Seguin and Thomas F. Parkerton for reviewing the manuscripts. The author appreciates the assistance of Henry C. Cobb, Mike Hornsby, Doug Kilgour, Vijay Loganathan, Gordon K. Porter, Brian Schwieker, Jan Szechi and especially, Joseph M. Aderholdt.

Style manual used: Journal of the Air and Waste Management Association

Computer software used: Microsoft Office 2003

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CHAPTER I

INTRODUCTION

The blending of fuel oxygenates in gasoline raises combustion temperatures and improves engine efficiencies. The results are lower levels of carbon monoxide and unburned hydrocarbons in automobile exhaust emissions [1]. The United States Environmental Protection Agency (EPA) estimates that 97,441,000 tons of carbon monoxide and 8,529,000 tons of hydrocarbons were released into the atmosphere in the United States by mobile sources, principally automobile and truck exhaust, in 1999* [2]. These amounts represent 56% of the total carbon monoxide and 47% of the total hydrocarbons released. As point source emissions control steadily improves, transportation source emissions reduction will play an increasingly important role in air pollution prevention. Since efforts directed towards pollution prevention have always proven more successful than those directed at pollution remediation, research efforts directed towards improving the technology of producing cleaner-burning fuels will continue to play a vital role in atmospheric pollution prevention.

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* Latest year for which emissions inventory data were available at the time of the publication of this dissertation.

Emission standards imposed by the 1990 U.S. Clean Air Act Amendments were expected to require oxygenates in nearly 70% of the U.S. gasoline pool by the year 2000. However, due to environmental concerns, actual usage peaked at about 32% in the late 1990s [3], as discussed in more detail in Appendix A of this dissertation. In January 1992, the Clean Air Act's oxygenated fuels program (OXY) began, requiring gasolines to be formulated to contain 2.7% by weight of oxygen in carbon monoxide nonattainment areas during the winter months [4]. In January 1995, areas that failed to comply with national ozone standards were required to begin using reformulated gasolines (RFG) year round [5]. The law required refiners to reformulate gasolines in order to reduce vapor pressure, decrease the aromatics content, and increase the oxygen content to 2.0% by weight in the nine most polluted cities in the country. Similar requirements in other regions were expected to follow.

In order to comply with these requirements, refiners typically use either alcohols or ethers as the oxygen source. Conveniently, oxygenates such as methanol, ethanol and methyl tertiary-butyl ether (MtBE), act both to provide oxygen and enhance the fuel's octane rating. However, blending problems limit methanol's appeal, and under current law both methanol and ethanol are too volatile for use in RFG. Moreover, both methanol and ethanol are miscible with water, which leads to phase separation during storage and transport. To avoid this problem, methanol and ethanol may be reacted with an iso-olefin feedstock such as isobutylene. The resulting ethers, namely MtBE and ethyl tertiary-butyl ether (EtBE), respectively, retain the benefits of octane enhancement and oxygen enrichment, but have considerably lower volatilities and water solubilities. Although

EtBE offers some performance advantages over MtBE, including higher blending octane and lower vapor pressure, MtBE has dominated the fuel oxygenates market for years, and its production base far outweighs that of competing oxygenates. However, MtBE has proven to be an environmental liability and the search for replacement blend components, including other oxygenates, is well underway.

Historically, ethers have proven to be the preferred oxygenate, and new ethers are currently being developed for use as replacements for MtBE in gasoline [6,7], as well as for directly replacing diesel fuel [8]. For ethers to be acceptable blend components or replacements for motor fuels, they must be of sufficiently high carbon number to boil in the same range as the motor fuel concerned. Unlike alcohols, ethers do not hydrogen bond and therefore have boiling points that are about the same as those of alkanes with comparable molecular weights [9]. In order to serve as effective replacement oxygenates for MtBE in gasoline, the ethers should be of carbon number C_4 to C_8, whereas ethers for use as replacements for diesel fuel should be of carbon number C_9 to C_{12}. From an environmental perspective, the ethers should have low water solubility and low vapor pressure. This environmental constraint favors the use of ethers with a carbon number of C_7 or higher. In this dissertation, the ethers selected for study as potential replacement oxygenates for MtBE in gasoline were of carbon numbers C_7 and C_8, while those studied as potential replacements for diesel fuel were of carbon numbers C_9, C_{10} and C_{12}.

Synthetic Aspects

Virtually all MtBE is currently made from isobutylene obtained from petroleum refinery olefin streams and methanol that is derived from natural gas. However, it would be preferable to be able to produce the methanol from coal, since coal is the most abundant domestic energy resource in many countries, including the United States. For a number of years, the Fossil Energy Program within the U.S. Department of Energy (DOE) has been supporting a coal liquefaction program to develop improved technologies for converting coal to clean and cost-effective liquid fuels and/or chemicals to complement the dwindling supply of domestic petroleum crude [10]. One area of research that is currently being supported by this program is the preparation of higher oxygenates from synthesis gas for use as fuels and fuel blend components.

Synthesis gas, or syngas, is a mixture of hydrogen and carbon monoxide. Methanol is frequently an intermediate in the synthesis of higher oxygenates by this route, being formed from syngas in the presence of a methanol synthesis catalyst according to the following reaction:

$$CO + 2\ H_2 \leftrightarrow CH_3OH$$

The production of methanol is favored by high pressures and low temperatures. However, low temperatures inhibit the reaction kinetics. At temperatures sufficient to produce good reaction rates at the pressures typically employed in syngas conversion, the equilibrium is decidedly to the left. The equilibrium can be shifted to the right, thus enhancing MeOH production, by physically removing the MeOH as it is formed, for example, by distillation, but this is costly and inefficient. Alternatively, the equilibrium can be shifted to the right chemically by reacting the methanol as it is formed to make value-added chemicals.

One such approach would be to introduce an olefin with the synthesis gas and an etherification catalyst with the methanol synthesis catalyst. Thus, a value-added higher oxygenate would be produced from synthesis gas in a single reaction vessel, without the necessity of removing intermediates. The methanol, once formed, will add to the olefin according to the following equation:

$$(CO + 2\ H_2 \rightarrow)\ CH_3OH + C_nH_{2n} \rightarrow\ CH_3OC_nH_{2n+1}$$

The author termed this process the single-step etherification of olefins with synthesis gas.

Environmental Aspects

As was the case with MtBE, the introduction of higher carbon ethers into fuel supplies guarantees that these materials will find their way into the environment [11]. Before introducing these compounds into the transport fuel supply at the rate of hundreds of millions of gallons per year, it would be worthwhile to look at their potential environmental impact. The EPA estimates that 11 million gallons of gasoline leaks from underground storage tanks every year [12]. If 32% of that gasoline is RFG containing approximately 15% MtBE, then over 500,000 gallons of MtBE will find its way into the environment every year from leaking underground fuel tanks (LUFT) alone. An equal amount of MtBE is estimated to enter the environment from non-point sources, primarily automobile emissions [13]. Since the higher ethers contain less oxygen than MtBE, they must be blended into gasoline at higher ratios to achieve the same oxygen levels.

Therefore, both automobile emissions and releases from underground fuel tanks will be increased compared to the current MtBE usage. Two homologues of MtBE are of particular industrial importance, and therefore of potential environmental importance, because they can be prepared from readily available petroleum refinery feedstocks. These two homologues are methyl tertiary hexyl ether and methyl tertiary octyl ether. Beginning in 1995, limited quantities of methyl tertiary hexyl ether were introduced into gasolines in Finland as a supplementary oxygenate to MtBE [14].

Goals/Objectives of the Dissertation

The major goals and objectives of this dissertation are:

1) To conduct a series of batch reactions to determine the optimum conditions for the preparation of higher carbon ethers (with carbon numbers of C_7 and C_9) from methanol and C_6- and C_8-olefins. The results can then be used to determine the optimum initial conditions for the development of a continuous single-step etherification reactor. This dissertation presents the first systematic evaluation of parametric data relevant to the design of a single-step process for producing higher ethers from olefins and synthesis gas known to the author.
2) To provide a screening-level risk assessment of the potential hazards to humans and ecosystems resulting from exposure to methyl tertiary hexyl ether and methyl tertiary octyl ether by atmospheric dispersion and deposition if these compounds were to completely replace MtBE in gasoline. This is the first work known to the author to provide such a risk assessment.

3) To evaluate the potential risks to groundwater resources as a result of contamination caused by leakage of these ethers from underground fuel tanks. This is the first work known to the author to provide such a risk assessment.

Organization of the Dissertation

Chapter II presents a detailed review of the literature relevant to the synthesis of higher carbon ethers from olefins and synthesis gas. Additionally, the literature relevant to predicting, by analog considerations, the toxicity of methyl tertiary hexyl ether and methyl tertiary octyl ether, from data available for methyl tertiary amyl ether and MtBE, is reviewed.

The research described in Chapter III evaluated the degree of reactivity of C_6- and C_8-olefins and the selectivity for the production of higher ethers. A detailed description of the experimental methodology is presented in Appendices D and E, and the thermodynamic constraints governing ether production are discussed in Appendix F. Appendix G presents an analysis of the reaction kinetics in the synthesis of higher ethers. The development of a simultaneous process for both alcohol and ether syntheses constitutes future work. The material in Chapter III was previously published by the author in *Fuel Processing Technology*, 2003, *83*, 219-234, and is reprinted here with the permission of the copyright holder.

Chapter IV addresses issues concerning potential environmental contamination by atmospheric dispersion and deposition of methyl tertiary hexyl ether and methyl tertiary octyl ether. In this study, a screening-level risk assessment was performed by comparing predicted environmental concentrations (PEC) of these ethers to concentrations that might cause adverse effects to humans or ecosystems. Since MtHxE and MtOcE form part of a homologous chemical series with MtBE, the basic mechanisms of atmospheric transport and reaction for these compounds are expected to be similar. A simple box model that has successfully been used to estimate urban air concentrations of MtBE was adapted to predict atmospheric concentrations of MtHxE and MtOcE. Expected atmospheric concentrations of these ethers were also estimated using the European Union System for the Evaluation of Substances (EUSES) multimedia fate model, which simultaneously calculates PECs in the various environmental compartments of air, water, soil and sediment. Because little or no data are available on the physicochemical, environmental and toxicological properties of MtHxE and MtOcE, estimation methods were employed in conjunction with EUSES to predict both the PECs and the concentrations at which these ethers might pose a threat to humans or ecosystems. Comparison of the PECs with concentrations that are thought to be hazardous yielded a preliminary assessment of risk. The results can then be used in a determination of whether these ethers should undergo more rigorous toxicological testing before they are used to replace MtBE in gasoline. The material in Chapter IV was previously published by the author in the *Journal of the Air and Waste Management Association*, 2006, *56(10)*, 1484-1492, and is reprinted here with the permission of the copyright holder.

Chapter V examines the potential for groundwater contamination due to leakage of methyl tertiary hexyl ether and methyl tertiary octyl ether from LUFTs. In this study, a screening-level risk assessment compared predicted well water concentrations of these ethers to concentrations that are likely to cause adverse effects. Since MtHxE and MtOcE form part of a homologous chemical series with MtBE, the basic mechanisms of subterranean transport are expected to be similar. A physicochemical model that has been successfully applied to the prediction of MtBE concentrations in community water supply wells was used to predict well water concentrations of MtHxE and MtOcE. Because very little data are available on the physicochemical and environmental properties of MtHxE and MtOcE, estimation methods were employed in conjunction with the model to predict well water concentrations. The predicted well water concentrations for MtHxE and MtOcE were then compared with concentrations at which MtBE is known to cause adverse effects in well water, thereby giving a preliminary indication of risk. These results can then be used in a determination of whether these ethers should undergo more rigorous toxicological testing before they are used to replace MtBE in gasoline. The material in Chapter V has been accepted for publication by the journal *Environmental Toxicology and Chemistry*.

Chapter VI concludes the dissertation by summarizing the conclusions that can be drawn from the current investigation and suggesting avenues for future work.

CHAPTER II

LITERATURE REVIEW

The preparation of fuels and value-added chemicals from coal and/or biomass is an area of much current research interest worldwide. Synthesis gas is an intermediate in the indirect conversion of coal or biomass to fuels and value-added chemicals. Likewise, methanol is frequently an intermediate in these processes. The isolation of the intermediate methanol is costly and inefficient, and it would be preferable to develop processes that produce fuels and value-added chemicals without isolating the methanol. One such process is the single-step dimethyl ether (DME) process [15]. Here, a dehydration catalyst, which is an acid catalyst, is placed in the reaction vessel with the MeOH synthesis catalyst, which consists of a mixture of copper oxide and zinc oxide on an alumina support. As MeOH is formed, it is dehydrated to DME and the DME is removed from the reaction vessel.

There are two versions of the single-step DME process, a gas phase version and a liquid phase version. In the gas phase process [15, 16], carbon monoxide, carbon dioxide and hydrogen are fed under pressure to a vessel containing both the methanol synthesis and dehydration catalysts. Any unreacted synthesis gas is either recycled or used as fuel. MeOH and DME are recovered and used to produce fuels or chemicals. The use of a single-step process offers economic advantages over a multi-step process for methanol synthesis, where removal and subsequent dehydration to DME in a separate reactor is required. However, both the synthesis reaction and the dehydration reaction are exothermic, and high temperatures not only inhibit the conversion of synthesis gas to DME, but also tend to deactivate the catalyst. Heat removal is thus an important aspect of this process, which led to the development of the liquid phase technology.

In the liquid phase DME synthesis, a three phase system comprising a liquid phase of an inert hydrocarbon oil, a solid phase of the methanol synthesis and dehydration catalysts, and a gas phase of the reactants and products is employed in a slurry reactor [17, 18]. The principal advantage of the liquid phase technology is the ready dissipation of the heat from the reactions by the hydrocarbon oil. Synthesis gas conversion to DME is increased and catalyst life is extended.

A process design is proposed here that is based on a modification of the single-step DME process. It is reasonable to assume that the equilibrium can be shifted to the right by introducing an olefin with the synthesis gas and replacing the dehydration catalyst with an etherification catalyst. Thus, a value-added higher oxygenate would be produced from synthesis gas in a single reaction vessel, without the necessity of removing intermediates. The methanol, once formed, will add to the olefin according to the following equation:

$$(CO + 2\ H_2 \rightarrow)\ CH_3OH + C_nH_{2n} \rightarrow\ CH_3OC_nH_{2n+1}$$

The author termed this process the single-step etherification of olefins with synthesis gas. A more detailed description of the proposed approach is provided in Appendix B, while Appendix C gives a more detailed description of the addition reactions of olefins.

In an alternative approach, Kazi et al. produced MtBE from isobutylene and synthesis gas in a single-step reactor [19]. A dual catalyst system was used with Pd/SiO_2 as the methanol synthesis catalyst and a zeolite as the etherification catalyst. However, the yield of ether from this reaction, which was operated at 175 ^oC and 7 atm, was very low, probably due to the choice of catalyst. While Pd/SiO_2 is an excellent choice for a methanol synthesis catalyst, finely divided noble metals are known to act as hydrogenation catalysts for olefins [20]. In this case, the olefin was isobutylene and yields of butanes were correspondingly high. In the current work, HZSM-5, which consists of CuO/ZnO on alumina, was used as the methanol synthesis catalyst and dry Amberlyst 15 was used as the etherification catalyst. The reaction temperatures ranged from 60 to 100 ^oC. This is the first work to propose the direct etherification of higher olefins with synthesis gas in a single-step reactor. This is also the first study to employ a dual catalyst system comprised of an etherification catalyst and a methanol synthesis catalyst that did not also hydrogenate the olefin.

The reaction of alcohols with olefins is well known [21], and several companies have developed commercial ether processes based on it [22-27]. The reaction requires the presence of an acidic catalyst, and sulfuric acid [28], ion-exchange resins [29], silicotungstic acid [30] and zeolyte catalysts [31] have all been successfully employed in this capacity. A long range goal of this project is to develop a catalytic reaction system that can convert synthesis gas and olefins to ethers in a single-step process. One objective of this dissertation is to use a series of batch reactions to determine the optimum conditions for the preparation of higher carbon ethers (with carbon numbers of C_7 and C_9) from methanol and C_6- and C_8-olefins. Since the methanol will ultimately be derived from synthesis gas, the process conditions for the etherification must be compatible with the methanol synthesis reaction conditions. A number of technologies have been developed for the preparation of methanol from synthesis gas at temperatures in the 60 to 150 ^{o}C range and at pressures from 150 to 750 psig [32-35].

The synthesis of methanol is a classic example of an exothermic equilibrium-limited reaction. Recently, there has been an emphasis on improving the synthesis of methanol by removing the alcohol as it is formed, thereby lowering the thermodynamic constraints on methanol conversion. The physical removal of methanol is one way of overcoming thermodynamic limitations in the synthesis of methanol. Another interesting and promising approach is to convert methanol into a chemical species whose removal affects the equilibrium conditions. The *in situ* dehydration of methanol to dimethyl ether (DME) in the presence of an added catalyst, such as gamma-Al_2O_3, is based on the second option [32]. An alternative way to remove the methanol, also based on ether synthesis, would be to react the methanol with an olefin and remove the resulting ether. Here, an etherification catalyst replaces the dehydration catalyst and an olefin is introduced. Depending on the olefin supplied, mixed methyl ethers may be produced. Accordingly, MeOEt can be prepared from ethylene, MeOPr from propylene, MtBE from isobutylene, TAME from isoamylene, or higher ethers from higher olefins. As the etherification catalyst possesses acid sites, it may also exhibit dehydration activity towards the methanol. However, the production of DME by dehydration of methanol is not likely under etherification conditions. Dimethyl ether has not been observed as a byproduct in the preparation of MtBE, and is therefore not expected here.

According to Selwitz and McNulty [30], any olefin, or mixture of olefins is suitable for use in this process. Furthermore, any alcohol, or mixture of alcohols is appropriate for use in this process. This particular process employs a silicotungstic acid catalyst, but a host of acid catalysts are suitable, including ion-exchange resins such as Amberlyst [27] and zeolite catalysts [36], such as HZSM-5 and HZSM-11 [31].

Advantages of the Etherification Process

In the single-step DME process, the dehydration typically takes place at temperatures ranging from 250 to 350 ^{o}C. Since the entire process occurs in a single step, the methanol synthesis also necessarily takes place at 250 to 350 ^{o}C. However, methanol synthesis is favorable at lower temperatures, and it is very desirable to develop a process that exploits this fact. The etherification proceeds in the temperature range from 50 to 200 ^{o}C, but preferably from 80 to 120 ^{o}C. If employed in a single step, the entire process would proceed in this temperature range, thus reducing the severity of the reaction conditions. Partial pressures of carbon monoxide and hydrogen would likely have to be high to encourage the methanol synthesis reaction.

There are two principal reactions involved in the single-step etherification, namely the methanol synthesis and the etherification of the methanol that is produced. A detailed literature review will be presented for both of these reactions. The dehydration reaction to produce DME will also be examined in some detail. Although this reaction is undesirable in the proposed process, it may serve as a useful model for the etherification step, as discussed below.

The Preparation of Synthesis Gas for Methanol Manufacture

The preparation of synthesis gas is a very mature chemical technology. The first demonstration of the catalytic conversion of synthesis gas to hydrocarbons was accomplished in 1902 [37]. Articles on its manufacture and uses fill volumes, and significant portions of national fuel economies have been based on it, most notably in South Africa. The discussion here will be limited to the preparation of synthesis gas intended for methanol manufacture.

Synthesis gas is a mixture of carbon monoxide and hydrogen, and is obtained by reacting steam with a carbon source. Petroleum hydrocarbons, natural gas, peat, solid and liquid wastes, and biomass have all proven suitable carbon sources, but the Department of Energy’s emphasis during their sponsorship of this research was on the preparation of syngas from coal. In the current commercial practice, the coal is first coked to remove volatiles. Then steam is allowed to react with the coke or, more formally, the carbon in the coke, according to the following equation:

$$C + H_2O \rightarrow CO + H_2 \qquad \text{Eq. 2-1}$$

Thus, if equimolar amounts of carbon and water react, the resulting syngas is an equimolar mixture of carbon monoxide and hydrogen. However, for the preparation of methanol from syngas, the stoichiometric requirement is two moles of hydrogen per mole of carbon monoxide:

$$CO + 2\ H_2 \rightarrow CH_3OH \qquad \text{Eq. 2-2}$$

The ratio of hydrogen to carbon monoxide in syngas can be increased by increasing the steam to carbon ratio, because carbon monoxide also reacts with steam to give carbon dioxide and additional hydrogen by the water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{Eq. 2-3}$$

The carbon dioxide is easily removed from the syngas mixture by absorption in water [38]. The proper ratio of carbon to steam to give a methanol synthesis gas is arrived at as follows:

Three times Equation 2-1 gives

$$3\ C + 3\ H_2O \rightarrow 3\ CO + 3\ H_2 \qquad \text{Eq. 2-4}$$

From equation 2-3,

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{Eq. 2-3}$$

Equation 2-4 plus Equation 2-3 gives

$$3\ C + 4\ H_2O \rightarrow 2\ CO + 4\ H_2 + CO_2 \qquad \text{Eq. 2-5}$$

or

$$1.5\ C + 2\ H_2O \rightarrow CO + 2\ H_2 \qquad \text{Eq. 2-6}$$

once the carbon dioxide is scrubbed out. Thus, an increase in steam of 33% over the equimolar ratio provides the optimum synthesis gas with which to manufacture methanol. Unfortunately, this means that fully one-third of the coal is lost as carbon dioxide, which constitutes not only a process inefficiency but also an environmental liability in the form of a greenhouse gas.

The Methanol Synthesis Process

Methanol is one of the most important chemical raw materials. Worldwide production capacity in 1989 was around 21 million tons per year, rising to 22.4 million tons per year by 1993, and production capacity continues to increase [39]. The methanol synthesis process is a mature commercial process. Numerous articles and textbooks have appeared on the subject, and hundreds of patents have been granted [39, 40]. Badische Anilin und Soda Fabrik (BASF corporation) produced methanol by the hydrogenation of carbon monoxide in the presence of iron oxide catalysts as early as 1913, and commercialized the process in 1923 using a zinc oxide/chromium oxide catalyst. The process operated under conditions of high pressure (25 - 35 MPa) and high temperature (320 - 450 ^{o}C). A significant amount of DME was also produced by this process, about 3 - 5 wt%. In the 1960s, Imperial Chemical Industries (ICI) developed a low pressure methanol process that utilized highly selective copper oxide catalysts. This and other related low pressure processes are characterized by relatively mild reaction conditions (5 - 10 MPa, 200 - 300 ^{o}C). By 1980, the high pressure plants had been almost completely replaced by the new low pressure technology.

There are numerous large plants based on the low pressure methanol synthesis process currently in operation all over the world. All of these plants employ copper and zinc oxides with alumina or chromium oxide. Much current research is directed towards the development of alternate processes, such as the liquid-phase methanol synthesis process and the low temperature, homogeneous catalysis process. However, these processes have yet to be proven commercially feasible, and there have been no major developments of scientific significance in conventional vapor-phase synthesis technology since the 1970s [41].

In contrast to the high pressure process, the low pressure process produces only very small amounts of DME, and a new synthetic route to DME had to be developed to meet market demand.

The Dimethyl Ether Synthesis Process

Dimethyl ether is industrially important as the starting material in the production of the methylating agent dimethyl sulfate and is also finding increasing use as an aerosol propellant and fuel additive [42].

In general, aliphatic ethers are prepared by heating alcohols in the presence of an acidic catalyst. Suitable catalysts include sulfuric acid, zinc, iron, copper, aluminum or manganese chloride, copper, aluminum or chromium sulfate, aluminum, titanium or barium oxides, silica gel, and a host of others. Aluminum oxide and aluminum silicate, with or without doping, are the most important catalysts for industrial applications.

The preparation of DME from methanol in the presence of acidic catalysts has been known for many years. Numerous methods have been discussed in the open and patent literature. In a typical two-step process, methanol is obtained from synthesis gas in the first step, and then dehydrated to DME in a separate reactor in the second step. Of particular interest for the current study is the direct synthesis of dimethyl ether from synthesis gas in a single-step process [43].

The Single-Step DME Process - A Synopsis of Current Technologies

The single-step conversion of syngas to DME offers certain advantages over the two-step process with methanol as an isolated intermediate. The principal advantage is that the equilibrium limited conversion to methanol is overcome by removing DME as a gas. The single-step DME process thus benefits from the high syngas conversion per pass compared to the traditional two-step process, in which methanol is produced from syngas over a methanol synthesis catalyst and then converted to DME over a dehydration catalyst in a subsequent reaction [44].

The catalyst system for the single-step DME process has two functionalities, a methanol synthesis functionality and a dehydration functionality. In addition, the methanol synthesis catalyst possesses water gas shift activity. These reactions are shown below:

$$CO + 2\ H_2 \rightarrow CH_3OH$$

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The single-step synthesis may be achieved in one of two ways. It requires the use of two catalytic systems, the first catalyst being the methanol synthesis catalyst and the second being the methanol dehydration catalyst. In the first process, the methanol synthesis catalyst and the methanol dehydration catalyst are physically mixed, the mixture being known as the dual catalyst system. In the second process, the two functionalities are built into a single catalyst and referred to as a bifunctional catalyst system. The methanol synthesis catalyst is generally a copper and/or zinc and/or aluminum and/or chromium based catalyst, while the dehydration catalyst may be selected from a host of solid acid materials. Bifunctional catalysts are prepared by either coprecipitating MeOH synthesis and MeOH dehydration components together or by precipitating MeOH synthesis components onto an existing, high surface area solid acid support. Regardless of which type of catalyst system is employed, it cannot be overemphasized that maintenance of the catalyst activity is a major challenge.

The single-step DME technology has reached a certain maturity, with over 30 related U.S. and foreign patents having been granted. Also, numerous studies designed to investigate the complexity of the overall conversion, to show the importance of the choice of catalyst components and to address issues associated with the bifunctional character of the catalyst systems (for instance, deactivation and regeneration problems) have appeared in the literature [15, 45].

The single-step liquid phase DME processes are based on the Liquid-Phase Methanol (LPMeOH) technology, which was conceived and patented by Chem Systems, Inc. [46] A number of variations on this process have been described in the combined open/patent literature, three of which will be examined in some detail in this section.

The liquid phase technologies offer significant advantages over existing gas phase technologies for MeOH/DME production [18]. Economic considerations dictate that viable processes must utilize syngas mixtures derived from low cost feedstocks. Liquid phase technologies are particularly suited to the conversion of syngas with high CO/H_2 ratios, such as those typically derived from coal. The process is also suitable to hydrogen rich mixtures. A principal advantage is the ease of heat dissipation offered by the oil-based slurry mixture. The heat generated by the three exothermic reactions (methanol synthesis, methanol dehydration and water gas shift) leads very quickly to high temperatures in the gas phase (essentially adiabatic) processes. Since the slurry is able to remove the generated heat more efficiently, a lower temperature is maintained and overall conversion is enhanced. This better heat dissipation reduces problems due to coking, sintering and deactivation of the catalyst. Typically, the same catalysts are employed as for the gas phase processes. Furthermore, backmixing of the slurry prevents the development of hot spots in the reactor. Finally, the liquid phase technologies offer significant energy savings over the gas phase technologies.

Air Products and Chemicals has described a slurry-based process that produces DME/MeOH in a three phase reactor using methanol synthesis and methanol dehydration catalysts in a single step [17, 47]. The 1999 Chemical Week Buyers Guide lists Air Products as the only commercial supplier of DME. The Electric Power Research Institute describes a similar process, but the main emphasis in this patent is the production of gasoline, with DME as an intermediate [48]. Both the Air Products and Electric Power processes operate in the 200 to 300 ^{o}C range.

A related article, although this may only be of academic interest, has appeared in the open literature. Iwasa et al. [49] reported that methanol is dehydrated to DME on

Pd/Al_20_3 in 70% yield with 90% selectivity. In this study, it was not determined whether Pd/Al_20_3 could be used as the dehydration catalyst in a single-step DME synthesis.

Preparation of Ethers from Alcohols and Olefins

The acid catalyzed addition of alcohols to olefins to form ethers is a classic example of the electrophilic addition reaction which is characteristic of the carbon-carbon double bond in olefins [50]. A host of substances are suitable for use as the catalyst, including sulfuric acid [51], silicotungstic acid [30], ion-exchange resins [52, 53] and zeolites [31, 36, 54]. The reactions undoubtedly proceed through a carbocation intermediate [21] and, consequently, rearrangements of the olefinic chain to the more stable secondary and tertiary carbocations occur whenever possible. Moreover, tertiary carbocations are more readily formed than secondary carbocations, which, in turn are more readily formed than primary carbocations, so a tertiary olefin was chosen for the initial portion of this work. This should allow the reaction to proceed under the lowest severity conditions. The simplest olefin that is capable of providing a tertiary carbocation is isobutylene. The reaction of methanol with isobutylene to produce methyl tertiary butyl ether (MtBE) is a commercial process, and numerous detailed studies on the technology have appeared in the literature [55]. Thus, this reaction was chosen as a good starting point for the development of the single-step etherification process.

The preparation of MtBE using synthesis gas as the only carbon source has also been studied [56-58]. Most of these studies involved a multistep process in which CO was hydrogenated to MeOH and isobutanol in separate reactors, with subsequent dehydration of the isobutanol to isobutylene and addition of the MeOH to the isobutylene. The only study found to date that has addressed the direct addition of an olefin to a carbon monoxide hydrogenation reaction, with the stated goal of etherifying the MeOH as it was formed, was by Kazi et al. [19] However, the authors stated that the rate of formation of MtBE was "very low". In this study, Pd/SiO_2 was used as the methanol synthesis catalyst in a dual catalyst system, which also contained a zeolite as the etherification catalyst. While Pd/SiO_2 is highly selective for methanol formation in CO hydrogenations and is therefore a very good methanol synthesis catalyst, finely dispersed noble metals are well known catalysts for the hydrogenation of olefins to paraffins [59]. Thus, much of the isobutylene was hydrogenated to isobutane before it could react with the methanol to produce MtBE. Kazi et al. suggested the use of a lower temperature methanol synthesis catalyst but did not specify its composition, noting that the use of this type of catalyst would make it possible to conduct cocurrent MtBE synthesis under conditions that were less favorable for both side reactions and acid site deactivation, while at the same time thermodynamically favoring MtBE production. In the current work, a CuO/ZnO on alumina methanol synthesis catalyst was employed, as this was not expected to exhibit hydrogenation activity towards the olefin.

Study Design

A long term goal of this project is to develop a process that etherifies olefins with synthesis gas in a single reaction vessel. Many of the advantageous features of the reactions outlined above will be utilized for the design of a continuous etherification reactor. Thus, a low pressure methanol synthesis reaction utilizing a low temperature methanol synthesis catalyst will be employed. Likewise, the slurry phase technology will be borrowed from the DME process. Zeolite HZSM-11 may be the best candidate to replace the methanol dehydration catalyst, as it seems to give the highest yields of and selectivity to MtBE [31]. However, HZSM-11 is still in the developmental phase and consequently is not yet commercially available. The literature search revealed that HZSM-5 gives the second best yields of and selectivity to MtBE [31], and since it is commercially available, was chosen for use in this study.

The olefin of choice for the initial portion of this work was isobutylene. Due to environmental concerns over MtBE finding its way into drinking water supplies, which mounted steadily during the course of this investigation, the DOE has shifted its attention from the preparation of MtBE to the preparation of higher carbon ethers. The higher carbon ethers have lower vapor pressures and higher boiling points than MtBE [60], which makes them good candidates for blending in reformulated gasolines or for use as diesel fuels. The ethers selected to be produced in this project were of carbon number C_7 to C_{12}. The C_7- and C_8-ethers are likely to be useful as oxygenates in reformulated gasolines, with a number of patents having been issued for the preparation of methyl tertiary hexyl ether [7, 61, 62]. The C_7- and C_8-ethers have blending octane numbers that are about the same as MtBE [6]. The C_9- to C_{12}-ethers may be used neat as a replacement for diesel fuel. Although the boiling range of the C_9-ether methyl tertiary octyl ether suggests its use as diesel fuel, it has a calculated blending octane number of 149 in gasoline [63] and so may also prove useful as a gasoline blend component. These ethers can be synthesized from C_6- and C_8-olefins by etherification with alcohols in the C_1 to C_4 range. The C_6- and C_8-olefins were selected because they are readily obtained from refinery process streams by dimerization of propylene [64, 65] and isobutylene [66], respectively.

It should be pointed out that the oxygenates constitute fuel blend components rather than additives, because they are "blended" into gasolines at the rate of three to fifteen percent, whereas the term "additive" designates compounds like detergents and dispersants, corrosion inhibitors, gum inhibitors, anti-icing additives, and anti-knock additives like tetraethyl lead, which is "added" at the several hundred parts per million level [67]. The misusage permeates the open, patent and regulatory literature.

In response to the DOE’s new directive, a literature search was conducted to identify the optimum processes for preparing higher carbon ethers. In 1936, Evans and Edlund first described the preparation of methyl tertiary hexyl ether [28]. A number of patents, both US and European, describe the preparation of tertiary alkyl ethers from C_6- and higher olefins [68]. These ethers are widely used in the formulation of resins, medicines, preservatives, dyes, plastics, solvents and chemical intermediates [69]. In addition, etherification of gasoline has been practiced as a means of reducing olefin content by converting the olefins to ethers. Olefins, and particularly conjugated diolefins, being highly reactive, are notorious for their tendency to polymerize and form gums during gasoline storage [70], whereas the ether linkage is very stable. The resulting gasoline is more suitable for blending in finished gasolines [71]. However, little or no attention has been paid to the isolation, synthesis or characterization of these ethers in the open literature in the period from the late 1930s through the 1970s.

The situation changed in the early 1980s. The first oxygenated fuels programs in this country utilized alcohols blended directly into gasoline. The corn belt states employed government subsidized ethanol successfully, but the national market was dominated by far by the more economical methanol. However, the direct blending of methanol into gasoline raises many problems. Besides its toxicity, it has a low calorific value, a high latent heat of vaporization, and a high vapor pressure blending value. Above all, its great affinity for water induces phase separation, even when only a very small amount of water comes into contact with the gasoline during the motor fuel distribution steps [64]. As a consequence, the direct blending of methanol into gasolines resulted in a rash of stalled vehicles that seriously damaged methanol's marketability. An indirect way of blending methanol into gasoline was sought. The solution chosen was methanolation of the olefins in gasoline [72]. The most reactive olefin found in gasoline is isobutylene, but olefins of carbon number C_5 to C_7 are also present. As the isobutylene is methanolated to MtBE, the higher olefins are necessarily also methanolated, although the conversion is lower. It was at this point that the scientific community became interested in the synthesis of higher carbon ethers from the olefins found in gasoline. The seminal paper discussing the mechanisms and kinetics of etherification of higher olefins with alcohols appears to be that of Krause et al., which appeared in 1984 [73]. They studied the reaction kinetics of etherification of C_6-olefins (in gasoline and in hydrocarbon blends) with methanol in plug flow reactors. They showed that both methanolation and isomerization of the olefins occur. They further showed that the structure of the olefin plays an important role in etherification, both in the rate of formation of the carbocation intermediate, and in the steric hindrance to methanolation exerted by the methyl groups.

A number of papers studying the syntheses of higher carbon ethers followed, although only those that investigated the alkanolation of dipropylene (the 2,3-dimethylbutenes) and di-isobutylene (the 2,4,4-trimethylpentenes) are of relevance to this discussion. Zhang and Datta studied the kinetics of simultaneous etherification and isomerization reactions of C_6-olefins with ethanol over Amberlyst 15 [74, 75]. Liu et al., studied the etherification of C_6-olefins in a large excess of methanol (mole fraction of methanol of 0.975) [76]. Wang and Guin developed better catalysts for use in etherification of C_6-olefins in hexane. In their studies, the activity of Amberlyst 15 was used as a baseline for comparison [77, 78]. Karinen et al. studied the isomerization and etherification of C_8-olefins in iso-octane [63, 79, 80]. They demonstrated that longer carbon chains decreased the rate of etherification. The rate of etherification depended strongly on the characteristics of the reactants, such as the bulkiness of the olefins. The same group also developed a kinetic model for the etherification of C_8-olefins with methanol in iso-octane [60].

Interestingly, almost all of the investigators who studied the etherification of higher olefins employed an inert diluent in their reaction mixtures. This may be a carryover from the initial efforts, which were directed towards etherifying gasoline directly [73]. This would have allowed the researchers to more easily compare their results to those of previous investigators [81]. What makes this particularly interesting is that inert hydrocarbons have been shown to have an inhibitory effect on the etherification of isobutylene [82]. Nonreactive butylenes compete for the active sites on the catalyst, thus blocking the access of the reactive isobutylene. It seems reasonable that nonreactive higher alkanes, such as hexane or iso-octane, would likewise block access of the reactive alkenes. Only two previous investigations were found that studied the etherification of higher olefins in the absence of an inert diluent. Liu et al. [76] etherified dipropylenes in excess methanol. However, they employed such a large excess of methanol (0.975 molar) that the methanol itself likely acted as a diluent. At very high methanol concentrations, the cross-linking in the polymeric chains that form the backbone of the ion-exchange resin catalyst are deeply disturbed [83, 84], and the results obtained from such studies may therefore not be directly comparable to those obtained when more equal molar ratios of olefins and alcohols are employed. The work of Zhang and Datta [74, 75], who ethanolated di-isobutylene at equimolar ratios of olefin and alcohol, appears to be the only report in the literature that focused on the etherification of higher olefins in the absence of any diluent. Thus, the investigation of the etherification reactions of neat higher olefins with neat lower alcohols seems to offer a promising avenue for research. For this reason, it was decided to study the etherification of both C_6- and C_8-olefins with lower alcohols in the absence of any diluent. The effect of an inert diluent on these reactions could then be investigated separately at a later time. This is the first work to study the etherification of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene with methanol in the absence of an inert diluent.

It should also be noted that under current practice the only higher carbon ether of any industrial importance is methyl tertiary octyl ether, which is important only as a byproduct of MtBE manufacture. Even under the mild conditions employed in etherification reactions, isobutylene dimerizes to di-isobutylene, which is a mixture of two isomers, namely 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. The equilibrium mixture consists of about four parts 2,4,4-trimethyl-1-pentene and 1 part 2,4,4-trimethyl-2-pentene [85]. Di-isobutylene is the main byproduct of MtBE manufacture [86]. Although di-isobutylene is not as reactive toward etherification as isobutylene [87], it does react, forming 2-methoxy-2,4,4-trimethylpentane, one of the seventeen isomeric methyl tertiary octyl ethers [88].

This study was divided into two parts, the first of which analyzed the ether production from the reaction of C_6- and C_8-olefins with alcohols. The second part will be the development of a single-step process where both alcohol and ether synthesis reactions are performed simultaneously. A goal of this dissertation is to determine, by a parametric evaluation of various reaction conditions, the conditions most favorable to ether production from C_6- and C_8-olefins and alcohols. The knowledge gained from this dissertation will then be available for use in the development of a continuous process for the preparation of higher carbon ethers from olefins and synthesis gas in a single-step etherification reactor.

Higher carbon ethers are readily synthesized by the reaction of methanol with a branched olefin over an ion exchange resin catalyst [60, 89]. In this study, commercially available Amberlyst 15 catalyst was used to produce higher carbon number (C_7 and C_9)

ether compounds from C_6- and C_8-olefins and methanol. Since alcohols in the C_2 to C_4 range can be prepared from synthesis gas with the proper choice of catalyst and conditions [56, 90], this work will be extended to the higher alcohols ethanol and 2-butanol, from which ethers of carbon number C_8, C_{10} and C_{12} can be prepared using the same starting olefins. The effect of process variables, such as the molar ratio between olefin and methanol, reaction temperature, reaction pressure, reaction time, reaction medium, and catalyst loading, will be determined for etherification in a batch reactor. The implications of the proposed research to the design of a continuous process for the preparation of higher carbon ethers from olefins and synthesis gas in a single-step etherification reactor will be discussed. This dissertation presents the first systematic evaluation of parametric data relevant to the design of a single-step process for producing higher ethers from olefins and synthesis gas. Additional details on the research plan are presented in Appendix B.

Human Toxicities of Methyl Tertiary Alkyl Ethers

No studies on the toxicities to human beings of methyl tertiary hexyl ether or methyl tertiary octyl ether were found in the literature. Considering the widespread publicity associated with MtBE contamination and the fear of environmental exposure, surprisingly few studies on the toxicity of MtBE have been published. Even fewer such studies have appeared for methyl tertiary amyl ether (TAME). Only those studies that can be used to compare the toxicity of MtBE and TAME, and therefore, by analog considerations, be used to establish a "trend" for predicting the toxicities of MtHxE and MtOcE, are relevant to this discussion.

With the possible exception of inhalatory exposure of refinery workers, tanker truck drivers, gasoline station attendants, and self-service customers, acute exposure to MtHxE and MtOcE is likely to be very limited, and was not the focus of this study. The principal hazard associated with human exposure to methyl tertiary alkyl ethers is long-term exposure to small concentrations of these ethers by inhalation of contaminated air or ingestion of contaminated water. For the purposes of evaluating long-term human exposure hazards, EUSES divides the risk assessment into five categories, namely, repeated dose effects, fertility impairment, maternal toxicity, developmental toxicity, and carcinogenicity.

Repeated Dose Effects. No data on the effects of chronic human inhalatory exposure to methyl tertiary alkyl ethers are available. In the absence of human exposure data, exposure assessment data for other mammals can be used to estimate toxicities to human beings. Some no observed adverse effect concentrations (NOAEC) for chronic rodent inhalatory exposure are available for MtBE and TAME. The only NOAEC for systemic noncancerous toxicological effects for inhaled TAME found in the literature is 500 ppm [91], while the NOAEC for MtBE ranges from 400 ppm [92] to 800 ppm [93]. These data indicate that these two ethers are likely to be of similar systemic toxicity. Based on analog considerations, MtHxE and MtOcE are also likely to be of similar repeated dose inhalatory toxicity. The matter is discussed in greater detail in Chapter IV.

There are no studies of the effects on humans of long-term ingestion of MtBE. All of the studies available for risk assessment are laboratory animal studies [94], and they are few in number. The most notable systemic (non-cancer) effect of long-term ingestion of MtBE is increased liver and kidney weights in rodents. Risk assessment studies for TAME are even fewer in number than those for MtBE. Only one study that is directly comparable to an MtBE study was found in the literature for TAME [95]. In 28-day gavage studies in rats, the lowest observed adverse effect levels (LOAEL) for liver and kidney abnormalities from MtBE were 440 mg per kg body weight per day (mg/kg/day), while the lowest level for TAME was 500 mg/kg/day. Since the molecular weights of MtBE and TAME are 88 and 102 daltons, respectively, their systemic toxicities are virtually identical on a molar basis. Based on analog considerations, MtHxE and MtOcE are also likely to be of similar repeated dose toxicity by ingestion. The matter is discussed in greater detail in Chapter V.

Fertility Impairment. In testing with rats, no effects on fertility were observed at MtBE concentrations as high as 3400 ppm [96] or for TAME concentrations as high as 3000 ppm [97]. It therefore seems unlikely that MtHxE and MtOcE will exhibit fertility impairment effects.

Maternal and Developmental Toxicities. In testing with mice, an NOAEC for maternal and developmental toxicities of 1000 ppm has been reported for MtBE [98], while that for TAME has been reported as 250 ppm [99]. However, the results of these tests are not directly comparable, in that the dosages in the MtBE test were 0, 1000, 4000 and 8000 ppm, while those for TAME were 0, 250, 1500 and 3500 ppm. That is to say that the actual NOAEC for MtBE could be lower. These results suggest that MtBE and TAME are probably of similar maternal and developmental toxicities, and it seems unlikely that MtHxE and MtOcE would differ very greatly.

Carcinogenicity. The primary health effect of interest in chronic methyl tertiary alkyl ether exposure studies is cancer. No data are available on the carcinogenicity of methyl tertiary alkyl ethers to humans. Both MtBE [100] and TAME [101] have been shown to be carcinogenic to rodents. The potential human carcinogenicity risks of MtBE exposure are based upon extrapolation from rodent carcinogenicity tests. Only a limited number of such studies have been performed and there is a great deal of controversy over their results and the interpretation of those results, particularly as to how the findings might be extrapolated to predict human carcinogenicity effects. The USEPA has tentatively classified MtBE as a possible human carcinogen, and therefore it seems plausible that MtHxE and MtOcE are also potential human carcinogens. TAME has not been classified as to its carcinogenicity to humans. The matter of the carcinogenicity of methyl tertiary alkyl ethers is discussed further in Chapters IV and V.

CHAPTER III

SYNTHESIS OF HIGHER CARBON ETHERS FROM OLEFINS AND METHANOL

1. Introduction

The objective of this research is to develop improved transportation fuels by producing higher ethers and oxygenates for use as blending agents in reformulated gasolines and ultra-clean diesel fuels. The addition of oxygenates to gasoline and diesel fuels raises combustion temperatures, improves engine efficiencies, and causes the fuel to burn more cleanly, resulting in lower levels of carbon monoxide and unburned hydrocarbons in the exhaust stream [1]. Ethers are the favored oxygen-containing additives for reformulated gasoline since they produce high octane gasolines that burn cleanly. MtBE (methyl-*tert*-butyl ether) has been extensively utilized in the fuel oxygenates market for years due mainly to favorable physicochemical properties. However, its significant solubility in water evokes environmental concerns and stimulates the development of alternatives [13]. For the product ethers to be acceptable additives in motor fuels, the ethers must be of sufficient carbon number to boil in the same range as the motor fuel to which they are being added. From an environmental perspective, the ethers should have low water solubility and low vapor pressure. In this study, the ethers selected to be produced were of carbon number C_7 and C_9.

1.1 Single-Step Liquid Phase Process

The focus of this research is to develop a single-step liquid phase process to produce higher ethers from synthesis gas. The conventional method of producing ethers is first to produce methanol from synthesis gas and then to convert the methanol to an ether. For example, this process is typically used to produce dimethyl ether (DME) from methanol by either a gas phase or liquid phase reaction [15, 43, 44, 46]. The conversion of syngas to methanol can be increased by removing, either physically or chemically, the alcohol as it is formed, because this removal lowers the thermodynamic constraints and promotes syngas conversion [32]. A single-step, liquid phase DME synthesis reaction has been developed that produces DME directly from synthesis gas using a bifunctional catalyst system that promotes both methanol synthesis and methanol dehydration to DME [17]. Performing this single-step reaction in a liquid phase offers the advantage of heat dissipation, thereby allowing a lower temperature to be maintained. The liquid phase reaction results in less catalyst deactivation and longer catalyst lifetime [18].

The ultimate objective of this research is to develop a catalytic reaction system to produce higher ethers from synthesis gas and olefins using a single-step liquid phase process. In this system, as methanol is produced from syngas, the methanol would react with olefins to produce higher ethers. The thermodynamic constraint to methanol synthesis can thus be overcome by removing the methanol in an ether.

The methanol synthesis reaction is exothermic and therefore the equilibrium production of methanol is favored by low temperatures. A number of processes have been developed that produce methanol from syngas at temperatures from 60 to 120 ^{o}C and 1-5 MPa [32, 34]. These conditions were found to be quite suitable for the etherification reaction also, as discussed below. One study has been found in which synthesis gas was etherified with isobutene in a single-step reaction [19]. A dual catalyst system was used with Pd/SiO_2 as the methanol synthesis catalyst and a zeolite as the etherification catalyst. The yield of ether from this reaction, which was operated at 7 atm and 175 °C, was very low. This result was most likely caused by the choice of catalyst. Not only is Pd/SiO_2 a methanol synthesis catalyst, it also serves as an effective hydrogenation catalyst for the added olefin, in this case, isobutene, and yields of butanes were correspondingly high. In the current work, HZSM-5, which consists of CuO/ZnO on alumina, was used as the methanol synthesis catalyst and dry Amberlyst 15 was used as the etherification catalyst. The reaction temperatures ranged from 60 to 100 °C.

1.2 Proof of Concept

A comprehensive literature review has been performed to determine the state of the literature for single-step synthesis reactions producing ethers from synthesis gas and olefins. The patent literature pertaining to DME formation and the production of higher ethers, along with the processes for synthesizing methanol at lower temperatures, plus the article by Kazi et al. [19], indicate the feasibility of developing this process. For the initial investigation, the study was divided into two parts: the first part was an analysis of ether production from the reaction of C_6- and C_8-olefins with alcohols, and the second part is the development of a single-step process where both alcohol and ether synthesis reactions are performed simultaneously. The work described herein evaluated the degree of reactivity of C_6- and C_8- olefins with methanol and the selectivity for the production of higher ethers. An evaluation of the degree of the reactivity of C_6- and C_8-olefins with ethanol and 2-butanol is presented in Appendix E. Additional details on the reactivities of C_6- and C_8-olefins with methanol can also be found there. The initial parametric conditions were selected on the basis of the conditions expected to be encountered in the methanol synthesis reaction. An excess of olefin over the stoichiometric amount required would help shift the etherification equilibrium to ether and increase methanol consumption. This in turn would help drive the methanol synthesis reaction by consuming the product thereof. For this reason, the molar ratio of olefin to methanol for the initial experiments was chosen as 2:1.

Karinen and Krause [63] produced C_9-ether compounds from C_8-olefins and methanol. They demonstrated that longer carbon chains decreased the rate of etherification. The rate of etherification depended strongly on the characteristics of the reactants, such as the bulkiness of the olefins.

Higher carbon ethers are readily synthesized by the reaction of methanol with a branched olefin over an ion exchange resin catalyst [63, 73, 89]. In this study, commercially available Amberlyst 15 catalyst was used to produce high carbon number (C_7 and C_9) ether compounds from (C_6 and C_8) olefins and methanol. The effect of process variables such as molar ratio between olefin and methanol, reaction temperature, reaction pressure, reaction time, reaction medium, and catalyst loading are presented for etherification in a batch reactor.

2. Experimental

A series of four reactions were performed to determine the efficacy of ether production from the reactions of olefins with methanol. Those reactions were thermal with olefin only (to demonstrate olefin stability); thermal with olefin and methanol; catalytic with olefin only (again, to demonstrate olefin stability) and catalytic with olefin and methanol. The first and third sets of reactions were conducted to establish baseline reactivity of the system without methanol, that is, to investigate any rearrangement of the olefinic structure. The reactions were performed using 25 cm^3 stainless steel batch reactors, which were immersed and agitated at 100 cpm in a temperature controlled sand bath. In general, duplicate trials were conducted at each of the experimental conditions by utilizing side-by-side batch reactors in the same sand bath. For any given test, the analytical results presented in Table 3-1 represent an average of the results obtained from the individual reactors. The only exception to this rule was in the case of the determination of the effect of changing a single process variable, such as pressure, on the process yield, all other parameters being held constant. A description of the experimental apparatus (Tubing Bomb Microreactor system) appears in Appendix D. The reactions were performed at temperatures of 60 to 100 ^{o}C and reaction times from 15 min to 24 hr using a pressure of 1.5 MPa H_2. Hydrogen was chosen as a blanketing gas as it represents a less toxic alternative to synthesis gas. One experiment was performed at an elevated pressure of 5.5 MPa H_2 to investigate the effect of pressure on etherification.

2.1. Materials

The olefins used in this study were straight-chain olefins, 1-hexene, 1-heptene and 1-octene, and the branched olefins, 2,3-dimethyl-1-butene (23DM1B), 2,3-dimethyl-2-butene (23DM2B), 2,4,4-trimethyl-1-pentene (244TM1P) and 2,4,4-trimethyl-2-pentene (244TM2P). The reactions with the straight chain olefins were conducted at 100 ^{o}C while the reactions with the branched olefins were conducted at temperatures ranging from 60 to 100 ^{o}C with most of the experiments being conducted at 70 ^{o}C. Reactions were initially performed at a 2:1 molar ratio of olefin (C_6 = 1.4 g; C_8 = 1.44 g) to methanol (for C_6 = 0.26 g; C_8 = 0.2 g) and then the molar ratio was changed to a 1:8 ratio of olefins (C_6 = 0.48 g; C_8 = 0.53 g) to methanol (for C_6 = 1.5 g; C_8 = 1.2 g) so that an excess of methanol would be present in the reactor. The olefins were obtained from Sigma Aldrich Chemical Company (97% pure) and used as received. The methanol was obtained from Fisher Scientific Company (99.9% pure, $\leq$ 0.05% water) and was dried over molecular sieves prior to use. The etherification catalyst used in the reactions was Amberlyst 15 (0.2 g) and was initially charged to the reactor at 10 wt% of the total charge. Catalyst studies were conducted in which dry Amberlyst 15 was compared to wet Amberlyst 15 and to crushed and extruded HZSM-5. Only the dry Amberlyst 15 promoted any reactivity and hence was used for the rest of the experiments. Additional reactions using 23DM1B and 244TM1P were performed in which the amount of dry Amberlyst 15 was halved to 5 wt%, doubled to 20 wt% and tripled to 30 wt% of the total charge; the Amberlyst 15 was also crushed and charged at 10 wt%. Additionally, HZSM-5 was used alone and HZSM-5 and Amberlyst 15 were used together to test the effect of the HZSM-5 on the etherification. Both dry and wet Amberlyst 15 were obtained from Sigma-Aldrich Chemical Co. and used as received. The HZSM-5 was obtained from United Catalysts and activated prior to use. The pretreatment consisted of heating the HZSM-5 under a nitrogen flow for two hours at 200 °C, followed by two hours at 400 °C.

2.2. Analysis

Reaction products were analyzed by gas chromatography (GC) using a Varian model 3400 equipped with a J&W Scientific DB-5 phase capillary, 25m × 0.32 mm I.D. with 0.52 μm film thickness. The injector was maintained at 200 °C and the flame ionization detector was maintained at 210 °C. The initial column temperature was 50 °C and the column was maintained at that temperature. 2,2,4-trimethylpentane was used as an internal standard. Response factors were obtained for all available reactants and products. Response factors for those products that were not commercially available were estimated by obtaining the response factors for structurally similar available compounds. For this reason, some of the product distributions presented in Table 3-1 may not sum to 100%.

3. Results and Discussion

In etherification, there are a number of reaction variables that determine the extent of reaction and product distribution. In this study, reaction temperature, reaction time, amount of catalyst loading, molar ratio of olefin to methanol, and concentration of reactants were selected for investigation. Table 3-1 presents the experimental conditions used in 50 etherification experiments performed in batch reactors. The product distributions are reported on a methanol free basis. Table 3-1 also presents the conversions for methanol and the α-olefins as well as the selectivity to ether production, defined as the ratio of the desired product, the ether, to the undesired β-olefin.

3.1. Straight Chain Olefins

The initial experimental work focused on determining the reactivity and selectivity of straight-chain olefins when reacted with methanol using dry Amberlyst 15 catalyst. The reaction sets performed were thermal reaction conditions with olefin only, catalytic reaction with olefin only, and thermal and catalytic reactions with olefins and methanol. In reactions using 1-hexene, 1-heptene, and 1-octene, performed at 100 ^{o}C, no reactivity was observed under thermal conditions, i.e., in the absence of catalyst, with or without methanol. Rearrangement of the olefins was observed in the presence of a catalyst regardless of whether methanol was present. While in the presence of methanol, a small amount of unidentified higher boiling material was produced, but no ethers were observed in the product mixture.

3.2 Branched Olefins

The next phase of the experimental work involved reactions of branched C_6- (23DM1B and 23DM2B) and C_8- (244TM1P and 244TM2P) olefins with methanol using 10 wt% dry Amberlyst. Baseline reactions were performed at 80 ^{o}C in the absence of methanol to determine the amount of rearrangement that occurred under thermal and catalytic conditions with the 1- and 2-pentene isomers of 2,4,4-trimethylpentene and 1- and 2-butene isomers of 2,3-dimethylbutene. The reaction schemes are presented in Figures 3-1 [60] and 3-2 [73]. In the catalytic reaction, the 1-pentene isomer

Table 3-1 Experimental Conditions and Results

Run No.	olefin	temp [°C]	time [hr]	$r_{O/A}$[1]	cat'st [wt%]	$r_{R/S}$[2]	1B[3]	2B[3]	1P[4]	2P[4]	MtHxE[5]	MtOcE[6]	Alc[7]	MeOH conv[8a]	MeOH conv[8b]	α-ole conv[9]	sel[10]
B1	23DM1B	80	2	2:1	10		8.5	63			27		1.5	55	54	91	0.43
B2	23DM2B						3.1	84			11		1.9	---	---	---	---
P1	244TM1P								85	8.0		7.0		14		15	0.88
P2	244TM2P								5.0	92		3.0		---	---	---	---
P3	244TM1P	70	1	2:1	10				96	2.2		2.5		5.0		4.7	1.1
P4			2						92	3.4		5.1		10		8.5	1.5
P5			4						87	5.4		7.5		15		13	1.4
P6			8						82	9.2		9.0		18		18	0.98
P7			24						70	20		9.6		19		30	0.48
P8		80	0.25						93	3.3		3.8		7.6		7.1	1.2
P9			0.5						91	4.3		5.0		10		9.3	1.2
P10			1						84	8.5		7.8		16		16	0.92
P11[11]			2						85	8		7.3		15		15	0.91
P12			4						77	16		7.6		15		23	0.48
P13		100	0.25						80	14		5.4		11		20	0.39
P14			0.5						76	18		5.6		11		24	0.31
P15			1						76	18		6.2		12		24	0.34
P16			2						79	16		5.4		11		21	0.34
B3	23DM1B	60	2	2:1	10		60	18			16		4.3	34	33	36	0.89
B4		70					14	53			32		1.2	65	64	86	0.6
B5[12]		80					8.5	63			27		1.5	55	54	91	0.43
B6		100					6.8	61			30		2.4	61	60	93	0.49

Table 3.1 (cont.)

Run No.	olefin	temp [°C]	time [hr]	$r_{O/A}$[1]	cat'st [wt%]	$r_{R/S}$[2]	1B[3]	2B[3]	1P[4]	2P[4]	MtHxE[5]	MtOcE[6]	Alc[7]	MeOH conv[8a]	MeOH conv[8b]	α-ole conv[9]	sel[10]
B7	23DM1B	70	4	2:1	10		6.4	58			34		1.3	69	68	93	0.59
B8			6				6.3	60			34		0.8	68	67	94	0.57
B9			8				4.9	58			36		0.87	73	72	95	0.62
B10			24				6.8	59			30		4.5	63	60	93	0.51
B11	23DM1B	70	2	1:8	10		5.9	36			54		3.9	7.0	7.0	94	1.5
P17	244TM1P	70	1	1:8	10				82	5.3		13		1.6		18	2.5
P18			2						73	9.2		18		2.2		27	2.0
B12[13]	23DM1B	70	2	2:1	10		7.2	59			33		1.2	67	66	93	0.56
B13	23DM1B	70	2	1:8	20		2.2	29			66		2.3	8.5	8.3	98	2.3
B14					30		1.1	27			66		5.8	8.8	8.3	99	2.4
B15					CR[14]		2.6	29			65		3.2	8.4	8.1	97	2.2
P19	244TM1P	70	2	1:8	20				63	14		23		2.9		37	1.7
P20					30				62	16		22		2.8		38	1.4
P21					CR[14]				73	9.0		18		2.2		27	2.0
B16[15]	23DM1B	70	2	1:8	5:0		5.2	33			59		3.1	7.6	7.4	95	1.8
B17[15]					5:7.5		16	32			50		2.6	6.4	6.2	84	1.6
P22[15]	244TM1P				10:7.5				77	7.1		15		1.9		22	2.1
P23[15]					0:7.5				99	0.4		0		0		0.4	0

Table 3.1 (cont.)

Run No.	olefin	temp [°C]	time [hr]	$r_{O/A}$[1]	cat'st [wt%]	$r_{R/S}$[2]	1B[3]	2B[3]	1P[4]	2P[4]	MtHxE[5]	MtOcE[6]	Alc[7]	MeOH conv[8a]	MeOH conv[8b]	α-ole conv[9]	sel[10]
B18	23DM1B	70	2	1:8	10	1:1	16	37			45		2.0	5.7	5.6	84	1.2
B19						2:1	41	27			30		1.7	3.8	3.8	58	1.1
B20					20	1:1	8.3	42			47		2.1	6	5.9	91	1.1
B21						2:1	22	38			38		2.0	4.8	4.8	78	1.0
B22			4		10	1:1	11	41			45		2.1	5.8	5.7	89	1.1
P24	244TM1P	70	2	1:8	10	1:1			89	3.6		7.9		0.98		11	2.2
P25						2:1			93	2.5		4.8		0.6		7.3	1.9
P26					20	1:1			83	5.4		11		1.4		16	2.0
P27						2:1			90	3.4		7.1		0.88		10	2.1
P28			4		10	1:1			84	5.5		11		1.4		16	2.0

1. $r_{O/A}$: molar ratio between olefin and methanol
2. $r_{R/S}$: mass ratio between reactants and decalin
3. 1B: 2,3-dimethyl-1-butene (23DM1B); 2B: 2,3-dimethyl-2-butene (23DM2B)
4. 1P: 2,4,4-trimethyl-1-pentene (244TM1P); 2P: 2,4,4-trimethyl-2-pentene (244TM2P)
5. MtHxE (methyl tertiary hexyl ether): 2-methoxy-2,3-dimethylbutane
6. MtOcE (methyl tertiary octyl ether): 2-methoxy-2,4,4-trimethylpentane
7. Alc: 2,3-dimethyl-2-butanol (23DM2BOH)

3-7: mole scheme in product, methanol free basis

8a. Conversion of methanol (%) in the absence of alcohol as a product

8b. Conversion of methanol (%) in the presence of alcohol as a product

9. Conversion of α-olefin (%)
10. Selectivity (molar ratio of ether in product to β-olefin in product)
11. Duplicates run P1 to verify reproducibility
12. Duplicates run B1 to verify reproducibility
13. 5.5 MPa
14. CR: crushed Amberlyst 15, 10 wt %
15. wt % Amberlyst 15/ wt % HZSM-5

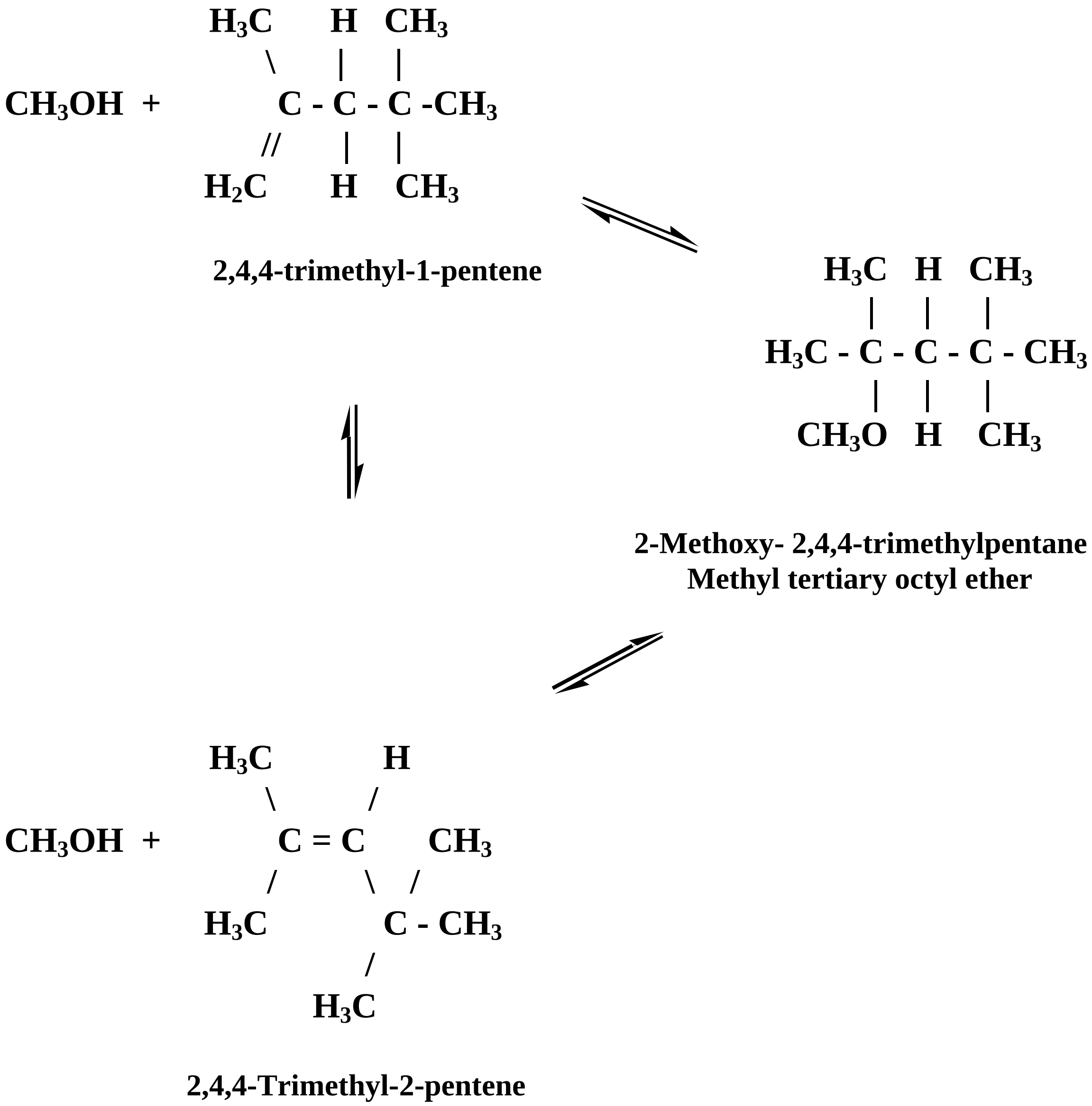


Figure 3-1

Reaction Scheme for Etherification of the 2,4,4-Trimethylpentenes with Methanol

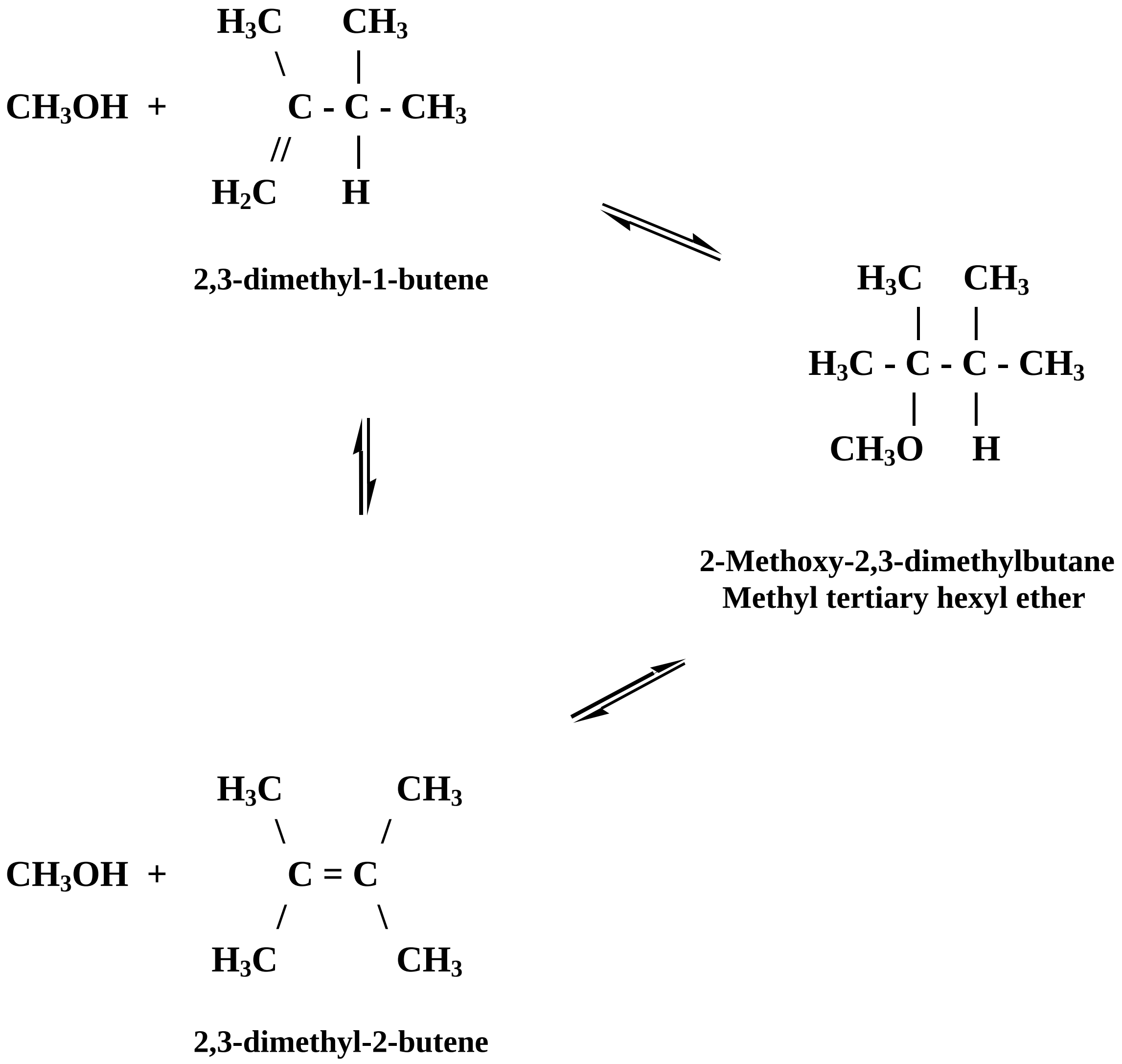


Figure 3-2

Reaction Scheme for the Etherification of the 2,3-Dimethylbutenes with Methanol

rearranged forming 22% of the 2-pentene isomer, while the 2-pentene isomer rearranged yielding 80% of the 1-pentene isomer. After reacting for 2 hr, the product distributions from both isomers were similar. Similar results were obtained for the C_6-olefin. After 2 hr of catalytic reaction, regardless of the initial isomer, the reaction composition was similar, yielding ~ 90% 23DM2B.

When the 2-pentene isomer was reacted in the presence of methanol, 3 mole% of the ether (run P2), 2-methoxy-2,4,4-trimethylpentane (MtOcE; methyl tertiary octyl ether), was formed while the 1-pentene isomer yielded 7 mole% of MtOcE (run P1). Similarly, the reaction with 2-butene yielded 11 mole% (run B2) 2-methoxy-2,3-dimethylbutane (MtHxE; methyl tertiary hexyl ether), while the 1-butene ismer yielded 27 mole% of MtHxE (run B1). In both cases, the reaction of the α-olefin isomer with methanol was favored. Hence, once the 2-butene or 2-pentene isomer was formed, the reaction proceeded very slowly yielding much less ether than the 1-butene or 1-pentene in an equivalent amount of time. It may be noted that the β-olefin is structurally more stable than the α-olefin and is, consequently, less reactive in etherification [75].

In many experimental studies of the synthesis of higher ethers from mixtures of methanol and olefins, ether compounds have been the primary products along with small amounts of alcohols [63, 76, 77]. In this study, the formation of 2,3-dimethyl-2-butanol (23DM2BOH) from C_6-olefin and water was detected as a side reaction in all the C_6-olefin runs. Under identical conditions, no hydration of the C_8-olefin was observed. The presence of a higher alcohol in the products from the C_6-olefins reactions indicates a small amount of water may have been present in the reactants, or may have adsorbed onto the surface of the Amberlyst during weighing and loading. Pretreatment of the Amberlyst by drying in a vacuum oven at 90 ^oC overnight did not reduce the amount of higher alcohol formed, so the pretreatment process was abandoned and the Amberlyst was used as received thereafter.

3.2.1. Effect of Reaction Temperature and Time

The effect of reaction temperature and time on the production of ethers from 244TM1P and 23DM1B was evaluated. The production of MtOcE from 244TM1P in reactions performed at 70, 80 and 100 ^oC (runs P3-P16) is shown in Table 3-1. The reactions performed at 70 ^oC from 1 to 24 hrs (runs P3-P7) showed an increase in ether production from 2.5 to ~10 mole%. The reactions performed at 80 ^oC (runs P8-P12) and 100 ^oC (runs P13-P16) produced similar amounts of ether as the 70 ^oC reaction but at shorter reaction times. The amount of rearrangement of the 1-pentene isomer to the 2-pentene isomer increases as both temperature and reaction time are increased (Figure 3-3). Ether production from 23DM1B after 2 hr reactions at 70, 80 and 100 ^oC (runs B4-B6) was not greatly affected by temperature, with all the reactions yielding 30 to 32 mole% ether (Figure 3-4). However, a substantial increase in ether production from 16 to 27 mole% was observed between 60 and 70 ^oC (runs B3 and B4). The effect of longer reaction times of 2, 4, 6, 8 and 24 hr was minimal on ether production, which ranged from 30 to 36 mole% (runs B4, B7-B10). In all of these reactions, the amount of rearrangement to 23DM2B was substantial, yielding nearly 60 mole% of the 2-butene

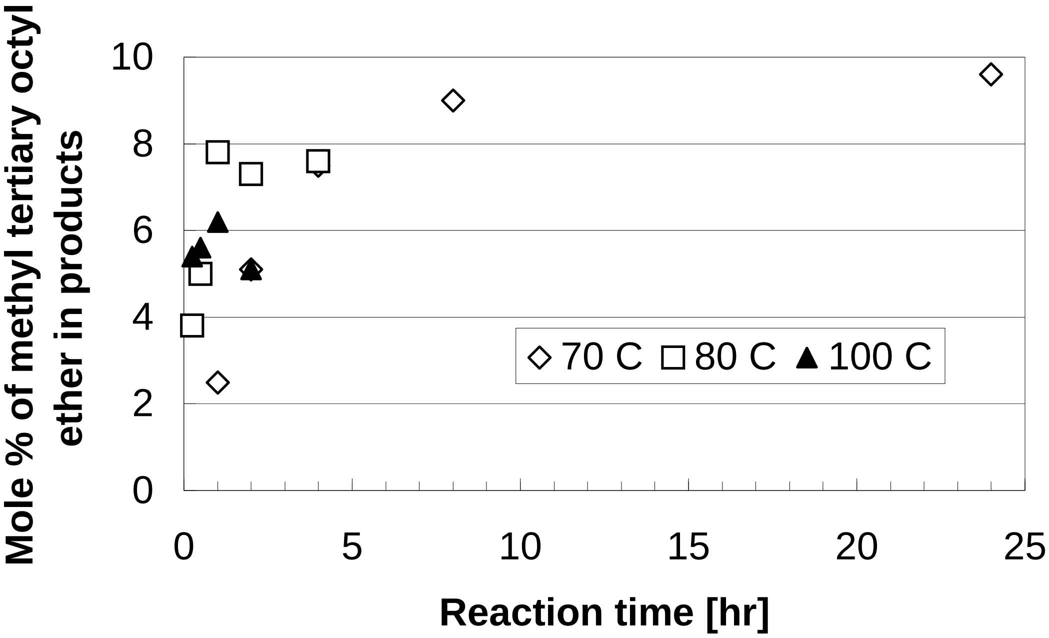


Figure 3-3

Effect of reaction temperature in the production of C_9-ether from C_8-olefin and methanol. $r_{O/A}$ = 2:1, 10 wt% of Amberlyst 15 (runs P3-P16).

isomer after 6 hr (runs B8-B10), as shown in Figure 3-5. The effect of temperature on the isomerization of C_6-olefins is more significant than it is on C_8-olefins.

The reactivity of 23DM1B increases greatly (from 36 to 86%) in the temperature range from 60 to 70 ^{o}C (runs B3 and B4) but increases only slightly (from 86 to 93%) in the temperature range from 70 to 100 ^{o}C (runs B4-B6), as shown by the conversion of 23DM1B (Figure 3-6). The conversion is approaching a limiting value at temperatures over 70 ^{o}C. This partially explains why there is such a dramatic increase in ether

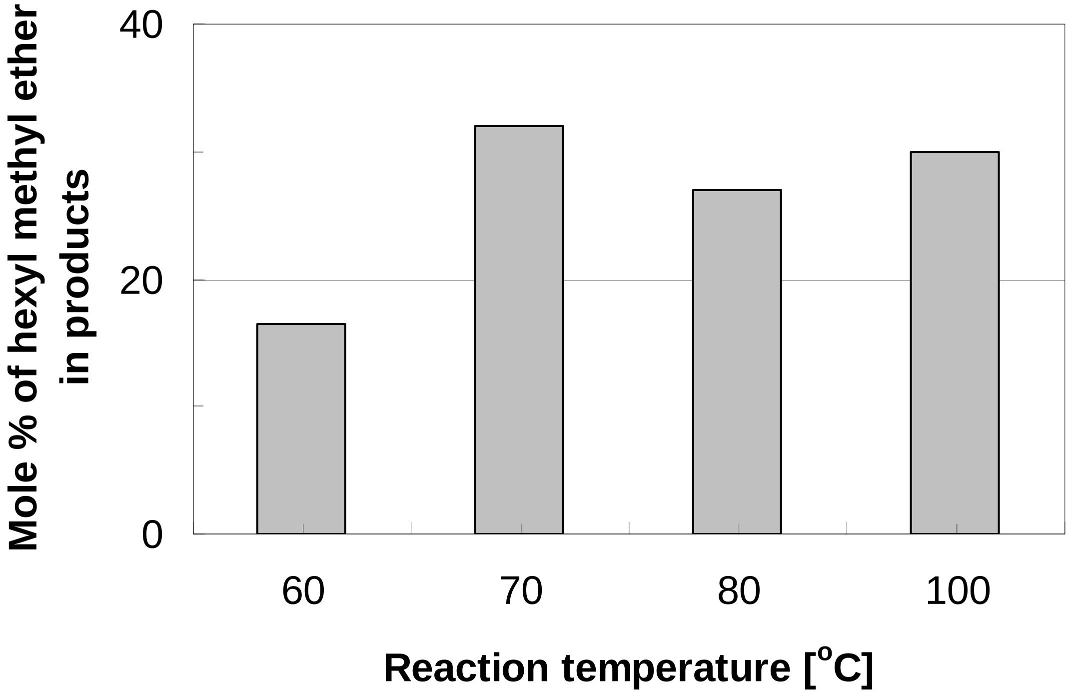


Figure 3-4

Effect of reaction temperature in the production of C_7-ether from C_6-olefin and methanol. reaction time = 2 hr, $r_{O/A}$ = 2:1, 10 wt% of Amberlyst 15 (runs B3-B6).

production in the temperature range from 60 to 70 ^oC, but no temperature effect is observed after 70 ^oC.

It should also be noted that the selectivity to MtHxE production drops markedly in the range from 60 to 80 ^oC. The lower temperature gave good selectivity but low yields due to the low conversion. Increasing the temperature to enhance the reactivity resulted in too much α-olefin being converted to the less reactive β-olefin. Therefore, the choice

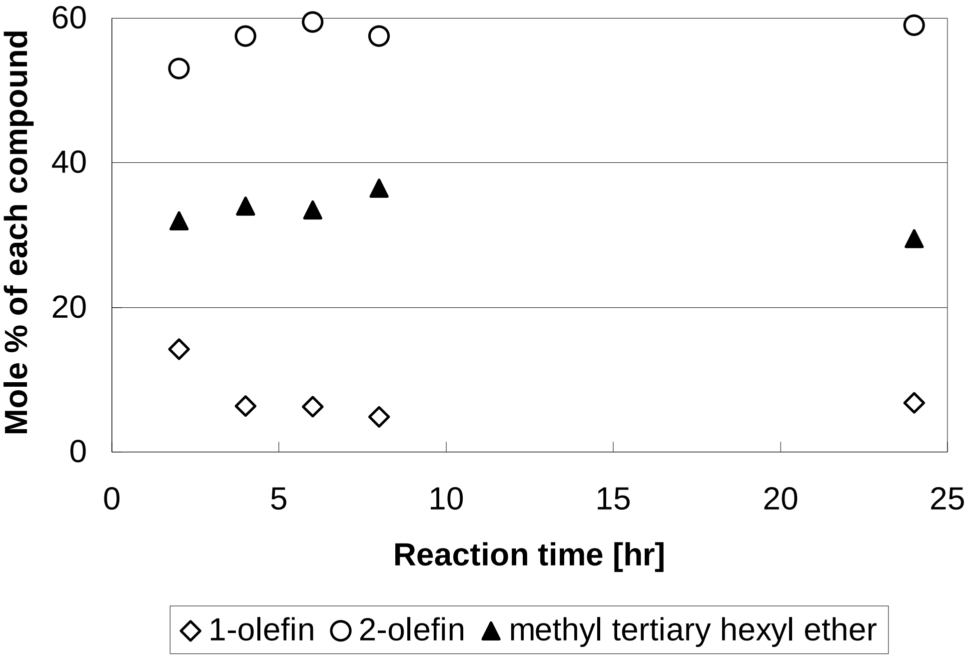


Figure 3-5

Effect of reaction time in the production of C_7-ether from C_6-olefin and methanol. reaction temperature= 70 ^oC, $r_{O/A}$ = 2:1, 10 wt% of Amberlyst 15 (runs B4, B7-B10)

of an optimum temperature for ether synthesis must involve a trade-off between α-olefin conversion and selectivity to ether production. From Figure 3-6, the optimum temperature for MtHxE synthesis seems to be about 70 ^oC.

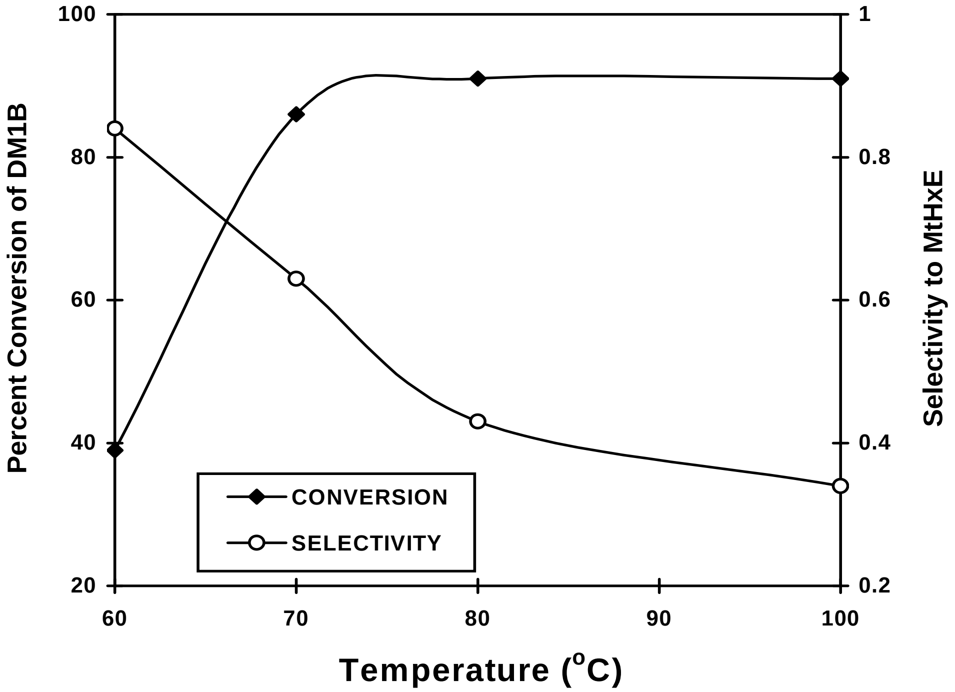


Figure 3-6

Effect of reaction temperature in the production of C_7-ether from C_6-olefin and methanol. reaction time = 2 hr, $r_{O/A}$ = 2:1, 10 wt% of Amberlyst 15 (runs B3-B6).

Similar results were obtained for the production of MtOcE, with the optimum temperature being about 80 °C. However, so that direct comparisons could be made between the reactivities of C_6- and C_8-olefins, a temperature of 70 °C was used for the reactions of both olefins in subsequent experimentation.

3.2.2. Effect of Olefin to Methanol Ratio

Another important reaction condition, the molar ratio between olefin and methanol, was also investigated because it affects the mechanism in the course of etherification [102], as well as the product distribution. The reactions discussed heretofore used a 2:1 olefin to methanol ratio. This ratio was selected because the methanol, which is ultimately to be derived from synthesis gas, would most likely react as soon as it is formed. The amount of ether produced using the 2:1 olefin to methanol ratio was only about 35%. In order to increase the yields of ethers from olefins, it was decided to employ a large excess of methanol in subsequent reactions. The molar ratio of olefin to methanol selected was 1:8. Several parametric factors may have affected the conversion of olefin to ether. Figure 3-7 shows that changing the ratio between olefin and methanol from 2:1 to 1:8 has a significant effect on product yields at both 1 (run P3 and P17) and 2 hr (run P4 and P18) reaction times when 244TM1P reacts with methanol. Similar experimental results were obtained for the reaction of 23DM1B with methanol at 2 hr. In the 1-butene reaction at a 1:8 ratio an additional as yet unidentified product was formed. The amount of ether formed using the 1:8 olefin to methanol ratio was nearly double that obtained in the reaction with the 2:1 ratio (runs B4 and B11). In the 1-pentene reaction, the increased ratio had the effect of more than tripling the ether formation (runs P3 and P17, P4 and P18), indicating that the reaction had been limited for the methanol reactant. This result is in good agreement with the results of other researchers [63, 103].

The conversion of 23DM1B increased slightly (less than 10%) when the molar ratio of olefin to alcohol was changed from 2:1 to 1:8, while the selctivity to MtHxE production increased by a factor of 2.5 (runs B4 and B11). The enhanced selctivity due to the presence of excess methanol explains the increased ether production. In the case of 244TM1P, both olefin conversion and selectivity were significantly increased (runs P3 and P17, P4 and P18).

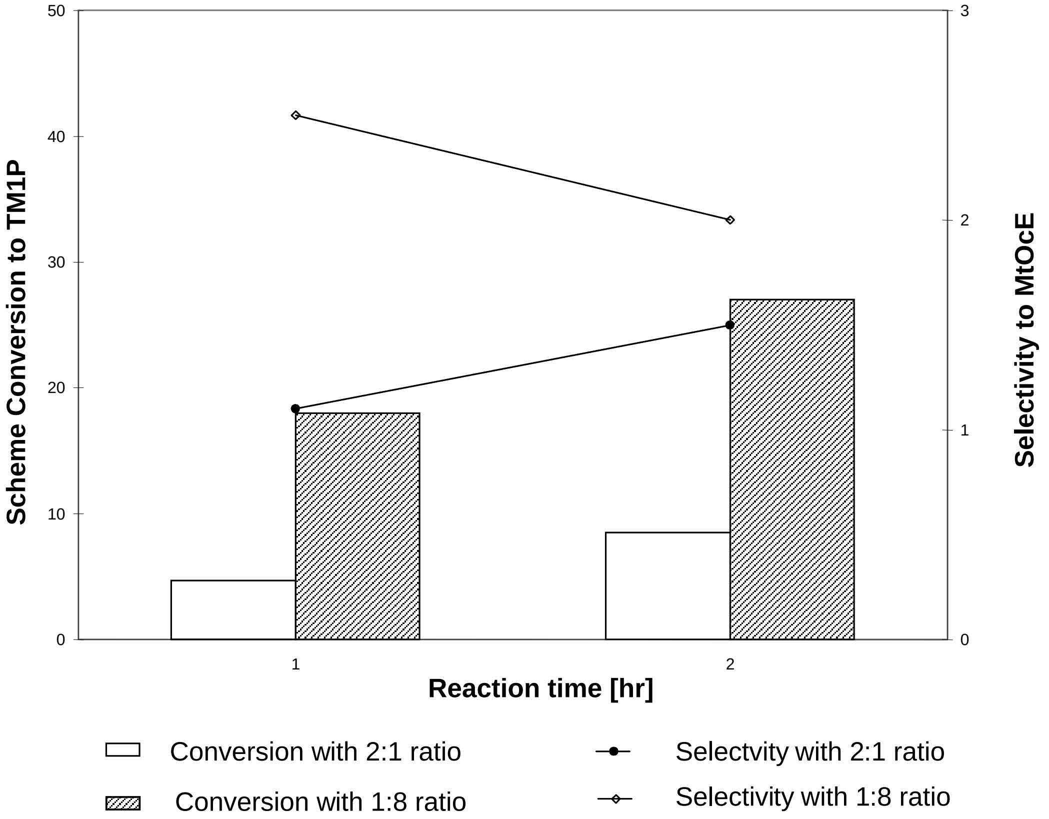


Figure 3-7

Effect of molar ratio between olefin and alcohol in the production of C_9-ether from C_8-olefin and methanol. Reaction temperature = 70 ^oC, 10 wt% of Amberlyst 15 (runs P3 and P17, P4 and P18).

3.2.3. Effect of Catalyst Loading

The effect of catalyst loading on the conversion of 23DM1B and 244TM1P was also determined. The initial catalyst loading (single loading, Amberlyst 15 dry, as received) was 10 wt% of the total reactor charge. Tests were also conducted using one-half, double and triple the single loading, or 5 wt%, 20 wt% and 30 wt% of the total reactor charge, respectively. In addition, the single loading was crushed and tested to ensure that the process was not diffusion limited. In the case of the C_6-olefin, crushing the Amberlyst had very little effect on the olefin conversion, but a significant effect on the selectivty to MtHxE production (runs B11 and B15). The etherification yield was increased by about 20%, indicating that the methanolation may be diffusion limited. Curiously, no such limitation was observed in the case of the C_8-olefin, with the results obtained for conversion, selectivity and ether production all being identical with the values obtained using an equal weight of uncrushed catalyst (runs P18 and P21) .

For the C_6-olefin, the one-half, single and double loading of catalyst all gave ether yields in the 54 to 58 mole% range at a reaction temperature of 70 ^oC and reaction time of 2 hrs (runs B16, B11and B13). The triple loading increased the etherification yield to 66 mole%, an increase of about 20% (run B14). For the C_8-olefin, the yield of ether from the single loading was 18 mole% (run P18). Both the double and triple loading of catalyst increased the ether production from 244TM1P (runs P19 and P20), but the yield seems to have reached a maximum at about 22% by the time the double loading was reached. As in the case of the C_6-olefin, the increase in yield from tripling the catalyst loading was about 20%. From a process economics standpoint, doubling or tripling the catalyst loading to effect a 20% increase in product yield would probably not be justified because of the cost of maintaining the catalyst in the reaction system. Therefore, the optimum catalyst loading seems to be in the 5 to 10 wt% range.

3.2.4 Effect of reaction pressure

Since it may be necessary to employ high pressures to drive the conversion of synthesis gas to methanol in the single-step etherification reactor, the effect on etherification yields of an increase in reaction pressure was also investigated. The reactions described above were performed under a 1.5 MPa hydrogen blanket. Increasing the pressure from 1.5 MPa to 5.5 MPa hydrogen in the reaction that utilized a 2:1 ratio of 23DM1B to methanol and reaction time of 2 hr had very little effect on the etherification yield (runs B4 and B12).

3.2.5 Effect of reaction medium

Since the single-step etherification reactor will likely utilize a slurry phase design, the effect of employing an inert diluent on etherification yields was also investigated. In the reactions described above, the reactants were introduced into the reaction vessel and allowed to react, i.e., no diluent was employed. In order to investigate the effect of an inert reaction medium, decalin (*cis:trans* = 50:50) was employed as diluent in the following reactions.

In the case of the C_6-olefin, when the reactants were diluted with decalin at a 1:1 combined reactants to solvent mass ratio, the amount of ether produced decreased due to the reduction in concentration of the reactants (runs B11 and B18, runs B13 and B20). This concentration effect is even more evident when the ratio between reactants and solvent is decreased to 1:2 (runs B18 and B19, runs B20 and B21). This effect of dilution was also observed in the reaction with the C_8 olefin (compare runs P18, P24 and P25, and P19, P26 and P27), as shown in Figure 3-8. For 23DM1B, doubling the amount of Amberlyst in the 1:1 diluted reaction mixture gave a slight increase (< 5%) in yield of MtHxE (runs B18 and B20), while doubling the amount of Amberlyst in the 1:2 diluted reaction mixture gave an increase of over 25% in yield of MtHxE (runsB19 and B21).

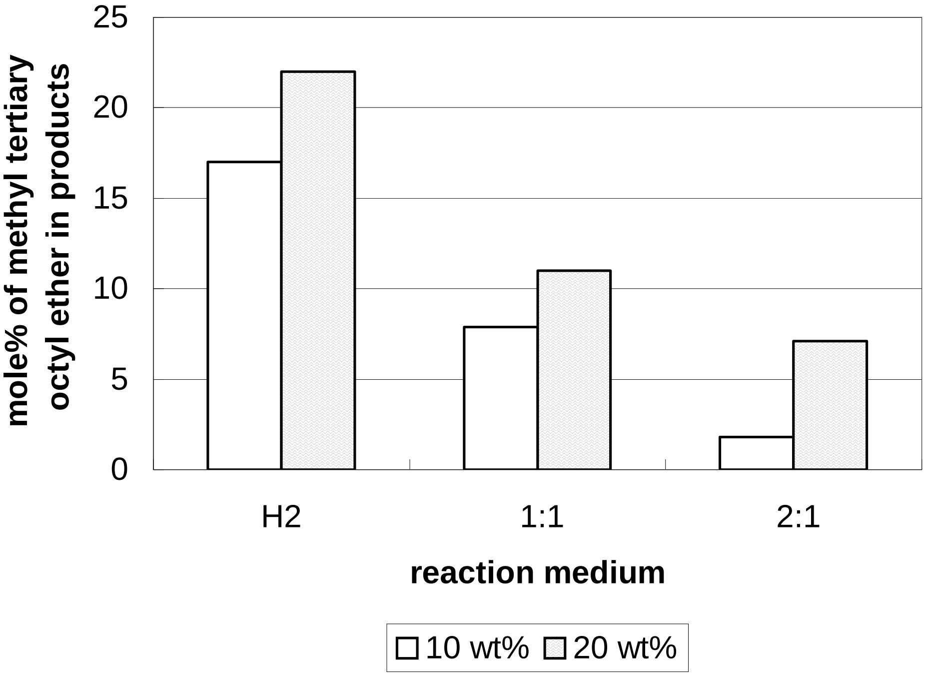


Figure 3-8

Effect of reaction medium in the production of C_9-ether from C_8-olefin and methanol. Reaction temperature = 70 °C, reaction time = 2hr, $r_{O/A}$ = 1:8, 10 wt% of Amberlyst 15 (runs P18, P24, and P25 and P19, P26, and P27).

For 244TM1P, doubling the amount of Amberlyst in the 1:1 diluted reaction mixture gave an increase of over 45% in yield of MtOcE (runs P24 and P26), while doubling the amount of Amberlyst in the 1:2 diluted reaction mixture gave an increase of over 35% in yield of MtOcE (runs P25 and P27). It is interesting to note that while the amount of diluent and catalyst employed affected the conversions of α-olefins, the selectvity to ether production remained fairly constant. For 23DM1B, the selectivty to MtHxE production stayed at about 1.1, while for 244TM1P, the selectivity to MtOcE production stayed at about 2.0.

3.2.6 Effect of the methanol synthesis catalyst

The effect of employing dual catalysts of both Amberlyst 15 and methanol synthesis catalyst on etherification yields was also investigated. The methanol synthesis catalyst itself, HZSM-5, showed no etherification activity, nor did it promote isomerization of the olefin (run P23). In mixed catalyst testing, at mass ratios of 1:1.5 (run B17) and 1.33:1 (run P22) of Amberlyst 15 to HZSM-5, the methanol synthesis catalyst had little or no effect on etherification yields.

3.2.7 Analysis of Variance (ANOVA)

The statistical experimental design method of ANOVA was applied as a means of interpreting the degree of importance of catalyst loading and reaction medium on the production of methyl tertiary hexyl ether and methyl tertiary octyl ether. Production of methyl tertiary hexyl ether was performed at six different combinations of catalyst loading (10 and 20 wt%) and reaction media (200 psig H_2, 1:1, and 1:2 reactants to decalin) at 70 ^{o}C, 2 hr reaction time, and 1:8 ratio of 23DM1B to methanol (runs B11, B13, B18~B21). Synthesis of methyl tertiary octyl ether was also performed at six different combinations using the same catalyst loadings, reaction media, temperature, reaction time and olefin to methanol ratio (runs P18, P19, P24~P27).

A reaction time of two hours, temperature of 70 ^{o}C, and a ratio between olefin and methanol of 1:8 seem to be reasonable reaction conditions to produce the higher carbon ether compounds. Two reaction parameters, catalyst loading and reaction medium, were selected, and their effect on the production of methyl tertiary hexyl ether and methyl tertiary octyl ether was determined. Tables 3-2 and 3-3 show the results of the ANOVA.

Table 3-2

ANOVA of MtHxE production from 23DM1B and methanol

		production of methyl tertiary hexyl ether		
Factor[a]	df[b]	SS[c]	MS	Fo
Total	5	453		
C	1	92.83	92.83	5.52[d]
R	2	326.52	163.26	9.70[e]
C*R	2	33.65	16.83	
Residual[f]	2		16.83	

[a] C = catalyst loading and R = reaction medium

[b] df=degree of freedom

[c] SS = sum of squares, MS = mean square = SS/df, and Fo = F distribution points

[d] Significant at 25%

[e] Significant at 10%

[f] Residual is the interaction of C*R

Table 3-3

ANOVA of MtOcE production from 244TM1P and methanol

		production of methyl tertiary octyl ether		
Factor[a]	df[b]	SS[c]	MS	Fo
Total	5	278.92		
C	1	25.63	25.63	42.02[d]
R	2	257.07	128.535	210.71[e]
C*R	2	1.22	0.61	
Residual[f]	2		0.61	

[a] C = catalyst loading and R = reaction medium

[b] df=degree of freedom

[c] SS = sum of squares, MS = mean square = SS/df, and Fo = F distribution points

[d] Significant at 2.5%

[e] Significant at 1%

[f] Residual is the interaction of C*R

A residual mean square was created by pooling sums of squares and degrees of freedom from sources of variation that were obviously statistically weak or insignificant to conduct the ANOVA statistical tests. The details of these calculations are available elsewhere [104].

The ANOVA presented in Table 3-2 shows that catalyst loading and reaction medium were significant at the 25% and 2.5% level for the production of methyl tertiary hexyl ether, respectively. The ANOVA presented in Table 3-3 indicates that catalyst loading and reaction medium were significant at the 2.5% and 1% level for the production of methyl tertiary octyl ether, respectively.

4. Conclusions and Future Work

The feasibility of producing the higher ethers 2-methoxy-2,3-dimethylbutane (methyl tertiary hexyl ether) and 2-methoxy-2,4,4-trimethylpentane (methyl tertiary octyl ether) from olefins (2,3-dimethyl-1-butene; 2,3-dimethyl-2-butene and 2,4,4-trimethyl-1-pentene; 2,4,4-trimethyl-2-pentene, respectively) and methanol has been demonstrated at temperatures between 70 and 100 ^{o}C. Branched olefins have a greater reactivity than straight chain olefins and are better candidates for producing higher ethers for use as fuel additives. β-olefins are structurally more stable than α-olefins and are, consequently, less reactive in etherification.

Increasing the amount of methanol available for the reaction raised the ether production to a reasonable level. Temperatures in the range from 70 to 100 ^{o}C were found to be suitable for ether production. However, the rate of isomerization between α- and β-olefins increases with increasing temperature, yielding more of the less reactive β-olefin. Therefore, serious consideration must be given to both the etherification reaction and the isomerization reaction when choosing the optimum temperature at which to conduct this synthesis.

The concentration of reactants played a key role in determining the rate of formation of ether compounds. The reactivity of C_6-olefins in etherification with methanol was greater than that of C_8-olefins.

The authors fully appreciate that there are conflicting thermodynamic constraints here. On the one hand, the concentration of methanol should be kept to a minimum in order to drive the methanol synthesis reaction. On the other hand, high concentrations of methanol help shift the etherification equilibrium to ether. These conflicting constraints present just one of the challenges to the single-step etherification reactor design.

The next challenge will be the selection of the low-temperature methanol synthesis process that is the most compatible with the etherification reaction. The optimization of the various reaction parameters (temperature, pressure, reaction time, catalyst loading, mass ratio of etherification catalyst to methanol synthesis catalyst, molar ratio of synthesis gas feed to olefin feed, recycle ratio of unreacted reactants, etc.) should provide promising avenues for future research.

CHAPTER IV

METHYL TERTIARY HEXYL ETHER AND METHYL TERTIARY OCTYL ETHER AS GASOLINE OXYGENATES: ASSESSING RISKS FROM ATMOSPHERIC DISPERSION AND DEPOSITION

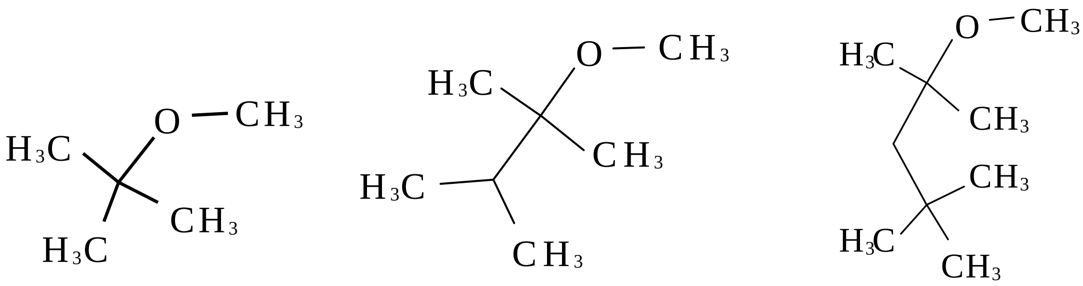
Homologues of methyl tertiary butyl ether (MtBE) are currently being developed as replacement oxygenates for MtBE in gasoline [6, 7], and have also been proposed for use as ultra-clean diesel fuels [8]. Increasing the hydrocarbon content of an ether reduces both the vapor pressure and water solubility [105]. Compared to MtBE, the lower volatility and water solubility would be expected to result in lower environmental exposure for the higher homologues. Two homologues of MtBE are of particular interest because they can be prepared from readily available olefinic feedstocks. These two homologues are methyl tertiary hexyl ether (MtHxE) and methyl tertiary octyl ether (MtOcE). Beginning in 1995, limited quantities of MtHxE were introduced into Finnish gasolines as a supplementary oxygenate to MtBE [14].

Commercially, MtBE is prepared almost exclusively by the methanolation of the four-carbon olefin isobutylene, the isobutylene being available in commercial quantities from petroleum refinery cracking processes. Similarly, the methanolation of olefins of carbon numbers C_6 and C_8 is the most likely industrial route to MtHxE [73, 106] and

MtOcE [63]. However, the quantity of higher olefins in refinery cracking streams is limited and decreases with increasing carbon number after C_5 [70]. It may be that the most feasible industrial route to these ethers is by the methanolation of the dimerization products of propylene [76, 107] and isobutylene [66, 108], respectively. Both propylene and isobutylene are readily available from cracking streams, and are easily dimerized to dipropylene (a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) and di-isobutylene (a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene), respectively.

Although there are three isomers of MtHxE and seventeen isomers of MtOcE [109], the methanolation of dipropylene leads only to the methyl tertiary hexyl ether designated as 2-methoxy-2,3-dimethylbutane (CAS # 26356-10-5), while the methanolation of di-isobutylene leads only to the methyl tertiary octyl ether designated as 2-methoxy-2,4,4-trimethylpentane (CAS # 62108-41-2), in accord with Markovnikov's rule. Figure 4-1 presents the chemical structures of these compounds. Because of the potential importance of higher ethers as high production volume (HPV) fuel blend components, a number of studies of the preparation of MtHxE and MtOcE have recently appeared in the literature [63, 76, 78, 80, 108, 110].

As was the case with MtBE, the introduction of these ethers into fuel supplies also guarantees their introduction into the environment. It is therefore of interest to assess the potential risk that these higher ethers may pose to the environment. In this chapter, a simple box model was employed to predict the atmospheric concentrations of these homologues of MtBE that might be expected in an urban airshed if either MtHxE or



Methyl t-Butyl Ether
MtBE

Methyl t-Hexyl Ether
MtHxE (Dimethyl-MtBE)

Methyl t-Octyl Ether
MtOcE (t-Butyl-MtBE)

Figure 4-1

Chemical Structures of MtBE, MtHxE and MtOcE

MtOcE were to completely replace MtBE in reformulated gasoline (RFG). Ambient air concentrations of these ethers were also assessed using a multimedia, steady-state equilibrium (Mackay Level III) model [111], which simultaneously predicts the expected concentrations of these contaminants in the various environmental media of air, water, soil and sediment. The predicted environmental concentrations were then compared to the concentrations that might be expected to cause adverse effects to humans or ecosystems, thereby giving an indication of risk.

Modeling Considerations and Parameter Estimation

The model chosen for the current study is from the recently published work of Kawamoto et al. [112], who developed a model that correlates MtBE emissions in an RFG usage area with ambient MtBE concentrations measured in the local airshed. They further showed that all the modeling calculations could be performed without extensive *a priori* information about the behavior of MtBE in the environment or in gasoline. This is of particular interest to the current work because there is little or no physicochemical or environmental property data available for MtHxE and MtOcE. The most important implication of their study is that careful analysis of emissions and transport can be used as a screening tool to evaluate expected urban air concentrations of volatile components of future fuel formulations. Ambient air concentration estimates, along with appropriate intermedia partition coefficients and degradation rate constants, can then be used to estimate the concentration of ethers in water, soil and sediment. The predicted concentrations within these media can be compared to the levels that are expected to pose a threat to humans or have ecotoxicological consequences, thereby giving an indication of risk.

Because the principal sources of releases of volatile gasoline components are evaporation and tailpipe emissions [113, 114], these releases are highly dispersed and diffuse. Therefore, the multimedia fate model is suitable for quantitatively predicting exposure concentrations for these ethers by atmospheric dispersion and deposition [115]. Pierson et al. [116], estimated that nontailpipe emissions from automobiles may increase by a factor of four in the interval from -5 ^{o}C to 20 ^{o}C. Therefore, the emissions loading input to the model was seasonally adjusted, assuming a temperature of -5 ^{o}C in the winter and 20 ^{o}C in the summer. Apart from this seasonal adjustment, we assumed a relatively constant diurnally averaged loading of ethers to the atmosphere. This allowed the application of a multimedia steady-state (Level III) model [111] that subdivides the environment into a number of homogeneous compartments, with chemical equilibrium within, but not between, the compartments. Since transient or impulsive releases of ethers to the atmosphere, such as those typically produced by spills, will likely account for only a very small fraction of the total released, the Level III model is sufficiently complex for the present purpose and application of a dynamic Level IV-type model is not necessary [117].

MtHxE and MtOcE may also pose a threat to the environment if they are released from leaking underground fuel tanks (LUFT). The principal danger here is the contamination of groundwater supplies. As was the case with MtBE, this will constitute a highly localized issue and, as such, is not well modeled by the regional equilibrium compartmentalization type models. The potential impact on groundwater resources of leakage of these ethers from LUFTs is addressed in Chapter V.

Since MtHxE and MtOcE form part of a homologous chemical series with MtBE, the basic mechanisms of transport and reaction in the environment for these compounds are expected to be similar. A model that successfully predicts environmental concentrations of MtBE should also allow for a realistic prediction of environmental concentrations of MtHxE and MtOcE by adjusting the model inputs to reflect the expected emissions loadings of MtHxE and MtOcE and their different physicochemical properties. The model of Kawamoto et al. [112] was adapted for this study because of its ability to successfully predict atmospheric MtBE concentrations in an urban airshed, from which the concentrations of MtBE in other environmental media can be estimated. Reliable estimates of release loads, intermedia partition coefficients, and sink loads are needed to generate meaningful model outputs, i.e., reasonable predictions of steady-state concentrations of ethers in the various environmental media [111].

Because very little data on the properties of MtHxE and MtOcE are available in the literature, it was necessary to employ property estimation methods. The United States Environmental Protection Agency (USEPA) maintains a free, downloadable software package known as the Estimation Programs Interface (EPI Suite) for this purpose on its website [118]. EPI Suite was used to estimate the air-water partition coefficient (Henry's law constant), octanol-water partition coefficient, organic carbon-water partition coefficient, water solubility, and the rate constant for reaction with tropospheric hydroxyl radicals for MtHxE and MtOcE. Where allowed by EPI Suite, when experimental property data were available for a structurally similar compound, in this case MtBE, it was used to adjust the property calculations. Table 4-1 contains the estimated property data for MtHxE and MtOcE, along with other selected property data. Data for MtBE are also presented for comparison.

The Airshed Box Model

Kawamoto [112] and his colleagues showed that adequate estimates of MtBE concentrations in an urban airshed could be generated by using a relatively simple model. The urban airshed that they modeled was the Boston, Massachusetts, primary metropolitan statistical area (PMSA). The simple box model for the Boston PMSA is nested in a box representing the Northeast United States (defined as the states of New York, Rhode Island, Massachusetts, Connecticut, New Hampshire, Vermont and Maine),

Table 4-1

Physicochemical and environmental properties of MtBE, MtHxE and MtOcE

Property	**Value**		
	MtBE	**MtHxE**[a]	**MtOcE**[a]
Molecular formula	$C_5H_{12}O$	$C_7H_{16}O$	$C_9H_{20}O$
Molecular weight (daltons)	88	116	144
Melting point (^oC)	-109	-80	-50
Boiling point (^oC)	55.2	82	121
Henry's Law Constant K_H (-) at 20 ^oC	1.7×10^{-2}	3.3×10^{-2}	5.9×10^{-2}
Henry's Law Constant K_H (-) at -5 ^oC	1.4×10^{-3}	7.8×10^{-3}	1.4×10^{-2}
Vapor pressure (torr) at 20 ^oC	207	69	18
Vapor pressure (torr) at -5 ^oC	66.77	18	2.8
Solubility in water (mg/l) at 25 ^oC	48,000	8900	1400
Log K_{ow} at 25 ^oC	1.0	1.9	2.9
K_{oc} at 25 ^oC (l/kg)	8	17	42
$k_{.OH}$ air (cm^3/molecule/sec)	2.83×10^{-12}	8.91×10^{-12}	6.30×10^{-12}
k for degradation in air (day^{-1}) [b]	0.5 (summer)	1.5 (summer)	1 (summer)
	0.2 (winter)	0.8 (winter)	0.5 (winter)
Half-life in air (days)	1 (summer)	0.5 (summer)	0.6 (summer)
	3 (winter)	1 (winter)	1 (winter)

[a] properties predicted using EPI Suite [118]

[b] derived using an $^{\cdot}OH$ concentration of 2×10^6 molecules/cm^3 (summer) or 1×10^6 molecules/cm^3 (winter) [112]

as shown in Figure 4-2. For the purposes of the current study, a marine area of equal size to the Northeast United States land area was also incorporated in the model, in keeping with the guidelines for EUSES version 2.0, as discussed below.

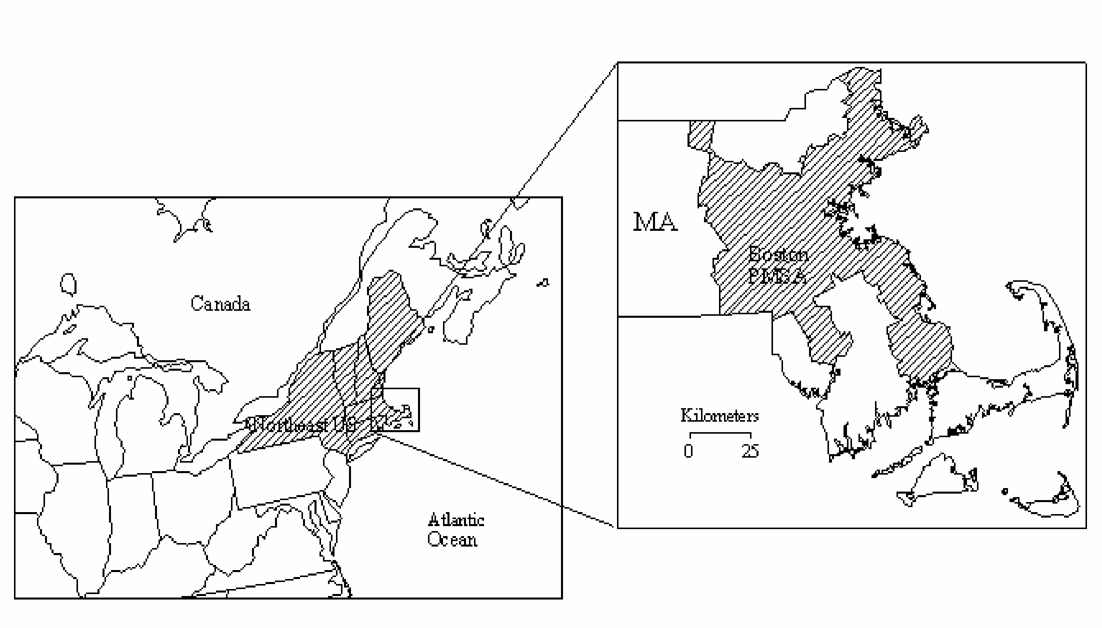


Figure 4-2

Map of the Northeast United States and Boston PMSA

used to parameterize the models (from [112], used with permission)

The basic assumptions of the Kawamoto et al. model are: (1) there is a constant emissions load during each season, adjusted for winter and summer, (2) the air entering the Northeast United States from outside is free of any MtBE, and (3) there are only two sinks, namely advection and reaction with tropospheric hydroxyl radicals. The parameters of the model can be adjusted to reflect seasonal variations in wind velocity, which controls advection, and temperature, which affects the concentration of hydroxyl radicals. The inputs for the model are presented in Table 4-2.

Table 4-2

Environmental characteristics of the Northeast United States and the Boston PMSA [112]

Characteristic	**Northeast United States**	**Boston PMSA**
Population	3.3×10^7	3.3×10^6
Area (km^2)	2.84×10^5	5.17×10^3
	Air	
Box height (m)	900 ± 200 (winter) 1000 ± 300 (summer)	900 ± 200 (winter) 1000 ± 300 (summer)
Temperature (°C)	-5 ± 4 (winter) 20 ± 4 (summer)	-5 ± 4 (winter) 20 ± 4 (summer)
Wind speed at 10 m elevation (m/sec)	4.0 ± 1.2	5.5 ± 1.4 (winter) 3.5 ± 0.9 (summer)
Effective lower troposphere air mass advection rate (m/sec)	8.0 ± 2.4	11.0 ± 2.8 (winter) 7.0 ± 1.8 (summer)
Precipitation (mm/yr)	1100	200 (winter) 470 (summer)
	Water	
Fraction of surface area	0.03	0.05
Average depth (m)	5	5
	Soil	
Volume fraction water	0.2	0.2
Volume fraction air	0.2	0.2
Fraction organic carbon	0.02	0.02
	Sediment	
Volume fraction solids	0.2	0.2
Fraction organic carbon	0.05	0.05

A simple box model, which holds for both the Northeast United States and the Boston PMSA, was applied. Using the stated assumptions, a mole balance on MtBE gives:

$$\frac{dn}{dt} = \text{emissions rate} + C_{\text{air, in}} \frac{dV_{air,\ in}}{dt} - C_{\text{air}} \frac{dV_{air}}{dt} - V_{\text{air}}\, k_{\bullet\text{OH}} [^{\bullet}\text{OH}]\, C_{\text{air}} \qquad (4\text{-}1)$$

where n is the number of moles of MtBE in the box at any time t, *dn/dt* is the rate of accumulation of MtBE in the box (mol/day), the emissions rate is the total of daily emissions within the box (mol/day), C_{air} is the spatially averaged MtBE concentration in the air mass in the box (mol/m^3), $C_{\text{air, in}}$ is the concentration of MtBE in the air entering the box from outside, $k_{\bullet\text{OH}}$ is the rate constant for the reaction with tropospheric hydroxyl radicals (m^3/molecule/day), [$^{\bullet}$OH] is the concentration of tropospheric hydroxyl radicals (molecules/m^3), V_{air} is the volume of the air mass in the box (m^3), and (dV_{air}/dt) reflects the rate at which the air mass volume is flushed with incoming wind (m^3/day). The first term on the right hand side of eq 4-1 represents the emissions load, the second and third terms are the advective load and sink, respectively, and the fourth term is the sink due to reaction with hydroxyl radicals. The air mass flushing rate was determined by assuming a square box model for the airsheds, with heights as listed in Table 4-2; the square root of the total area times the height gave the area normal to the wind. Thus, dV_{air}/dt (m^3/day) is given by the product of the wind velocity (m/day) and the cross-sectional area of the box normal to the wind (m^2) [119]. Diurnally averaged tropospheric hydroxyl radical concentrations for all calculations were assumed to be 2 x 10^6 molecules/cm^3 during the summer months and 1 x 10^6 molecules/cm^3 during the winter months [112].

Under steady-state conditions, the rate of accumulation of MtBE *(dn/dt)* in the box equals zero, and eq 4-1 can be solved for C_{air} in terms of the other (known) variables:

$$C_{air}^{steady-state} = \frac{\text{emissions rate} + C_{air,in}\frac{dV_{air,in}}{dt}}{\frac{dV_{air}}{dt} + V_{air}k_{\bullet OH}[\cdot OH]} \qquad (4\text{-}2)$$

The concentration of MtBE in the air entering the Northeast United States from outside, $C_{air,\ in}$, was set to zero and eq 4-2 was solved to give $C_{air,\ steady\text{-}state}$ for the Northeast United States. Then $C_{air,\ steady\text{-}state}$ for the Northeast United States was applied as $C_{air,\ in}$ for the Boston PMSA, and eq 4-2 was solved again to give $C_{air,\ steady\text{-}state}$ for the urban area. Equation 4-2 applies equally well to MtHxE and MtOcE; the only parameters in need of adjustment being the emissions loadings and the rate constants for the reaction with tropospheric hydroxyl radicals.

Emissions Loadings for MtHxE and MtOcE

Kawamoto et al. [112] provide order of magnitude estimates of MtBE emissions for the Boston PMSA and the Northeast United States, from which emissions of MtHxE and MtOcE can be estimated. Because MtHxE and MtOcE contain more hydrogen and carbon than MtBE, they necessarily contain proportionately less oxygen. Therefore, in order to meet mandated oxygen levels in fuels, they must be blended at higher ratios. MtBE, MtHxE and MtOcE contain about 18, 14 and 11% oxygen, respectively. Therefore, it will require about 32% more MtHxE and about 64% more MtOcE than MtBE in fuels to arrive at the mandated oxygen level.

The overwhelming majority (95+%) of releases of volatile gasoline components to the atmosphere are from a combination of tailpipe and nontailpipe emissions from automobiles [113, 114]. Unfortunately, there is no consensus on which of these two sources is more important, with different studies yielding vastly different results [116]. It is therefore of interest to consider the potential effects of replacing MtBE with MtHxE or MtOcE on both nontailpipe and tailpipe emissions.

MtHxE and MtOcE are significantly less volatile than MtBE (Table 4-1). As a first approximation, Raoult's law may be applied to scale expected evaporative emissions of MtHxE and MtOcE relative to MtBE. Taking into consideration the reduced volatilities and increased concentrations of these ethers in gasoline, Raoult's law calculations indicate that only about half as much MtHxE and about one-seventh as much MtOcE will enter the atmosphere as MtBE. Nontailpipe emissions include hot soak, diurnal, running loss, resting loss, crankcase loss, and refueling operations. There is no field experience with MtOcE to verify the Raoult's law prediction, and field observations with MtHxE are limited to refueling operations. Investigations at two Finnish self-service automobile refueling stations where gasoline containing ~3% each of MtBE and MtHxE was being dispensed revealed that the customers were exposed to about 1/15 as much MtHxE as MtBE [120]. This result strengthens the prediction that evaporative emissions will be reduced, even though the concentrations of higher ethers in gasoline must be greater to achieve the same oxygen levels. However, given that the MtBE emissions estimate used to scale MtHxE and MtOcE emissions estimates is only an order of magnitude estimate [112], Raoult's law calculations do not predict a very significant reduction in evaporative emissions of MtHxE and MtOcE relative to MtBE.

The exhaust emission characteristics of gasoline engines are largely dictated by the type of fuel used [121]. The main parameters affecting tailpipe emissions are density, boiling curve, composition, volatility, heating value, octane rating, and oxygen content [122]. The oxygen content would remain the same if higher ethers were to replace MtBE on an equimolar basis, and the effect on density and heating value would be minimal. While no value for the octane rating of MtHxE was found in the literature, MtBE and MtOcE both have blending octane numbers of 110 [6, 108], and it seems unlikely, from structural analog considerations, that MtHxE would differ very greatly. The major impact of higher ether use would likely be the reduction in volatility and shifting of the boiling curve to higher boilers. It may, therefore, be necessary to blend easily volatilized constituents into the resulting gasoline in order to meet the tunability requirements of spark-ignition engines. This type of component blending is a routine matter at refineries, and is an especially common practice during winter months [122]. Hence, there is nothing to suggest that tailpipe emissions of higher ethers would be significantly different than those found with MtBE usage.

Given that the reduction in nontailpipe emissions from replacing MtBE with higher ethers is probably less than an order of magnitude, and considering the current lack of consensus over which source, tailpipe or nontailpipe, contributes more to overall emissions, we chose to assume a one-to-one correspondence between increased ether levels in fuels and increased ether emissions to the atmosphere. This should suffice to provide risk-conservative "order of magnitude" estimates of ether concentrations in the atmosphere using the appropriate models. Table 4-3 presents the projected order of magnitude emissions loadings for MtHxE and MtOcE if these compounds were to completely replace MtBE in gasolines, independently, for the Northeast United States and the Boston PMSA.

Table 4-3

Emissions Loadings for MtBE, MtHxE and MtOcE (kg/day)

Area	MtBE [a]	MtHxE	MtOcE
Northeast United States	8×10^4 (winter)	1×10^5 (winter)	1.3×10^5 (winter)
	3×10^5 (summer)	4×10^5 (summer)	5×10^5 (summer)
Boston PMSA	6.7×10^3 (winter)	8.6×10^3 (winter)	1.1×10^4 (winter)
	2.7×10^4 (summer)	3.5×10^4 (summer)	4.4×10^4 (summer)

[a] from [112]

EUSES Multimedia Model

The prediction of the steady-state atmospheric concentrations of ethers using the airshed box model described above is straightforward. On the other hand, the calculation of predicted environmental concentrations in the various media of water, soil and sediment requires the simultaneous solution of multiple mass balance and equilibrium equations [111]. To this end, the European Union System for the Evaluation of Substances (EUSES) version 2.0 multimedia environmental fate model was employed [123]. EUSES was designed as a decision-support system to evaluate the risks of commercial and industrial substances to humans and the environment. EUSES 2.0

includes a nested multimedia mass balance model, SimpleBox 3.0, which is equipped to simultaneously calculate steady-state contaminant concentrations in air, water, soil and sediment on regional and continental scales. Based on these predicted environmental concentrations (PEC), the risk assessment module evaluates the potential risk to humans and the environment. The ratio of the PEC to the predicted no-effect concentration (PNEC) defines the risk characterization ratio (RCR) for the compartment; an RCR of unity or greater suggests a potential threat to ecosystems within that compartment and indicates the need for a more rigorous risk assessment. The ratio of the no observed adverse effect level (NOAEL) to the total daily exposure level is termed the margin of safety (MOS) and is used for human exposure risk assessment. An MOS of unity or smaller suggests a potential threat to humans and indicates the need for a more rigorous risk assessment.

EUSES version 2.0 allows the user to define both the regional and the continental scales. For this study, the region was defined to be the Boston PMSA and the continent was defined to be the Northeast United States. This definition of the continent includes the Northeast United States as defined above (exclusive of the Boston PMSA) and an equal area of sea water. Continental tropospheric air mass velocities were used in the EUSES modeling. Unless specified otherwise, EUSES version 2.0 defaults were used for all model parameters. Degradation rates in surface water, soil and sediment were assumed to be zero, and the predicted exposure concentrations are thus conservative.

Estimates of intermedia partition coefficients generated by EPI Suite are generally considered accurate to within about one-half of a log unit [118]. The EUSES model is not particularly sensitive to this level of variability in the partition coefficients. The variability in the predicted rate constants for reaction with tropospheric hydroxyl radical is considered to be about one-eighth of a log unit [123]. Its effect on the variability in the atmospheric degradation sink is small compared to the variability in the emissions load and advective sink. A detailed variability/sensitivity analysis for the airshed box model is presented elsewhere [112].

Predicted Environmental Concentrations of MtHxE and MtOcE

Table 4-4 presents the EUSES predictions for the concentrations of MtBE, MtHxE and MtOcE in the various environmental media. The atmospheric concentrations of these ethers predicted by the airshed box model described above (eq 4-2) are also presented here for comparison. EUSES predicted steady-state atmospheric concentrations of 0.8 and 1 $\mu g/m^3$ for MtHxE and MtOcE in the summer and 0.3 and 0.4 $\mu g/m^3$ for MtHxE and MtOcE in the winter, respectively, in the Boston PMSA. The predicted concentrations for MtHxE and MtOcE in the Northeast United States were 0.3 and 0.4 $\mu g/m^3$ in the summer and 0.1 and 0.2 $\mu g/m^3$ in the winter, respectively. In all cases, the predicted concentrations of MtOcE were greater than those for MtHxE, which is to be expected due to the increased emissions loading.

Atmospheric concentrations of MtHxE and MtOcE predicted by the airshed box model (eq 4-2) were in good agreement with those generated by EUSES. This implied that, according to the EUSES model, the processes reflected in eq 4-2 (emission, advection due to wind, and reaction with hydroxyl radical) constituted the dominant

Table 4-4

Predicted environmental concentrations of MtBE, MtHxE and MtOcE in the Northeast United States and Boston PMSA for two seasons

Predicted Environmental Concentrations	**MtBE**		**MtHxE**		**MtOcE**	
	summer	**winter**	**summer**	**winter**	**summer**	**winter**
			Northeast United States			
In air, box model ($\mu g/m^3$)	0.4	0.1	0.3	0.1	0.4	0.2
In air, EUSES ($\mu g/m^3$)	0.4	0.1	0.3	0.1	0.4	0.2
In surface water, EUSES (μg/liter)	0.02	0.04	0.006	0.009	0.004	0.007
In soil, EUSES (μg/kgdwt)	0.005	0.01	0.005	0.009	0.008	0.01
In sediment, EUSES (μg/kgdwt)	0.06	0.1	0.03	0.05	0.03	0.05
			Boston PMSA			
In air, box model ($\mu g/m^3$)	0.8	0.3	0.9	0.3	1	0.4
In air, EUSES ($\mu g/m^3$)	0.8	0.3	0.8	0.3	1	0.4
In surface water, EUSES (μg/liter)	0.04	0.05	0.02	0.02	0.01	0.01
In soil, EUSES (μg/kgdwt)	0.01	0.02	0.01	0.02	0.02	0.03
In sediment, EUSES (μg/kgdwt)	0.1	0.2	0.07	0.1	0.08	0.1

sources and sinks for these compounds. It should also be noted that the predicted atmospheric concentrations of MtHxE and MtOcE are generally close to those predicted for MtBE. With the exception of MtHxE in the summer months in the Northeast United States, the predicted atmospheric concentrations of the higher ethers were equal to or greater than those predicted for MtBE, as would be expected due to the increased emissions loadings. As the calculated half-life in air of MtHxE is only one-third that of MtBE, the sink due to reaction with tropospheric hydroxyl radicals is expected to actually exceed the advective sink, comprising about 54% of the total of the two sinks, which accounts for the reduced concentration of MtHxE predicted in the summer. The effect is less pronounced for MtOcE, whose calculated half-life is only about half that of MtBE. In the winter months, the concentration of tropospheric hydroxyl radicals is reduced due to the reduction in sunlight, and advection is therefore the dominant sink for all three ethers.

Predicted concentrations of MtHxE and MtOcE in surface water were consistently lower than those predicted for MtBE, as would be expected from their larger Henry’s law constants (lesser tendency to partition from air into water).

Predicted concentrations of MtHxE and MtOcE in soil were about the same or somewhat greater than the predicted concentrations of MtBE. Owing to their more hydrocarbon-like natures, both are likely to have a greater affinity for organic matter in soil than MtBE does. On the other hand, predicted concentrations of MtHxE and MtOcE in sediment were consistently less than the predicted concentrations of MtBE, presumably due to the decreased concentration of these ethers in surface water compared to MtBE.

Risk Assessment

Risk Characterization Ratios. EUSES includes a risk characterization module that generates an RCR from the ratio of the PEC to the Predicted No Effect Concentration (PNEC). EUSES estimates the PNECs from user-supplied toxicological endpoints. In this study, toxicological endpoints in the aquatic compartment were estimated for three trophic levels, producers (EC_{50} for green algae), primary consumers (LC_{50} for daphnids), and secondary consumers (LC_{50} for fish), using ecological structure-activity relationships (ECOSAR) [118]. ECOSAR was also used to predict a toxicological endpoint for one decomposer in the terrestrial compartment (LC_{50} for earthworms). EUSES calculates PNECs for sediment dwelling organisms internally using extrapolations from data for aquatic organisms. Table 4-5 presents the results of these predictions for MtBE, MtHxE and MtOcE. Experimental values for MtBE toxicological endpoints found in the literature are also presented here for comparison. The comparison indicates that ECOSAR predicts greater toxicities for MtBE than experimental observation actually showed.

Table 4-5

ECOSAR predicted toxicological endpoints for MtBE, MtHxE and MtOcE for aquatic and terrestrial organisms

Endpoint	MtBE[a]	MtHxE	MtOcE
96-hr LC_{50} for fish (mg/L)	220 (672)	45	6.4
48-hr LC_{50} for daphnids (mg/L)	230 (542)	49	7.5
96-hr EC_{50} for green algae (mg/L)	140 (184)	31	5.1
14-day LC_{50} for earthworms (mg/kgdwt)	800 (Not found)	600	350

[a] Experimental values for MtBE given in parentheses, from [93].

Inspection of Table 4-5 shows that the ethers grow progressively more ecotoxic in proportion to their hydrophobicity, as would be expected in a homologous series of nonpolar organic chemicals that act by a nonspecific narcosis mechanism [124].

EUSES calculations of the RCRs in the surface water, sediment, and soil compartments for MtHxE are of the order of 10^{-3}, while those for MtOcE are of the order of 10^{-2}, projecting that these ethers will pose only a minimal risk to ecosystems at the expected environmental concentrations.

Margins of Safety for Human Exposure. Humans may be exposed to ethers in the environment by any of a number of routes. Risk assessment for exposed workers (refinery workers, tanker truck drivers, gasoline station attendants) and consumers by inhalation or direct contact is a highly localized issue and was not the focus of this study. The PECs for MtHxE and MtOcE in surface and ground water that can be attributed to atmospheric deposition were very low, 0.01 to 0.1 μg/l, suggesting that no significant exposure will occur due to recreational activities, bathing, cooking or drinking. The EUSES predicted concentrations of these ethers in fish, meat and milk are in the parts per billion to parts per trillion range, suggesting that significant human exposure through food chain accumulation is unlikely. The principal route of human exposure to environmental MtBE is thought to be by inhalation of ambient air [125]. The EUSES analysis suggests this will also hold true for MtHxE and MtOcE.

Safety concerns arise largely due to the potential for a lifetime of exposure to methyl tertiary alkyl ethers in ambient air. However, no data on the effects of chronic human inhalatory exposure to methyl tertiary alkyl ethers are available. In the absence of human exposure data, exposure assessment data for other mammals can be used to estimate toxicities to human beings. Some no observed adverse effect concentrations (NOAEC) for chronic rodent inhalatory exposure are available for the first two members of the methyl tertiary alkyl ether series, namely MtBE and methyl tertiary amyl ether (TAME). The only NOAEC for systemic noncancerous toxicological effects for TAME found in the literature is 500 ppm [91], while the NOAEC for MtBE ranges from 400 ppm [92] to 800 ppm [93]. Based on the results of rodent testing, in which a concentration of 403 ppm was considered to be a NOAEC, the USEPA has calculated a chronic reference concentration of 3 mg/m^3 for MtBE [126]. The chronic reference concentration is an order of magnitude estimate of a continuous inhalation exposure level for the human population (including sensitive subpopulations) that is likely to be without appreciable risk of deleterious non-cancer effects during a lifetime. Taking 1440 mg/m^3 (400 ppm) to be a NOAEC and using a risk assessment factor of ten for interspecies extrapolation, a margin of safety for human exposure in the range of 10^5 to 10^6 can be calculated for MtBE using the PECs in Table 4-4. This result is in good agreement with the results of previous researchers [112].

Since no mammalian inhalatory exposure data were found for MtHxE and MtOcE, we sought an approach to predict their toxicities. The results of numerous studies compiled by both the USEPA and the European Union Organisation for Economic Co-operation and Development (OECD) HPV Chemicals Programme demonstrate that while structure-activity relationship based methods perform very well for predicting short-term nonmammalian toxicity, these methods do not perform well in predicting chronic toxicity in mammals [127]. Given the complexity of health endpoints and the amount of uncertainty in many models, USEPA has historically used an expert judgment/nearest analog approach for predicting health effects in assessing new chemicals [128]. This type of approach is also accepted by the OECD [129].

MtBE and TAME may make suitable analogs for screening-level predictions of health effects for MtHxE and MtOcE because: 1) the compounds in this series have only minor structural differences that are not expected to have a direct impact on toxicity;

2) the ether linkage is known to be a biologically active site for this class of compounds; and 3) the most common mechanism of biotransformation for ethers in general is an oxidation process known as O-dealkylation. This mechanism of biotransformation is particularly well characterized for methyl alkyl ethers, in which case the primary metabolites are formaldehyde and the parent alcohol [130].

Since we expect the model employed here to only predict PECs to within an order of magnitude, the MOSs derived from them are, at best, order of magnitude estimates. In qualitative terms, MtHxE and MtOcE can only be predicted to be more toxic than, less toxic than, or of similar toxicity to their lower analogs [128]. Comparison of the NOAECs for MtBE and TAME shows that they are of similar toxicity. For the purposes of a screening-level assessment, we assumed that MtHxE and MtOcE are also of similar systemic toxicity. In this case, since the ambient air PECs for MtHxE and MtOcE were very close to the PECs for MtBE (Table 4-4), the MOSs for MtHxE and MtOcE would be close to the MOS for MtBE. These results suggest that MtHxE and MtOcE will also exhibit a wide margin of safety for human exposure (i.e., MOSs in the range of 10^5 to 10^6), at least for systemic effects.

However, the primary health effect of interest in chronic inhalation MtBE exposure studies is cancer. No data are available on the carcinogenicity of MTBE to humans [131]. Inhaled MtBE has been shown to be carcinogenic to both rats and mice [93]. The potential human carcinogenicity risks of MtBE inhalation are based upon extrapolation from rodent carcinogenicity tests. Only a very limited number of such studies have been performed and there is a great deal of controversy over their results and the interpretation of those results, particularly as to how the findings might be extrapolated to predict human carcinogenicity effects. The USEPA has tentatively classified MtBE as a possible human carcinogen, and therefore it seems plausible that MtHxE and MtOcE are also potential human carcinogens. The theoretical one in a million excess cancer death level is widely used for establishing public health goals for nonvoluntary human exposure to environmental carcinogens. MtBE is listed as a hazardous air pollutant under Title III of the 1990 Clean Air Act Amendments. As part of the Cumulative Exposure Project, the USEPA has determined a 10^{-6} increased cancer risk protective inhalation exposure concentration of 6 $\mu g/m^3$ for a human lifetime (70 years) of exposure to air contaminated with MtBE [132]. However, there are large uncertainties associated with this determination. Given that ambient air MtHxE and MtOcE concentrations predicted by the current model are only "order of magnitude" estimates, PECs ranging from 0.1 to 1 $\mu g/m^3$ for MtHxE and MtOcE (Table 4-4) could actually represent ambient air concentrations approaching the concentration where the cancer risk threshold has been set for MtBE. Although Boston was used as a case study, experience with MtBE [112] demonstrates that these PECs may easily be an order of magnitude higher for very large urban centers (e.g., Los Angeles). Therefore, this screening-level assessment indicates that in some cities, MtHxE and MtOcE concentrations in urban air could reach levels that pose an unacceptable cancer risk to the population. In light of this evidence, and given the large uncertainties involved in the determination of the cancer risk threshold for MtBE, we recommend testing of the carcinogenic potential of MtHxE and MtOcE before their widespread introduction into gasoline.

In conclusion, both the airshed box and EUSES models predict air concentrations of MtHxE and MtOcE that are of the same order of magnitude as air concentrations of MtBE for both the Boston PMSA and the Northeast United States [112]. EUSES calculations of the RCRs in the surface water, sediment, and soil compartments for MtHxE were of the order of 10^{-3}, while those for MtOcE were of the order of 10^{-2}, indicating that these ethers pose only a minimal risk to ecosystems at the expected environmental concentrations.

It is important to note that “megalopolis” urban centers such as Mexico City, Cairo and Los Angeles could expect to have ether concentrations in ambient air that are an order of magnitude higher than those expected for the Boston PMSA [112]. EUSES calculations for these conditions predict that the RCRs would likewise be unfavorably adjusted by an order of magnitude. Even so, the RCRs will still be in the 10^{-2} and 10^{-1} range for MtHxE and MtOcE, respectively. These results suggest that these ethers pose only a minimal risk to ecosystems even at these increased environmental concentrations.

Given the concern regarding MtBE as a potential human carcinogen, analogue considerations give rise to similar concerns for MtHxE and MtOcE as potential replacements. Moreover, some of the predicted ambient air concentrations of MtHxE and MtOcE in very large urban areas exceed the concentration where the cancer risk threshold has been set for MtBE. The screening-level risk assessment suggests the need for a more rigorous risk assessment for MtHxE and MtOcE before their widespread introduction into gasoline.

CHAPTER V

METHYL TERTIARY HEXYL ETHER AND METHYL TERTIARY OCTYL ETHER AS GASOLINE OXYGENATES: ANTICIPATING WIDESPREAD RISKS TO COMMUNITY WATER SUPPLY WELLS

Homologues of methyl tertiary butyl ether (MtBE) are currently being developed as replacement oxygenates for MtBE in gasoline [6, 7], and have also been proposed for use as ultra-clean diesel fuels [8]. Increasing the hydrocarbon content of an ether reduces the water solubility [105] and increases the organic matter-water partition coefficient (K_{om}) [133]. Therefore, these higher carbon number ethers are expected to be less likely to migrate from the site of a leaking underground fuel tank (LUFT) and contaminate groundwater resources than MtBE. Two homologues of MtBE are of particular interest because they can be prepared from readily available olefinic feedstocks. These two homologues are methyl tertiary hexyl ether (MtHxE) [76] and methyl tertiary octyl ether (MtOcE) [108]. Beginning in 1995, limited quantities of MtHxE were introduced into gasoline in Finland as a supplementary oxygenate to MtBE [14].

Commercially, MtBE is prepared almost exclusively by the methanolation of the four-carbon olefin isobutylene, the isobutylene being available in commercial quantities from petroleum refinery cracking streams. Similarly, the methanolation of olefins of carbon numbers C_6 and C_8 is the most likely industrial route to MtHxE [73, 106] and MtOcE [63]. However, the quantity of higher olefins in refinery cracking streams is limited and decreases with increasing carbon number after C_5 [70]. It may be that the most feasible industrial route to these ethers is by the methanolation of the dimerization products of propylene and isobutylene, respectively. Both propylene and isobutylene are readily available from cracking streams, and are easily dimerized to dipropylene (a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) and di-isobutylene (a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene), respectively.

Although there are three isomers of MtHxE and seventeen isomers of MtOcE [109], the methanolation of dipropylene leads only to the methyl tertiary hexyl ether designated as 2-methoxy-2,3-dimethylbutane (CAS # 26356-10-5), while the methanolation of di-isobutylene leads only to the methyl tertiary octyl ether designated as 2-methoxy-2,4,4-trimethylpentane (CAS # 62108-41-2), in accord with Marovnikov's rule. Figure 5-1 presents the chemical structures of these compounds. Because of the potential importance of higher ethers as high production volume (HPV) fuel blend components [106, 134, 135], a number of studies of the preparation of MtHxE and MtOcE have recently appeared in the literature [63, 76, 78, 80, 108, 110].

As was the case with MtBE, the introduction of these ethers into fuel supplies guarantees their introduction into the environment as well. Chapter IV addressed issues of environmental concern related to the atmospheric dispersion and deposition of MtHxE and MtOcE as a result of evaporative and tailpipe emissions. Although the greatest

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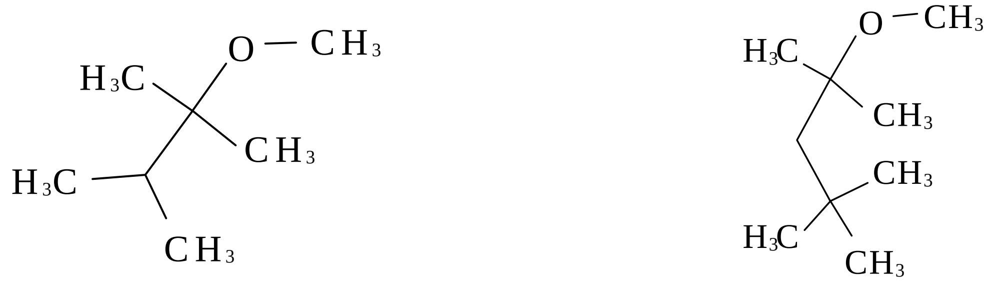
Methyl t-Butyl Ether
MtBE

Methyl t-Amyl Ether
TAME (Methyl-MtBE)



Methyl t-Hexyl Ether
MtHxE (Dimethyl-MtBE)

Methyl t-Octyl Ether
MtOcE (t-Butyl-MtBE)

Figure 5-1

Chemical Structures of MtBE, TAME, MtHxE and MtOcE

potential for human exposure to environmental MtBE is thought to be through inhalation, the threat posed by leakage of MtBE from LUFTs and its subsequent migration into groundwater resources has been the source of far greater public concern [125]. It is therefore of interest to assess the potential risk that these higher ethers might pose to well water supplies. Since MtHxE and MtOcE form part of a homologous chemical series with MtBE, the basic mechanisms of subterranean transport and degradation for these compounds are expected to be similar. In this paper, a simple physicochemical model is employed to predict the concentrations of these homologues of MtBE that might be expected in a typical community water supply well (CSW) if either MtHxE or MtOcE were to completely replace MtBE in reformulated gasoline (RFG). The predicted concentrations are then compared to the concentrations that might be expected to cause adverse effects, thereby giving a preliminary assessment of risk.

Modeling Considerations and Parameter Estimation

Arey and Gschwend [136] recently developed a model for predicting fuel component concentrations in a CSW resulting from fuel leakage from a nearby LUFT. These authors further showed that all the modeling calculations could be performed without extensive *a priori* information about the behavior of the fuel components in the subsurface. This is of particular interest to the current work because there are no existing data on or field experience with subsurface contamination resulting from MtHxE and MtOcE releases. The most important implication of their study is that a generalized screening model of subsurface transport can evaluate the expected range of well water concentrations of candidate fuel components resulting from subsurface contamination by nearby LUFTs. The predicted concentrations can then be compared to the levels that are thought to pose a threat to public health, thereby giving an indication of risk.

The Physicochemical Screening Model

Reports from LUFT sites reveal that many of the transport parameters needed to simulate contaminant transport and fate are usually not available, even for simplified models. Release dates, fuel compositions, and spill volumes are rarely known [137]. Environmental data from actual release sites are often not available for compounds that are being researched and developed for future use [6]. However, the goal of this screening approach is to evaluate the hazards associated with the use of a particular product in most typical situations, rather than to analyze site-specific contamination problems. Arey and Gschwend [136] showed that adequate estimates of MtBE concentrations in most affected CSWs could be generated by using a relatively simple physicochemical transport model.

The model assumes that the gasoline NAPL percolates through the vadose zone and spreads into a resting “pancake”, or pooled lens, on the water table. The loss of solute by vaporization from the NAPL through the vadose zone is considered negligible. The groundwater in immediate contact with the pooled gasoline is assumed to be chemically equilibrated with the NAPL, thereby creating an underlying plume of saturated water. A shallow, unconfined, sand and gravel aquifer is assumed. Groundwater advection, CSW drawdown, and sorption to solids (retardation) are assumed to control the rate of plume migration in the subsurface. Finally, the plume is assumed to be completely captured by a downgradient CSW and subsequently mixed (i.e., diluted) with adjacent, uncontaminated water in the well capture zone when drawn from the well. Figure 5-2 depicts this simplified model of a solute plume migrating from a gasoline release site to a CSW.

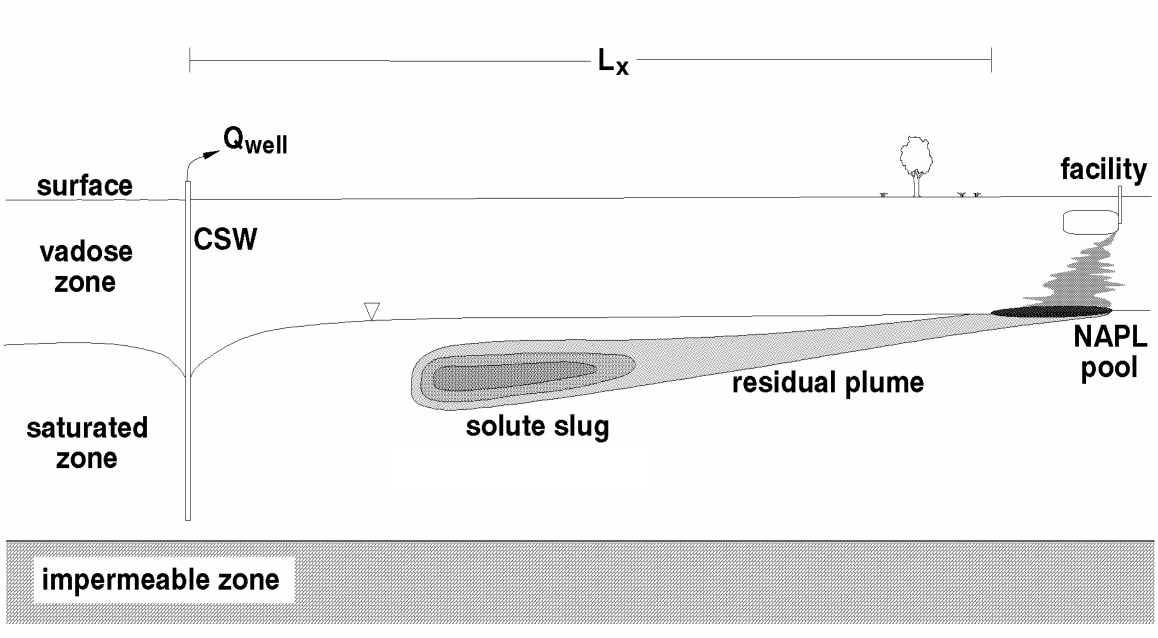


Figure 5-2

Depiction of a solute plume migrating from a gasoline release site to a CSW. The vertical scale is exaggerated to show detail. (From [136], used with permission.)

The main environmental transport parameters for the model involve the hydrogeologic setting; the distance of the CSW from the LUFT; the mass fraction of organic matter in the aquifer material; the ambient groundwater velocity; the non-aqueous phase layer (NAPL) dimensions; and the CSW pumping rate. As this model was intentionally designed so that only minimal additional information is necessary to tailor it to the behavior of a novel gasoline constituent, only three compound-specific model parameters are included: the concentration of the constituent in fuel (Cg), the gasoline-water partition coefficient (K_{gw}), and the organic matter-water partition coefficient (K_{om}).

Considering only the subset of CSWs that are affected by LUFT contamination, Arey and Gschwend (136) forecasted contamination levels in the "median" CSW using median or logarithmic average values of hydrogeologic parameters. For this type of estimate, they assumed: (1) the distance (L_x) from the CSW to the LUFT is 1400 m; (2) the mass fraction of organic matter in the aquifer material (f_{om}) is 0.003; (3) the ambient groundwater velocity (v_x) is 0.4 m/day; (4) the CSW pumping rate (Q_{well}) is 400 gal/min; and (5) the gasoline NAPL pooled lens volume (V_g) is 440 gal. The full list of field inputs for the model are presented in Table 5-1.

The model also assumes a retardation factor, R, of the contaminant, which reflects the decreased velocity of the contaminant as it is advected through the subsurface due to sorption to aquifer organic matter:

$$R = \frac{v_x}{v_{\text{contaminant}}} = 1 + \frac{f_{om} K_{om} \rho_s (1-\phi)}{\phi}, \tag{5-1}$$

where v_x is the linear velocity of the water (m/day), $v_{contaminant}$ is the linear velocity of the contaminant (m/day), ρ_s is the density of the aquifer solids material (kg/l), ϕ is the aquifer porosity (L/L), and K_{om} (L/kg) is estimated from K_{ow} (-) by [142]:

$$\log K_{om} = 0.82 \log K_{ow} + 0.14. \tag{5-2}$$

The inputs for the model are presented in Table 5-1. The rationale behind the model assumptions and a detailed description of the model development is presented elsewhere [136]. The resulting characteristic concentration of a contaminant in the well is estimated as [136]:

Table 5-1

Summary of model field transport parameters for a typical at-risk CSW[a]

Field parameter	**Symbol**	**Expected value**
Aquifer lithology	-	unconsolidated sand, gravel
Aquifer porosity	ϕ	0.25
Aquifer fraction of organic matter	f_{om}	0.003
Well pumping rate	Q_{well}	400 gal/min
Distance from LUFT to CSW	L_{x}	1400 m
NAPL volume	V_{g}	440 gal
NAPL saturation	S_{g}	0.35
NAPL lens thickness	h_{g}	0.2 m
Ambient groundwater velocity	v_{x}	0.4 m/day
Aquifer solids density	ρ_{s}	2.5 kg/l
Vertical dispersivity	a_{z}	0.002 m
Longitudinal dispersivity	a_{x}	20 m

[a] from [136]

$$\mathrm{C_{well}} = \frac{0.2\left(\dfrac{v_x C_g V_g}{R Q_{well}}\right)}{\sqrt{0.1\left(\dfrac{K_{gw}}{R}\right)^2 \left(\dfrac{V_g}{\phi}\right)^{1/2} \dfrac{(h_g S_g)^{3/2}}{a_z} + 2 a_x L_x}} \tag{5-3}$$

where a_z and a_x are the vertical and longitudinal dispersivities (m), respectively, h_g is the NAPL lens thickness (m), and S_g is the NAPL saturation (-), defined as the fraction of void space occupied by NAPL within the lens.

The screening model forecasted MtBE contamination levels of C_{well} = 23 μg/L for the median, at-risk CSW. Arey and Gschwend also showed that a variability analysis of the input parameters can be used to assess the precision, or expected distribution, of forecast CSW contamination levels [136]. The analysis suggests that C_{well} may vary from the typical value predicted by eq. 5-3 by a factor of as much as ~8x. The resulting forecast for MtBE was consistent with large scale field surveys of MtBE measurements in CSWs [136], suggesting that the model can provide "order of magnitude" estimates of concentrations of proposed novel fuel additives in CSWs.

Application of the Screening Model to MtHxE and MtOcE

Because we expect the biodegradability and sorption mechanisms of MtHxE and MtOcE in the subsurface to be similar to those of MtBE, the model should adequately predict well water concentrations of MtHxE and MtOcE, once the model parameters have been adjusted to reflect the expected fuel concentrations and physicochemical properties of MtHxE and MtOcE. Although there is currently no field experience to guide estimates of subsurface biodegradation rates for MtHxE or MtOcE, their structural similarity to MtBE, and particularly the degree of branching in their carbon skeletons, suggests that, like MtBE, they will degrade very slowly in the subsurface. Indeed, oxygenates containing a tertiary carbon atom have proven to be much more recalcitrant than their unbranched or moderately branched chemical analogs [138]. That is to say that the branching that makes these ethers useful as octane enhancers also makes them very resistant to biodegradation in the subsurface.

The model proposed by Arey and Gschwend [136] was chosen for this study because of its ability to adequately predict MtBE concentrations in a typical at-risk CSW. Representative estimates of C_g, along with reliable estimates of gasoline-water partition coefficients (K_{gw}) and organic matter-water partition coefficients (K_{om}), were therefore needed in order to generate meaningful model outputs, i.e., reasonable predictions of concentrations of ethers in a typical at-risk CSW.

Because very limited data on the properties of MtHxE and MtOcE are available in the literature, it was necessary to employ property estimation methods. The United States Environmental Protection Agency (USEPA) maintains a free, downloadable software package known as the Estimation Programs Interface (EPI Suite) for this purpose on its website [118]. EPI Suite was used to estimate the octanol-water partition coefficient (K_{ow}) and the water solubility (S_i) for both MtHxE and MtOcE. EPI Suite allows for the adjustment of property estimations when experimental data are available for a structurally similar compound. In this case, experimental property data are available for methyl tertiary amyl ether (TAME) and was thus used to adjust the calculations. Estimates of the octanol-water partition coefficient and the water solubility generated by EPI Suite are typically considered accurate to within about one-half of a log unit [118]. The model employed here is not particularly sensitive to this level of variability in K_{ow} and S_i. Specifically, the effect of the variability in K_{ow} and S_i on the model outputs, i.e., predicted contaminant concentrations in well water, is small compared to the effect of the variabilities in LUFT release parameters, subsurface hydrogeology characteristics, and CSW pumping rates. A detailed variability/sensitivity analysis for the current model is presented elsewhere [136].

The values of the gasoline-water partition coefficient, K_{gw}, were estimated from the water solubility. The gasoline-water partition coefficient, based on a component's molarities in the equilibrated phases, is given by

$$K_{gw,\,i} \quad = \quad \frac{M_{g,\,i}}{M_{w,\,i}}\,, \tag{5-4}$$

where M_g and M_w are the solute concentrations (mol/l) in the gasoline and water phases, respectively, and the subscript *i* designates the *i*th component. MtBE [139], TAME [139, 140] and MtOcE [79] have all been shown to form almost ideal solutions with gasoline components. We can thus assume that MtHxE will also behave ideally in solution with gasoline, based on the similarity in molecular structures of these ethers. Under these conditions, the solute concentration in the aqueous phase follows Raoult's law and is proportional to the mole fraction of solute in the gasoline phase [141]:

$$M_{w,\,i} = X_{g,\,i}\, S_{w,\,i} \tag{5-5}$$

where $X_{g,\,i}$ is the mole fraction of solute in the gasoline and $S_{w,\,i}$ is the aqueous molar solubility of neat solute. Assuming gasoline to be an ideal mixture of liquids, eqs. 5-4 and 5-5 can be combined to give

$$K_{gw,\,i} \quad = \quad \frac{M_{g,\,i}}{X_{g,\,i}\, S_{w,\,i}} \; = \; \frac{1000(\rho_g/\overline{MW_g})}{S_{w,\,i}}\,, \tag{5-6}$$

where ρ_g is the gasoline density (g/ml) and $\overline{MW}_g$ is the average molecular weight of the gasoline. Equation 5-6 assumes that the “dilute” activity coefficient of solute *i* in water is equivalent to the activity coefficient at saturation [142]. The density of gasoline is taken as 0.75 g/ml, and the average molecular weight is about 100 daltons [141, 143]. Insertion of the water solubility estimates from EPI Suite in eq. 5-6 provides estimates of K_{gw} for MtHxE and MtOcE. Table 5-2 contains the estimated values of K_{gw} and K_{ow} for MtHxE and MtOcE, along with other selected property data. Data for MtBE and TAME are also presented for comparison.

Concentrations of MtHxE and MtOcE in Gasoline

Because MtHxE and MtOcE contain more hydrogen and carbon than MtBE, they necessarily contain proportionately less oxygen. In order to provide the same oxygen levels in fuels, they must therefore be blended at higher ratios. MtBE, MtHxE and MtOcE contain about 18.2, 13.8 and 11.1 wt% oxygen, respectively. Therefore, it is necessary to use approximately 32% more MtHxE and about 64% more MtOcE than MtBE in fuels to arrive at the same oxygen level. Gasoline must contain 11 vol% MtBE to provide 2.0 wt% oxygen in gasoline. Table 5-2 presents the concentrations of MtHxE and MtOcE that would be needed to completely replace MtBE in gasoline at this level.

Table 5-2

Physicochemical and environmental properties of MtBE, TAME, MtHxE and MtOcE

Property	**Value**			
	MtBE	**TAME**	**MtHxE**	**MtOcE**
Molecular formula	$C_5H_{12}O$	$C_6H_{14}O$	$C_7H_{16}O$	$C_9H_{20}O$
Molecular weight (daltons)	88	102	116	144
Solubility in water at 25 °C (mg/L)	48000[a]	11000[b]	6100	900
Log K_{ow} at 25 °C	1.0[c]	1.6[b]	2.0	2.9
K_{om} at 25 °C (L/kg)	9.1	28	60	330
K_{gw}	16[a]	68	120	830
C_g (vol%)	11	12.8	14.5	18
C_g (ppm)	110000	128000	145000	180000
Predicted concentration in well water (μg/L)	23	19	15	5
Likely range of concentrations in well water (μg/L)	3 - 180	2 - 150	2 - 120	0.6 - 40

a. Experimental data fom reference [141].

b. Experimental data fom reference [144].

c. Experimental data fom reference [93].

Toxicological Effects and Odor and Taste Thresholds of Methyl Tertiary Alkyl Ethers in Drinking Water

Organoleptic Properties. While no data for the odor or taste thresholds in water for MtHxE and MtOcE were found in the literature, odor and taste thresholds in water of 15 and 40 μg/L, respectively, have been established for MtBE [93]. Additionally, odor and taste thresholds in water of 194 and 128 μg/L, respectively, have been determined for the next higher member of the homologous methyl tertiary alkyl ether series, namely methyl tertiary amyl ether (TAME) [144]. The addition of a single methylene group to MtBE results in significantly higher odor and taste thresholds in water for TAME. If this trend continues for MtHxE and MtOcE, they may not be detectable in drinking water by odor or taste at concentrations at which MtBE would be readily detectable by potential consumers. That is to say that the intense odor and taste of MtBE in drinking water serves as an indication of contamination, whereas MtHxE and MtOcE could be present in drinking water at potentially harmful concentrations without any warning signs.

The USEPA has established a drinking water advisory level of 20 to 40 μg/l for MtBE, based primarily on odor and taste thresholds [94]. The EPA goes on to stipulate that maintaining drinking water concentrations of MtBE below this range should also provide a large margin of safety (20,000 to 100,000x) against health-based risks.

Systemic Toxicological Effects. There are no studies of the effects on humans of long-term exposure to MtBE. All of the studies available for risk assessment are laboratory animal studies [94], and they are few in number. The most notable systemic (non-cancer) effect of long-term ingestion of MtBE is increased liver and kidney weights in rodents. Risk assessment studies for TAME are even fewer in number than those for MtBE. Only one study that is directly comparable to an MtBE study was found in the literature for TAME [95]. In 28-day gavage studies in rats, the lowest observed adverse effect levels (LOAEL) for liver and kidney abnormalities from MtBE were 440 mg per kg body weight per day (mg/kg/day), while the lowest level for TAME was 500 mg/kg/day. Since the molecular weights of MtBE and TAME are 88 and 102 daltons, respectively (Table 5-2), their systemic toxicities are virtually identical on a molar basis. For the purposes of estimating LOAELs in a screening-level risk assessment, we therefore assumed that MtHxE and MtOcE also have similar systemic toxicities. Based on this assumption, MtHxE and MtOcE will probably have significantly higher LOAELs for systemic toxicological effects than for carcinogenic toxicological effects.

Carcinogenic Toxicological Effects. The potential human carcinogenicity risks of MtBE ingestion are based upon extrapolation from rodent carcinogenicity tests. Only a very limited number of such studies have been performed and there is a great deal of controversy over their results and the interpretation of those results, particularly as to how the findings might be extended to predict human carcinogenicity effects. The EPA reviewed these studies and concluded that the data do not support confident, quantitative estimation of the risk to humans of the ingestion of low levels of MTBE in drinking water [94]. Despite these findings, the California Department of Toxic Substances Control (CDTSC) has calculated an MtBE concentration of 13 μg/L in drinking water to be protective of both cancer and non-cancer effects in humans. However, in this calculation the CDTSC used the rodent bioassay results that the EPA maintains are inadequate to quantitatively assess the potential risk of human exposure to MtBE [145]. A number of other states have issued health-based advisory levels in the 5 to 15 μg/l range, below the federal guideline of 20 to 40 μg/l, and additional states are considering revisions to existing advisories [146]. In spite of this controversy, public health goals for MtBE in drinking water have been and are being established based on health effects observed in experimental animals. Since the primary health effect of interest in oral MtBE exposure studies is cancer [131], it is prudent to consider the carcinogenicity of methyl tertiary alkyl ethers when assessing their potential risk to drinking water resources by applying a physicochemical screening model.

The only study found in the literature assessing the carcinogenic potential of any methyl tertiary alkyl ether other than MtBE was an investigation of TAME [101]. A similar study with MtBE had previously been published by the same group [100]. These studies showed that both MtBE and TAME are carcinogenic to rats at the 250 mg/kg/day dosage level. Since no trials were conducted at dosages between the control dosage (0 mg/kg/day) and the 250 mg/kg/day dosage, it is not possible to determine if MtBE is more or less carcinogenic than TAME from these data. Therefore, no trend can be suggested for an analog-based estimate of the potential carcinogenicity of MtHxE and MtOcE. It should also be noted that the mechanism of methyl tertiary alkyl ether carcinogenicity is not well understood [147], and that no correlations for relating carcinogenicity to structure for this class of compounds were found in the literature.

Therefore, for the purpose of the screening-level model employed here, the best alternative was to proceed with the risk calculations based on the assumption that all these ethers have similar carcinogenic potential, while bearing in mind that the carcinogenic potentials of MtHxE and MtOcE may in reality be greater than that of MtBE, as the carcinogenic potentials of larger, less water soluble homolgues often are.

Predicted Concentrations of MtHxE and MtOcE in Well Water

The physicochemical screening model predicted typical well water concentrations of 15 and 5 μg/L for MtHxE and MtOcE in at-risk CSWs, respectively, compared to 23 μg/L for MtBE (Table 5-2). Based on a variability analysis of the input parameters [136], the model also predicted likely concentration ranges of 2 to 120 μg/L and 0.6 to 40 μg/L for MtHxE and MtOcE, respectively, compared to 3 to 180 μg/L for MtBE. The lower well water concentrations predicted for MtHxE and MtOcE compared to MtBE are reasonable considering the higher gasoline-water partition coefficients and retardation factors for MtHxE and MtOcE relative to MtBE.

Risk Assessment

The predicted range of concentrations of MtHxE in affected CSWs, 2 to 120 μg/L, is comparable to drinking water advisory levels issued for MtBE by both the USEPA (20 to 40 μg/L) [94] and several U.S. states (5 to 15 μg/L) [146]. The predicted range of concentrations for MtOcE (0.6 to 40 μg/L) is about three times less, suggesting that MtOcE use may be relatively safer than MtHxE use. However, the purpose of the screening model is to identify compounds with predicted well water concentrations near or above a designated safe, compound specific threshold value, which should be considered as potential widespread contaminants. Compounds with predicted well water concentrations significantly below (e.g., by ~10x) a pre-determined acceptable drinking water level would then be considered unlikely to cause widespread contamination of drinking water resources [136]. Both MtHxE and MtOcE have predicted well water concentrations in the range of concentrations at which MtBE has caused and continues to cause widespread public health concern. It should also be borne in mind that MtHxE and MtOcE may be more carcinogenic than MtBE. Therefore, unless it can be clearly demonstrated that MtHxE and MtOcE are not carcinogenic at these concentrations in drinking water, their use in gasoline could lead to widespread health risks from consumption of contaminated water from community water supply wells.

Conclusions

The ranges of predicted well water concentrations of 2 to 120 μg/L for MtHxE and 0.6 to 40 μg/L for MtOcE are comparable to the range of concentrations (5 to 15 μg/L) where a number of states have placed drinking water advisory levels for MtBE, suggesting that both of these ethers have the potential to pose a threat of widespread contamination to community water supplies. Furthermore, unlike MtBE, the predicted well water concentrations for MtHxE and MtOcE are much lower than their projected odor and taste threshold values in water, suggesting that consumers would have little warning that they were drinking contaminated and potentially harmful water. The results of this screening-level risk assessment suggest that MtHxE and MtOcE should undergo more rigorous risk assessments, including both carcinogenicity testing and determination of odor and taste thresholds in water, before they are used to replace MtBE in gasoline.

CHAPTER VI

CONCLUSIONS AND FUTURE WORK

The development of a new chemical process, from concept to industrial realization, is an enormously complex task that involves many issues, including process feasibility, process economics, market development, environmental impact and frequently, legal and political issues. This is especially true of compounds that are to be used as fuels, since they have the potential to become high production volume chemicals. If the ethers produced in this research were to replace MtBE in gasoline, they would almost immediately become some of the most extensively manufactured industrial compounds, and because of their widespread distribution by automobiles and leaking underground fuel tanks, also the most widely released to the environment. No single study could address all of these issues, but this dissertation attempts to illuminate a small portion of this multifaceted process. The current work sheds some light on two of these aspects, namely the process feasibility and the potential environmental impact of these new ethers.

Feasibility Demonstration

The experimental work documented herein, by demonstrating the feasibility of synthesizing higher carbon ethers from olefins and preformed alcohols, lays the groundwork for the development of a process to produce higher carbon ethers from olefins and synthesis gas in a single-step reaction. An experimental methodology has been developed using hydrogen as the blanketing gas. In future work, hydrogen gas will be replaced by synthesis gas so that methanol is generated *in situ* for reaction with the olefin. A methanol synthesis catalyst will be employed in combination with the Amberlyst® 15 ion-exchange resin etherification catalyst so that the methanol synthesis and etherification reactions occur simultaneously. Catalysts for low temperature methanol syntheses are commercially available. The determination of which of the available low temperature methanol synthesis catalysts is most compatible with the ether synthesis and the exact physical arrangement of the dual catalyst system constitutes future work. Obviously, the catalyst must not promote the hydrogenation of olefins. Additionally, the current work has shown that methanol is more reactive in etherification than ethanol, and 2-butanol does not react under the conditions used in this study. Therefore, tailoring of the alkanol synthesis catalyst to produce alcohols other than methanol does not seem to be a promising avenue for further research.

The next step in this process development is the construction of a bench-scale flow through continuous reactor. The kinetics data reported in Appendix G can be used for the preliminary design of this reactor. A flow through reactor lends itself to kinetics studies more readily than a batch reactor, and the new data obtained from studies in the flow through reactor could be used to refine its design. Additionally, the flow system will allow for the optimization of the gas and liquid hourly space velocities.

Catalysts have been developed that promote methanol synthesis over a fairly wide range of temperatures, from 60 to 150 ^{o}C, so there should be no conflict with the optimum temperature for etherification. Additionally, the minimum requirement for pressure in the proposed reactor design is that it be sufficient to keep both the alcohol and the olefins liquefied. Since a liquid is being produced from a gas in the methanol synthesis reaction, the reaction is promoted by high partial pressures of synthesis gas. This research has shown that pressures as high as 800 psig do not inhibit the etherification reaction. Therefore, there should be no incompatibilities for the methanol synthesis and etherification reactions based on pressure. On the other hand, there is a conflicting thermodynamic constraint in that although low concentrations of methanol in the reactor favor syngas conversion, high concentrations of methanol increase the yield of ether. Therefore, the optimum concentration of methanol in the reactor for the simultaneous methanol synthesis and etherification reactions must be determined by experiment. Other parameters to be optimized in the bench scale reactor include the gas and liquid hourly space velocities, which determine the amount of time the reactants are in contact with the catalysts, and the recycle ratio of unreacted reactants to feed.

Since both the methanol synthesis and etherification reactions are exothermic, it may be necessary to employ a heat exchanger to dissipate the heat of reaction and maintain a constant temperature in the reactor. Additionally, depending on the heat dissipation characteristics of the reacting mixture, it may be necessary to employ an inert diluent to reduce the concentration of reactants, thereby reducing the rate of heat generation from the reactions. A three phase slurry reactor is envisaged. Synthesis gas will constitute the gas phase, and alcohol, olefin, product ether and diluent (if employed) the liquid phase. The catalysts, which are kept in suspension in the liquid phase by agitation, will constitute the solid phase.

The current work has shown that 2,3-dimethyl-1-butene gives much higher yields of ethers than 2,3-dimethyl-2-butene under identical reaction conditions. Therefore, 2,3-dimethyl-1-butene would be much preferred as a feedstock for an etherification reactor. However, the composition of commercially available 2,3-dimethylbutene is the same as the composition of the equilibrium mixture, that is, 90% of the less reactive 2,3-dimethyl-2-butene and only 10% of 2,3-dimethyl-1-butene. Fortunately, the boiling points of these isomers are far enough apart to that they can easily be separated by distillation, specifically 56 ^{o}C for 2,3-dimethyl-1-butene and 73 ^{o}C for 2,3-dimethyl-2-butene. Therefore, a separator (atmospheric still) could be used to produce a stream of almost (~ 98%) pure 2,3-dimethyl-1-butene for feed to the reactor, while the less reactive 2,3-dimethyl-2-butene could be directed to an isomerizer. In the isomerizer, which operates in the 80 to 100 ^{o}C range, the equilibrium composition is again attained, and the isomerized mixture is directed back to the still. Since both the distillation and the isomerization take place at or below 100 ^{o}C, the energy costs associated with these process units would be small.

Since the etherification reaction is equilibrium limited, there will be ether, methanol and olefins present in the liquid product mixture. Unreacted synthesis gas in the gas phase will remain in the reactor as the liquid product is withdrawn. Only traces of synthesis gas will dissolve in the liquid phase. Since the product ethers, methanol and olefins all have significantly different boiling points, they should be separable by atmospheric distillation, and the unreacted methanol can be recycled directly to the reaction vessel. In the case of the 2,3-dimethylbutenes, the alpha-isomer is more reactive and therefore will be depleted in the reaction vessel more rapidly than the beta-isomer. Moreover, isomerization to the less reactive beta-isomer will proceed simultaneously with the etherification. Consequently, the unreacted olefins stream leaving the reactor will be enriched in the less reactive beta-isomer. The alpha-olefin content of this stream can be increased by directing it to the isomerizer, also. In the case of the 2,4,4-trimethylpentenes, the reactivities of the two isomers are similar, and an isomerizer may not be required. The optimum process conditions in the liquid product separators and, in the case of the 2,3-dimethylbutenes, the still/isomerizer, must be determined experimentally.

Only one other reaction is known to occur with this type of etherification, namely oligomerization of the olefins. Dimerization of isobutylene is well known in MtBE units, although this only occurs at start-up. A high boiling material was detected in the some GC runs in the current work. This side reaction did not cause problems in the batch reactors. However, in a continuous reactor, a high boiling material could build up in the separator, which might necessitate the periodic cleaning of the separator.

Etherification of olefins with ethanol is an area of much current interest. Since the ethanol can be derived from renewable resources, research efforts directed toward developing such technologies qualify for government support. In the current work, yields of ethyl tertiary alkyl ethers were about half of those of methyl tertiary alkyl ethers under identical process conditions. Therefore, it would require a much larger and more expensive unit to achieve the same throughput with ethyl tertiary alkyl ethers than with methyl tertiary alkyl ethers. Given that methanol is much cheaper to produce than ethanol, substantial government subsidies would be required to enable an ethyl tertiary alkyl ethers unit to become economically competitive with a methyl tertiary alkyl ethers unit.

The kinetics data and the information gained by optimizing the process parameters in the bench-top model can be used in the next stage of the process development, namely the construction of a pilot plant unit. Similarly, experience gained at the pilot plant level can then be used in the design of a commercial scale unit. Then, even if an economic feasibility study indicates sufficient profitability to invest, there will still remain many hurdles to overcome before such a unit can become a commercial reality, not the least of which is a consideration of the environmental impact of the widespread use of these ethers in gasoline.

Environmental Aspects

The models used in the current research project that if methyl tertiary hexyl ether and methyl tertiary octyl ether were used to completely replace MtBE in gasoline, they would be present in ambient air at concentrations near the concentrations at which MtBE is currently present. The European Union System for the Evaluation of Substances multimedia fate model further projects that, on the basis of these concentrations in air, these ethers pose only a minimal threat to ecosystems when distributed through the various environmental compartments of air, soil, sediment and water. The assessment also indicates that these compounds are possible human carcinogens, and that they may be present in urban air at concentrations that pose an unacceptable cancer risk. Therefore, testing of the toxicological properties of these compounds is recommended before they are used to replace MtBE in gasoline.

It is also a projection of the current study that leakage of gasolines blended with methyl tertiary hexyl ether and methyl tertiary octyl ether from underground fuel tanks would result in the contamination of community water supply wells at levels near those currently being experienced with MtBE. These results suggest that these ethers have the potential to pose a threat of widespread contamination for community water supplies. Furthermore, unlike MtBE, the predicted well water concentrations for methyl tertiary hexyl ether and methyl tertiary octyl ether are much lower than their predicted odor and taste threshold values in water, suggesting that consumers would have little indication that they were drinking contaminated and potentially toxic water. These results emphasize the need for extensive toxicological testing of these ethers before they are approved to replace MtBE in gasoline.

REFERENCES

1. Shelley, S. and Fouhy, K. The Drive for Cleaner-Burning Fuel; *Chemical Engineering* **January 1994**, *101(1)*, 61-63.
2. U.S. Environmental Protection Agency, National Air Toxics Inventory, **1999**, Office of Mobile Sources, Pollutant Inventory, accessed at URL http://www.epa.gov/otaq/invntory/overview/pollutants/carbonmon.htm (accessed Nov 2006)
3. Garland, C. *History and Overview of the Reformulated Gasoline Program: A Briefing Book for Members of Congress and Staff*; National Reformulated Gasoline Hotline, Arlington, VA, 1997.
4. U.S. Environmental Protection Agency, The Clean Air Act Amendments. Washington, D.C., 101st Congress of the United States, 1990, Sec. 219, p. S.1630-1938, accessed at URL http://www.epa.gov/oar/caa/caaa.txt
5. Ainsworth, S. Oxygenates Seen as Hot Market by Industry; *Chemical and Engineering News* **May 11, 1992**, *70(19)*, 26-30.
6. Drogos, D.L.; Diaz, Arthur F. Physical Properties of Fuel Oxygenates and Additives; Oxygenates in Gasoline: Environmental Aspects; *American Chemical Society Symposium Series*, No. 799, **2002**, p. 258.

7. Hendrickson, D.E. *Use of Tertiary-Hexyl Methyl Ether as a Motor Gasoline Additive*; United States Patent US 5,752,992, assigned to EXXON Chemical Patents, Inc., May 19, 1998.

8. Huffman, G.P. *Cooperative Research in C1 Chemistry*; Consortium for Fossil Fuel Liquefaction Science, University of Kentucky, Lexington, KY, **1999**, p. 1.

9. Morrison, R.T.; Boyd, R.N. *Organic Chemistry*; Third Edition, Allyn and Bacon, Inc., Boston MA, 1975, p. 553.

10. Shen, J; Schmetz, E.; Stiegel, G.; Tischer, R. DOE Indirect Coal Liquefaction - Hurdles and Opportunities for its Early Commercialization; *Preprints of Papers, American Chemical Society - Division of Fuel Chemistry* **1997**, *42(2)*, 583-585.

11. Keller, A.A.; Fernandez, L. Beyond Methyl tert-Butyl Ether: Applying the Precautionary Principle to Gasoline Oxygenates, in Oxygenates in Gasoline: Environmental Aspects; *American Chemical Society Symposium Series*, No. 799, 2002, pp. 125- 136.

12. Tangley, L. Local Problems Become National Issue; *Bioscience* **March 1984**, *34(3)*, 142-148.

13. Squillace, P.H.; Pankow, J.F.; Korte, N.E.; Zogorski, J.S. Review of the Environmental Behavior and Fate of Methyl tert-Butyl Ether; *Environmental Toxicology and Chemistry* **1997**, *16(9)*, 1836-1844.

14. Koskinen, M.; Jarvelin, H. and Lindqvist, P. NExETHERS – New Way of Producing Ethers; *Oil Gas-Eur. Mag.* **1997**, *23(3)*, 31-35.

15. Sofianos, A.C.; Scurrell, M.S. Conversion of Synthesis Gas to Dimethyl Ether over Bifunctional Catalytic Systems; *Industrial and Engineering Chemistry - Research* **1991**, *30(11)*, 2372-2378.

16. Chang, C.D. Hydrocarbons from Methanol; *Catalysis Reviews: Science and Engineering* **1983**, *25(1)*, 1-118, and references therein.

17. Lewnard, J.J.; Hsiung, T.H.; White, J.F. and Brown, D.M. Single-Step Synthesis of Dimethyl Ether in a Slurry Reactor; *Chemical Engineering Science* **1990**, *45(8)*, 2735-2741.

18. Brown, D.M.; Bhatt, B.L.; Hsiung, T.H.; Lewnard, J.J.; Waller, F.J. Novel Technology for the Synthesis of Dimethyl Ether from Syngas; *Catalysis Today* **1991**, *8*, 279-304.

19. Kazi, A.M.; Goodwin, J.G.; Marcelin, G.; Rachid, O. Synthesis of MtBE during CO Hydrogenation: Reaction Sites Required; *Industrial and Engineering Chemistry - Research* **1995**, *34*, 718-721.

20. Roberts, J.D.; Caserio, M.C. *Basic Principles of Organic Chemistry*; W.A. Benjamin, Inc., New York, NY, 1965, p. 173.

21. Noller, C.R. *The Chemistry of Organic Compounds*; W.B. Saunders Company, Philadelphia, PA, Third Edition, 1966, p. 159-160.

22. Scholz, B.; Butzert, H.; Neumeister, J.; Nierlich, F. Methyl *Tert*-Butyl Ether; *Ullman's Encyclopedia of Industrial Chemistry*, 1985, Vol. A16, pp. 543-549, Weinheim, Federal Republic of Germany, Deerfield Beach, FL.

23. Groenveld, H.; Kwantes, A. Dutch Patent DE-OS 29 11 077, assigned to Shell Netherlands, 1979.

24. Guttman, A.T.; Grasselli, R.K. *Liquid Phase Process for the Manufacture of Methyl Tertiary Ethers*; US Patent 4,259,533, assigned to The Standard Oil Company, Cleveland, OH, March 31,1981.

25. Humberg, H.; Wegner, H. German Patent DE 27 06 465, assigned to Deutsche Texaco, 1987.

26. Dai, P.S.; Knifton, J.F. *Two-stage Etherification of Tertiary Butyl Alcohol Using Second Stage Zeolite Catalysts for the Intermediate Preparation of Isobutylene*; US Patent 5,856,588, assigned to Huntsman Specialty Chemicals Corporation, Austin, TX, January 5, 1999.

27. Bakshi, A.; Hickey, T.P. *Etherification Process*; US Patent 5,919,989, assigned to Catalytic Distillation Technologies, Pasadena, TX, July 6, 1999.

28. Evans, T.W.; Edlund, K.R. Tertiary Alkyl Ethers - Preparation and Properties; *Industrial and Engineering Chemistry* **1936**, *28(10)*, 1186-1188.

29. Ancillotti, F.; Mauri, M.M; Pescarollo, E. Ion Exchange Resin Catalyzed Addition of Alcohols to Olefins; *Journal of Catalysis* **1977**, *46*, 49-57.

30. Selwitz, C.M.; McNulty, J.G. *Etherification process*; US Patent 4,175,210, assigned to Gulf Research and Development Company.

31. Chu, P.; and Kühl, G.H. Preparation of Methyl tert-Butyl Ether (MTBE) over Zeolite Catalysts; *Industrial and Engineering Chemistry - Research* **1987**, *26,* 365-369.

32. Wender, I. Reactions of Synthesis Gas, *Fuel Processing Technology* **1996**, *48(3)*, 189-297.

33. Palekar, V.M.; Jung, H.; Tierney, J.W.; Wender, I. Slurry Phase Synthesis of Methanol With a Potassium Methoxide/Copper Chromite Catalytic System; *Applied Catalysis A: General* **1993**, *102*, 13-34.

34. Marchionna, M.; Lami, M.; Galletti, A.M.P. Synthesizing Methanol at Lower Temperatures; *CHEMTECH* **April 1997**, *27(4)*, 27-31.

35. Marchionna, M.; Basini, L.; Aragno, A.; Lami, M.; Ancillotti, F. Mechanistic Studies on the Homogeneous Nickel-Catalyzed Low Temperature Methanol Synthesis; *Journal of Molecular Catalysis, A, Chemical* **1992**, *75(2)*, 147-151.

36. Goodwin, J.G., Jr.; Natesakhawat, S.; Nikolopoulos, A.A.; Kim, S.Y. Etherification on Zeolites: MTBE Synthesis; *Catalysis Reviews* **2002**, *44(2)*, 287-320.

37. Baldwin, R.M. Coal Conversion Processes (Liquefaction); *Kirk-Othmer Encyclopedia of Chemical Technology*; Fourth Edition, John Wiley and Sons, New York, NY, 1993, p. 585.

38. Astle, M.J. *The Chemistry of Petrochemicals*; Reinhold Publishing Corporation, New York, NY, 1956, p. 6.

39. Fiedler, E.; Grossman, G.; Kersebohm, D.B.; Weiss, G.; Witte, C. Methanol; *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, Germany, 2003, Vol. 21, pp. 611-635.

40. Skrzypek, J.; Sloczynski, J.; Ledakowicz, S. Methanol Synthesis: Science and Engineering, Polish Scientific Publishers, Warsaw, Poland, 1994.

41. Lee, S. *Methanol Synthesis Technology*; CRC Press, Boca Raton, FL, 1990, p. 15.

42. Höver, H. Dimethyl Ether; *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim, Germany, 1985, Vol. A8, pp. 541-544.

43. Snamprogetti, SpA, German Patent DE 2 362 944.

44. Peng, X.D; Parris, G.E.; Toseland, B.A.; Battavio, P.J. *Use of Aluminum Phosphate as the Dehydration Catalyst in Single Step Dimethyl Ether Synthesis*; United States Patent US 5,753,716, assigned to Air Products and Chemicals, Allentown, PA, May 19, 1998.

45. Aguayo A.T.; Erena J.; Sierra I.; Olazar, M.; Bilbao, J. D Deactivation and regeneration of hybrid catalysts in the single-step synthesis of dimethyl ether from syngas and CO_2; *Catalysis Today* **2005**, *(1-4)*, 265-270.

46. Espino, R.L.; Pletzke, T.S. *Methanol Production*; United States Patent US 3,888,896, assigned to ChemSystems, Inc., New York, NY, May 29, 1973.

47. Lewnard, J.J.; Hsiung, T.H.; White, J.F.; Bhatt, B.L. *Liquid Phase Process for Dimethyl Ether Synthesis*; United States Patent US 5,218,003, assigned to Air Products and Chemicals, Inc., Allentown, PA, June 8, 1993.

48. Lee, S.; Gogate, M.R.; Fullerton, K.L.; Kulik, C.J. *Catalytic Process for Production of Gasoline from Synthesis Gas*; United States Patent US 5,459,166, assigned to Electric Power Research Institute, Palo Alto, CA, October 17,1995.

49. Iwasa, N.; Yamamoto, O.; Ohyama, S.; Takezawa, N. Dehydration of Methanol to Methyl Formate over Palladium/Zinc Oxide Catalysts; *Journal of the Chemical Society - Chemical Communications* **1991**, *18*, 1322-1323.

50. Noller, C.R. *The Chemistry of Organic Compounds*, W.B. Saunders Company, Philadelphia, PA, Third Edition, 1966, p. 100.

51. Francis, A.W. *Method of Making Ethers*; United States Patent US 2,077,042, assigned to Socony-Vacuum Oil Company, Incorporated, New York, NY, April 13, 1937.

52. Cruz, V.J.; Izquierdo, J.F.; Cunill, F.; Tejero, J.; Iborra M.; Fité, C. Acid ion-exchange resins catalysts for the liquid-phase dimerization/etherification of isoamylenes in methanol or ethanol presence, *Reactive and Functional Polymers* **2005**, *65(1-2)*, 149-60.

53. Parra, D.; Izquierdo, J.F; Cunill, F.; Tejero, J.; Fite, C.; Iborra, M.; Vila, M. Catalytic Activity and Deactivation of Acidic Ion-Exchange Resins in Methyl *tert*-Butyl Ether Liquid Phase Synthesis, *Industrial and Engineering Chemistry - Research* ***1998****, 37(9), 3575-3581.*

54. Collignon, F.; Mariani, M.; Moreno, S.; Remy, M.; Poncelet, G. Gas Phase Synthesis of MTBE from Methanol and Isobutene over Dealuminated Zeolites, *Journal of Catalysis* **1997**, *166*, 53-66.

55. Peters, U.; Nierlich, F.; Schulte-Körne, E.; Sakuth, M.; Deeb, R.; Laugier, M; Suominen, M.; Kavanaugh, M. Methyl Tert-Butyl Ether; *Ullmann's Encyclopedia*

of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, Germany, 2003, Vol. 21, pp. 701-717.

56. Micheli, E.; Antonelli, G.B.; Sanfilippo, D. Ethermix Process: Synthesis of Ethers from CO/H_2; *Studies in Surface Science and Catalysis* **1997**, *107, Natural Gas Conversion IV*, 139-144.

57. Kiem, W.; Falter, W. Isobutanol from Synthesis Gas; *Catalysis Letters* **1989**, *3*, 59-64.

58. Ververk, K.A.N.; Jaeger, B.; Finkeldei, C.H.; Keim, W. Recent Developments in Isobutanol Synthesis From Synthesis Gas; *Applied Catalysis A: General* **1999**, *186*, 407-431.

59. Morrison, R.T.; Boyd, R.N. *Organic Chemistry*; Third Edition, Allyn and Bacon, Inc., Boston, MA, 1975, p. 182.

60. Karinen, R.S.; Krause, A.O.I. Kinetic Model for the Etherification of 2,4,4-Trimethyl-1-pentene and 2,4,4-Trimethyl-2-pentene with Methanol; *Industrial and Engineering Chemistry - Research* **2001**, *40*, 6073-6080.

61. Lindquist, P. *Process for Preparing Tertiary Alkyl Ethers*; United States Patent US 5,998,675, assigned to Neste Oy, Espoo, Finland, December 7, 1999.

62. Smith, Jr., L.A.; Putman, H.M.; Semerak, H.J.; Crossland, C.S. *Process for the Production of Tertiary Alkyl Ethers*", United States Patent US 6,583,325, assigned to Catalytic Distillation Technologies, Pasadena, TX, June 24, 2003.

63. Karinen, R.S.; Krause, A.O.I. Reactivity of some C_8-alkenes in etherification with methanol; Applied Catalysis A: General **1999**, *188(1-2),* 247-256.

64. Torck, B.; Convers, A.; Chauvel, A. Methanol for Motor Fuel *via* the Ethers Route; *Chemical Engineering Progress* **August 1982**, 36-45.

65. Gary, J.H.; Handwerk, G.E. *Petroleum Refining - Technology and Economics*, Marcel Dekker, Inc., New York, NY, Second Edition, 1984, p. 176.

66. Scharfe, G. Convert Butenes to High Octane Oligomers; *Hydrocarbon Processing* **1973**, *52(4)*, 171-173.

67. Owen, K. Fuels for Spark-Ignition Engines, *Modern Petroleum Technology*; Fifth Edition, Part Two, John Wiley and Sons, Great Yarmouth, Great Britain, 1984, p. 815.

68. Verdol, J.A. *Tertiary Olefin Separation via Etherification with Small Surface Areas Catalysts*; United States Patent US 3,170,000, assigned to Sinclair Research, Inc., Wilmington, DE, February 16, 1965.

69. Holovka, J.M.; Hurley, Jr., E. *Preparation of Mixed Unsymmetrical Ethers*; United States Patent US 3,718,701, assigned to Marathon Oil Company, Findlay, OH, February 27, 1973.

70. Pescarollo, E.; Trotta, R.; Sarathy, P.R. Etherify Light Gasolines; *Hydrocarbon Processing* **1993**, *72(2)*, 53-58.

71. Kozlowski, R.H.; Sieg, R.P.; Scott, J.W. *Hydrocarbon Conversion Process*; United States Patent US 3,849,082, assigned to Chevron Research Company, San Francisco, CA, November 19, 1974.

72. Ancillotti, F.; Pescarollo, E. Fuel Blends Create Solubility Problems, *Hydrocarbon Processing* **1977**, *56(11)*, 295-299.

73. Krause, A.O.I.; Hammarstrom, L.G.; Joutsimo, M. Etherification of C_6-olefins with Methanol; *8th International Congress on Catalysis - Proceedings*, **1984**, *V*, V553-V563.

74. Zhang, T.; Datta, R. Ethers from Ethanol. 3. Equilibrium Conversion and Selectivity Limitations in the Liquid-Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers; *Industrial and Engineering Chemistry - Research* **1995**, *34(7)*, 2237-2246.

75. Zhang, T.; Datta, R. Ethers from Ethanol. 4. Kinetics of the Liquid Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers, *Industrial and Engineering Chemistry - Research* **1995**, *34(7)*, 2247-2257.

76. Liu, J; Wang, S.; Guin, J.A. Etherification of Dimethylbutenes in Excess Methanol; *Fuel Processing Technology* **2001**, *69*, 205-219.

77. Wang, S.; Guin, J.A. Silica-supported Sulfated Zirconia: A New Effective Acid Solid for Etherification; *Journal of the Chemical Society - Chemical Communications* **2000**, 2499-2500.

78. Wang, S.; Guin, J.A. Si-MCM41 Supported Sulfated Zirconia and Nafion for Ether Production, *Energy and Fuels* **2001**, *15*, 666-670.

79. Karinen, R.S.; Lylykangas, M.S. and Krause, A.O.I. Reaction Equilibrium in the Isomerization of 2,4,4-Trimethylpentenes; *Industrial and Engineering Chemistry - Research* **2001**, *40*, 1011-1015.

80. Karinen, R.S.; Linnekoski, J.A.; Krause, A.O.I. Etherification of C_5- and C_8-alkenes with C_1- to C_4-alcohols; *Catalysis Letters* **2001**, *76(1-2)*, 81-87.

81. Rihko, L.K; Krause, A.O.I. Etherification of FCC Light Gasoline with Methanol; *Industrial and Engineering Chemistry - Research* **1996**, *35*, 2500-2507.

82. Fité, C.; Tejero, J.; Iborra, M.; Cunill, F.; Izquierdo, J.F.; Parra, D. The Effect of the Liquid Reaction Medium on the Kinetics of the Liquid-phase Addition of Methanol to Isobutene; *Applied Catalysis A: General* **1998**, *169*, 165-177.

83. Gates, B.C.; Rodriguez, W. General and Specific Acid Catalysis in Sulfonic Acid Resins; *Journal of Catalysis* **1973**, *31*, 27-31.

84. Thornton, R.; Gates, B.C. Catalysis by Matrix-Bound Sulfonic Acid Groups: Olefin and Paraffin Formation from Butyl Alcohols; *Journal of Catalysis* **1974**, *34*, 275-287.

85. Noller, C.R. *The Chemistry of Organic Compounds*, W.B. Saunders Company, Philadelphia, PA, Third Edition, 1966, p. 103.

86. Rehfinger, A.; Hoffmann, U. Formation of Di-isobutene, Main Byproduct of Methyl Tertiary Butyl Ether Synthesis Catalyzed by Ion Exchange Resin; *Chemical Engineering and Technology* **1990**, *13(3)*, 150-156.

87. Grootjans, J. Catalysis in Modern Petroleum Refining, in Catalysis and Automotive Pollution Control; *Studies in Surface Science and Catalysis*, Crucq, A.; Frennet, A., eds., Elsevier Science Publishers B.V., The Netherlands, 1987, pp. 31-49.

88. Di Girolamo, M; Lami, M; Marchionna, M; Pescarollo, E; Tagliabue, L.; Ancillotti, F. Liquid Phase Etherification/Dimerization of Isobutene over Sulfonic

Acid Resins; *Industrial and Engineering Chemistry - Research* **1997**, *36*, 4452-4458.

89. Curtis, C.W.; Roberts, C.R.; Snelling, J. Production of Mixed Higher Ethers in Gas and Liquid Phase Reactions; Consortium for Fossil Fuel Liquefaction Science (CFFLS) 2000 Annual Report, DOE Cooperative Agreement No. DE-FC26-099FT40540.

90. Greene, M.I. Alcohol-Based Fuels from Syngases; *Chemical Engineering Progress* **August 1982**, 46-51.

91. White, R.D.; Daughtrey, W.C.; Wells, M. S. Health Effects of Inhaled Tertiary Amyl Methyl Ether and Ethyl Tertiary Butyl Ether; *Toxicol. Lett.* **1995**, *82-83*, 719-724.

92. *The MTBE Resource Guide*. European Fuel Oxygenates Association. http://www.efoa.org/mtbe/pdf/appendix8.pdf (accessed Dec 2005).

93. European Union Risk Assessment Report – TERT-BUTYL METHYL ETHER. http://ecb.jrc.it/Documents/Existing-Chemicals/RISK_ASSESSMENT/REPORT/mtbereport313.pdf (accessed Dec 2005).

94. USEPA, **1997**, *Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary Butyl Ether (MtBE)*, EPA-822-F-97-009, accessed at URL http://epa.gov/waterscience/drinking/mtbe.pdf

95. Australian Government, Department of Health and Ageing, National Industrial Chemicals Notification and Assessment, Summary Report: NA878; accessed at

URL http://www.nicnas.gov.au/PUBLICATIONS/CAR/NEW/NA/NASUMMR/NA0800SR/na878.asp

96. Biles, R.W.; Schroeder, R.E.; Holdsworth, C.E. Methyl Tertiary Butyl Ether Inhalation in Rats: A Single Generation Reproduction Study; *Toxicol. Ind. Health* **1987**, *3(4)*, 519-534.

97. Tyl, R.W.; Meyers, C.B.; Marr, M.C.; Fail, P.A.; Seely, J.C.; Elswick, B.; James, A.; Welsch, F. Two-generation Reproductive Toxicity Study of Inhaled Tertiary Amyl Methyl Ether; *Journal of Applied Toxicology* **2003**, *23(6)*, 397-410.

98. Bevan, C.; Tyl, R.W.; Neeper-Bradley, T.L.; Fisher, L.C.; Panson, R.D.; Douglas, J.F.; Andrews, L.S. Developmental Toxicity Evaluation of Methyl Tertiary-butyl Ether (MTBE) by Inhalation in Mice and Rabbits; *Journal of Applied Toxicology* **1997**, *17(S1)*, S21-S29.

99. Welsch, F.; Elswick, B.; James, R.A.; Marr, M.C., Myers, C.B.; Tyl, R.W. Developmental Toxicity Evaluation of Inhaled Tertiary- Amyl Methyl Ether in Mice and Rats; *Journal of Applied Toxicology* **2003**, *23(6)*, 387-395.

100. Belpoggi, F.; Soffritti, M.; Filippini F.; Maltoni, C. Results of Long-Term Experimental Studies on the Carcinogenicity of Methyl tert-Butyl Ether; *Ann. N.Y. Acad. Sci.* **1997**, *837*, 77-95.

101. Belpoggi, F.; Soffritti, M.; Minardi, F.; Cattin, E.; Maltoni, C. Results of Long-Term Carcinogenicity Bioassays on Tert-Amyl-Methyl-Ether (TAME) and Di-Isopropyl Ether (DIPE) in Rats; *Ann. N.Y. Acad. Sci.* **2002**, *982*, 70-86.

102. Ancillotti, F.; Mauri, M.; Pescarollo, E.; Romagnoni, J. Mechanisms in Reaction Between Olefins and Alcohols Catalyzed by Ion Exchange; *J. Mol. Catal*. **1978**, *4(1)*, 37-48.

103. Kiviranta-Paakkonen, P.K.; Struckmann, L.K.; Linnekoski J.A.; Krause, A.O.I. Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol; *Ind. Eng. Chem. Res*. **1998**, *37(1)*, 18-24.

104. Montgomery, D.C. *Design and Analysis of Experiments*, 3rd ed., John Wiley and Sons., New York, New York , 1991.

105. Piel, W.J. Diversify Future Fuel Needs with Ethers; *Fuel Reformulation* **1994**, *4(2)*, 28-33.

106. Ignatius, J.; Jarvelin, H.; Lindqvist, P. Use TAME and Heavier Ethers to Improve Gasoline Properties; *Hydrocarbon Process.* **1995**, *74(2),* 51-53.

107. Kohn, P. Process Provides Option for Non-leaded Gas Makers; *Chemical Engineering* **1977**, *84*, 114-116.

108. Rihko-Struckmann, L.K.; Karinen, R.S.; Krause, A.O.I.; Jakobsson, K.; Aittamaa, J.R. Process Configurations for the Production of the 2-Methoxy-2,4,4-trimethylpentane – a Novel Gasoline Oxygenate; *Chem. Eng. Process.* **2004**, *43*, 57-65.

109. Henze, H.R.; Blair, C.M. The Number of Structurally Isomeric Alcohols of the Methanol Series; *J. Am. Chem. Soc.* **1931**, *53,* 3042-3046.

110. Snelling, J.; Curtis, C.W.; Park, Y.K. Synthesis of Higher Carbon Ethers from Olefins and Alcohols I: Reactions with Methanol; *Fuel Process. Technol.* **2003**, *83*, 219-234.

111. Mackay, D.; Paterson, S. Evaluating the Multimedia Fate of Organic Chemicals: A Level III Fugacity Model; *Environ. Sci. Technol.* **1991**, 2*5(3)*, 427-436.

112. Kawamoto, K; Arey, J.S.; Gschwend, P.M. Emission and Fate Assessment of Methyl Tertiary Butyl Ether in the Boston Area Airshed Using a Simple Multimedia Box Model: Comparison with Urban Air Measurements; *J. Air & Waste Manage. Assoc.* **2003**, *53(12)*, 1426-1435.

113. Schifter, I.; Magdaleno, M.; Diaz, L.; Kruger, B.; Leon, J.; Palmerin, M.E.; Casas, R,; Melgarejo, A.; Lopez-Salinas, E. Contribution of the Gasoline Distribution Cycle to Volatile Organic Compound Emissions in the Metropolitan Area of Mexico City; *J. Air & Waste Manage. Assoc.* **2002**, *52(5)*, 535-541.

114. Brown, S.L. Atmospheric and Potable Water Exposures to Methyl tert-Butyl Ether (MTBE); *Regul. Toxicol. Pharm.* **1997**, *25*, 256-276.

115. Cowan, C.E.; Mackay, D.; Feijtel,T.C.J.; Meent, D. v. d.; Di Guardo, A.; Davies, J.; Mackay, N. *The Multi-Media Fate Model: A Vital Tool for Predicting the Fate of Chemicals*; SETAC Press, Pensacola, Florida, USA, 1995.

116. Pierson, W.R.; Schorran, D.E.; Fujita, E.M.; Sagebiel, J.C.; Lawson, D.R.; Tanner, R.L. Assessment of Nontailpipe Hydrocarbon Emissions from Motor Vehicles; *J. Air & Waste Manage. Assoc.* **1999**, *49(5)*, 498-519.

117. Cahill, T.M.; Mackay, D. Complexity in Multimedia Mass Balance Models: When are Simple Models Adequate and When are More Complex Models Necessary?; *Environ. Toxicol. Chem.* **2003**, *22(6)*, 1404-1412.

118. United States Environmental Protection Agency, Estimation Programs Interface, http://www.epa.gov/opptintr/exposure/docs/EPIsuitedl.htm (accessed Dec 2005).

119. Trapp, S.; Matthies, M. *Chemodynamics and Environmental Modeling;* Springer-Verlag, Berlin, Germany, 1998, p. 107.

120. Vainiotalo, S.; Peltonen, Y.; Ruonakangas, A.; Pfaffli, P. Customer Exposure to MTBE, TAME, C_6 Alkyl Methyl Ethers, and Benzene during Gasoline Refueling; *Env. Health Pers.* **1999,** *107(2)*, 133-140.

121. Abdel-Rahman, A.A. On the Emissions from Internal-Combustion Engines: A Review; *Int. J. Energy Res.* **1998**, *22*, 483-513.

122. Schafer, F.; Basshuysen, R. v. *Reduced Emissions and Fuel Consumption in Automobile Engines,* **1995**, SAE SP, ISBN 1-56091-681-8, p. 117.

123. EUSES, the European Union System for the Evaluation of Substances version 2.0. European Chemical Bureau, Joint Research Center, Ispra, Italy. http://ecb.jrc.it (accessed Dec 2005).

124. Rand, G.M., ed. *Fundamentals of Aquatic Toxicology;* Second Edition, Taylor and Francis, Washington, D.C., USA, 1995, p. 632.

125. MTBE (methyl tertiary butyl ether) Briefing Paper prepared by the California Environmental Protection Agency; accessed at URL http://www.arb.ca.gov/fuels/gasoline/oxy/mtbebp.pdf (accessed Dec 2005).

126. USEPA, Office of Pollution Prevention and Toxics, Chemical Summary for Methyl-tert-Butyl Ether, EPA 749-F-94-017a. http://www.epa.gov/chemfact/s_mtbe.txt (accessed Dec 2005).

127. Silbergeld, Ellen. *High Production Volume (HPV) Challenge Program*. http://www.epa.gov/chemrtk/silbrgld.htm (accessed Dec 2005).

128. USEPA. *The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program*. http://www.epa.gov/chemrtk/sarfinl1.htm (accessed Dec 2005).

129. Organisation for Economic Co-operation and Development. *Manual for Investigation of HPV Chemicals.* http://www.oecd.org/dataoecd/60/24/1947517.pdf (accessed Dec 2005).

130 Leeuwen, C.J. v.; Hermens, J.L.M., eds. *Risk Assessment of Chemicals: An Introduction*; Kluwer Academic Publishers, Dordrecht, The Netherlands, **1995**, p. 87.

131. Williams, P.D.R.; Scott, P.K.; Sheehan, P.J.; Paustenbach, D.J. A Probabilistic Assessment of Household Exposures to MTBE in California Drinking Water; *Human and Ecological Risk Assessment* **2000**, *6(5)*, 827-849.

132. Caldwell, J. C.; Woodruff. T.J.; Morelo-Frosch, R.; Axelrad, D.A. Application of Health Information to Hazardous Air Pollutants in EPA's Cumulative Exposure Project; *Tox. Ind. Health* **1998**, *14(3)*, 429-454.

133. Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry*, John Wiley & Sons, New York, NY, 1993, p. 273.

134. Boethling, R.S.; Lynch, D.G.; Thom, G.C. Predicting Ready Biodegradability of Premanufacture Notice Chemicals; *Environ. Toxicol. Chem.* **2002** *22(4)*, 837-844.

135. Papachristos, M.J.; Swithenbank, J.; Priestman, G.H.; Stournas, S.; Polysis, P.; Lois, E. The Effect of the Molecular Structure of Anti-knock Additives on Engine Performance; *J. Inst. Energy* **1991**, *64*, 113-123.

136. Arey, J.S.; Gschwend, P.M. A physical-chemical screening model for anticipating widespread contamination of community water supply wells by gasoline constituents; *J. Contam. Hydrol.* **2005**, *76(1-2)*, 109-138.

137. Weaver, J.W.; Charbeneau, R.J. *A Screening Approach to Simulation of Aquifer Contamination by Fuel Hydrocarbons (BTEX and MTBE)*; accessed at URL http://www.epa.gov.nerl/mtbe/approach.pdf

138. Sulfita, J.M.; Mormile, M.R. Anaerobic Biodegradation of Known and Potential Gasoline Oxygenates in the Terrestrial Subsurface; *Environ. Sci. Technol.* **1993**, *27(5)*, 976-978.

139. Bennett, A.; Orbey, H.; Sandler, S. Vapor-Liquid Equilibria of Hydrocarbons and Fuel Oxygenates. 2.; *J. Chem. Eng. Data* **1993,** *38*, 263-269.

140. Gonzalez, J.A.; Carmona, F.J.; Riesco, N.; de la Fuente, I.G.; Cobos, J.C. Thermodynamics of Mixtures Containing Ethers; *Phys. Chem. Chem. Phys.* **2000**, *2*, 2587-2597.

141. Cline, P.V.; Delfino, J.J.; Rao, P.S.C. Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures; *Environ. Sci. Technol.* **1991**, *25*, 914-920.

142. Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry*, Second Edition, John Wiley & Sons, New York, NY, 2003, p. 141.

143. Chevron – Gasoline Refining and Testing; accessed at URL http://www.chevron.com/products/prodserv/fuels/bulletin/motorgas/3_refining-testing/

144. European Union Risk Assessment Report – 2-METHOXY-2-METHYLBUTANE. http://ecb.jrc.it/Documents/Existing-Chemicals/RISK_ASSESSMENT/DRAFT/R413_0409_env.pdf (accessed Dec 2005).

145. Final Statement of Reasons, Primary Maximum Contaminant Level for Methyl tert-Butyl Ether, Title 22, California Code of Regulations; accessed at URL http://www.dhs.ca.gov/ps/ddwem/chemicals/mtbe/4-17-00MTBESOR.PDF

146. Delta Environmental Consultants, Inc. *Groundwater Oxygenate Cleanup Levels for LUST Sites*; accessed at http://epa.gov/oust/mtbe/oxytable.pdf

147. Ahmed, F.E. Toxicology and Human Health Effects Following Exposure to Oxygenated or Reformulated Gasoline; *Toxicol. Lett.* **2001**, *123(2-3)*, 89-113.

148. Goklany, I.M. *Clearing the Air - The Real Story of the War on Air Pollution*, Cato Institute, Washington, D.C., 1999, pp. 24-40.

149. Fischbeck, P.S.; Farrow, R.S., eds., *Improving Regulation*, Resources for the Future, Washington, D.C., 2001, pp. 70-94.

150. Bryner, G.C. *Blue Skies, Green Politics*, Second Edition, Congressional Quarterly, Inc., 1995, p. 169.

151. Kirschner, E. Growth of Top 50 Chemicals Slowed in 1996 from Very High 1995 Rate, *Chemical and Engineering News*, **April 8, 1996**, *74(15)*, 16-22.

152. Williams, P.; Benton, J.W.; Sheehan, P. Comparative Risk Analysis of Six Volatile Organic Compounds in California Drinking Water; *Environ. Sci. and Tech.* **2002**, *36(22)*, 472-4728.

153. Executive Order D-5-99, by Gray Davis, Governor of the State of California, March 25, 1999.

154. Piel, W.J. and Thomas, R.X. Oxygenates for Reformulated Gasoline; *Hydrocarbon Processing* **1990**, *69(7)*, 68-73.

155. Unzelman, G.H. U.S. Clean Air Act expands role for oxygenates; *Oil and Gas Journal* **April 15, 1991**, 44-48.

156. Bryner, G.C. *Blue Skies, Green Politics*, Second Edition, Congressional Quarterly, Inc., 1995, p. 200.

157. Astle, M.J. *The Chemistry of Petrochemicals*, Reinhold Publishing Corporation, New York, NY, 1956, pp. 10-12.

158. Asinger, F. *Mono-Olefins, Chemistry and Technology*, Pergamon Press Ltd., London, U.K., 1968, pp. 49, 50.

159. Carey, F.A. *Organic Chemistry*, McGraw-Hill Book Co., New York, NY, 1987, p. 160.

160. Lee, Sunggyu *Methanol Synthesis Technology*, CRC Press, Boca Raton, FL, 1990, p. 25.

161. Daubert, T.E. *Chemical Engineering Thermodynamics*, McGraw-Hill Book Company, New York, NY, 1985, p. 284.

162. Fogler, H.S., *Elements of Chemical Reaction Engineering,* Third Edition, Prentice-Hall PTR, Upper Saddle River, NJ, 1999.

APPENDIX A

A BRIEF HISTORY OF TRANSPORTATION FUEL INDUCED AIR POLLUTION

Although the problem of air pollution in general is much older, the story of cleaner-burning transportation fuels begins in Los Angeles in the early 1940s. It was here that an air pollution problem quite unlike the smoke and particulate matter (PM) problems that had plagued cities since the dawn of the Industrial Revolution first became noticeable. Dubbed smog, it irritated the eyes and reduced visibility. Even though control measures aimed at reducing sulfur dioxide and particulate matter from stationary sources had proven quite successful, the citizens of Los Angeles perceived little, if any, progress in controlling smog [148].

Time Line for Mobile Source Air Pollution

1950	A.J. Haagen-Smit is credited with being the first to point out that the smog in the Los Angeles basin could be due to automobile exhaust fumes. At that time, governmental efforts at air pollution control were restricted to the state and local levels. Although it was clear that state and local governments were not getting the job done, supporters of state’s rights

were opposed to "federal meddling". The resulting political battle did little to address pollution abatement issues.

1955 Air Pollution Control Act - The federal government provided research, training and technical assistance for state and local governments, but had no statutory authority.

1957 By this time most experts agreed that the smog in the Los Angeles basin was caused by the formation of secondary pollutants such as ozone, formed by the reactions of hydrocarbons and nitrogen oxides from power plants and other industrial sources, but also from motor vehicles.

1959 California adopted Ambient Air Quality Standards for ethylene, nitrogen oxides, photochemical oxidants, sulfur dioxide, and carbon monoxide. Carbon monoxide had long been known as a poisonous gas that would kill indoors if not vented properly. Thus, it is easy to understand the public’s alarm at the finding of significant concentrations of CO in ground level ambient air.

1961 Motor vehicle manufacturers voluntarily equipped new vehicles for sale in California with a crankcase emissions control device.

1963	The crankcase emissions control device was voluntarily extended throughout the United States.
1963	Clean Air Act - The U.S. Government was empowered to use the courts to enforce its recommendations, but this proved ineffective, as only one case ever went to court.
1964	California mandated the use of crankcase emissions control devices.
mid-to-late 60s	Automobile exhaust also became a problem in the urban areas of the Northeast.
1965	Motor Vehicle Air Pollution Control Act - gave the federal government authority to regulate hydrocarbon and carbon monoxide emissions.
1966	California mandated motor vehicle emissions standards for new cars.
1968	California’s standards were extended nationwide for new cars.

FULL-SCALE FEDERALIZATION

1970 Clean Air Act Amendments - substantially expanded the federal government’s role. The act put into place the basic framework for air pollution control that still exists today. It established federal National Ambient Air Quality Standards (NAAQS). The act set "rigid" deadlines to meet NAAQS’s, and most importantly for this research, mandated new motor vehicle emission standards requiring a 90% reduction (relative to pre-1968 levels) in unburned hydrocarbons and carbon monoxide by 1975 and in nitrogen oxides by 1976, although numerous extensions were granted.

1971 The EPA established NAAQS for sulfur dioxide, total suspended particulates, carbon monoxide, oxidants and nitrogen oxides.

LEAD IS PHASED OUT

Auto manufacturers resorted to post-combustion catalysts to reduce unburned hydrocarbons and carbon monoxide in exhaust. Since these catalysts are poisoned by lead, lead was phased out as catalyst-equipped vehicles came into the motor pool.

1978	NAAQS for lead was mandated. Compliance with the new standard proved to be relatively painless, since lead was already being phased out because of the damage it caused to post-combustion catalytic converters.

REMOVAL OF LEAD HURTS OCTANE

The removal of lead from the gasoline pool had a detrimental effect on octane. Refiners responded by increasing the aromatics content. Increased use of aromatics leads to poor mid-range volatility, higher benzene emissions, and increased emissions of toluene, ethyl benzene, xylenes and soot (PM). The need to replace aromatics in gasoline became apparent. Outside of metals, oxygenates are generally the only high octane alternative to aromatics in gasoline.

TIME LINE FOR OXYGENATES [149]

1969	tertiary Butyl alcohol - first oxygenate used commercially
1973	MtBE introduced in Europe
1978	U.S. government subsidized 10% ethanol - This was not an Air Pollution Control measure but an Energy Independence measure.
1979	EPA allowed 7 volume % MtBE in gasoline.
1981	EPA allowed 11 volume % MtBE in gasoline.
1988	EPA allowed 15 volume % MtBE in gasoline. Denver, CO, instituted the nation's first wintertime oxygenated fuels program.

EVENTS LEADING TO THE CLEAN AIR ACT AMENDMENTS OF 1990 (CAAA)

Urban air pollution caused by automobiles continued to be a problem through the 1980s. Two major issues were ozone pollution and the buildup of carbon monoxide levels in several cities during the winter months. Framing the Congressional debate about how to deal with these problems were proposals to mandate the use of vehicles that could use cleaner-burning alternative fuels like methanol and natural gas. The proposals were controversial and faced major opposition from both auto makers and the oil industry.

1989 President Bush proposed the mandatory use of alternative-fuel vehicles in the nine most polluted cities.

August 15, 1989 ARCO responded

ARCO announced the introduction of EC-1, the first gasoline especially formulated to control emissions, for use in southern California. ARCO heralded EC-1 as a particularly cost-effective way to clean up emissions of older, non-catalyst equipped vehicles by as much as 15%. It is one of the many ironies of clean air politics that no one in Congress or the EPA had pushed for the development of reformulated gasoline [150]. It was only after ARCO made the announcement that cleaner-burning gasolines could be produced that Congress imposed on oil refiners to do so. At this point, the focus of congressional debate shifted from alternative fuels to the details of gasoline formulation. Of particular concern was the oxygen level that would be required in fuels. Adding oxygen to fuels increases combustion temperatures, resulting in lower levels of carbon monoxide and unburned hydrocarbons in the exhaust [1]. In addition, oxygenates replace volatile organic compounds (VOC) in fuel. Some of these have high vapor pressures and thus increase ozone levels. Both ethanol and MtBE had been approved for use in gasoline and therefore were the leading contenders in the significantly expanded oxygenate market that would result from the Congressional deliberations over RFG. A debate raged in Congress over MtBE versus ethanol, the details of which, although far more interesting than anything presented here, are beyond the scope of this discussion. MtBE emerged as the environmentally preferred candidate.

November 15, 1990 President Bush signed the Clean Air Act Amendments. The amendments introduced two new programs that mandated oxygenate use in motor fuels.

1. Wintertime oxygenated fuels program - OXY program.

The goal was to reduce carbon monoxide pollution during the winter months in 39 non-attainment areas by requiring 2.7 % oxygen in gasoline. These areas were designated as OXY areas. Many of these areas, particularly the corn belt states, used ethanol to meet the oxygenate requirement, but some, notably Alaska and California, opted for MtBE use.

2. RFG program

Beginning in 1995, the reformulated gasoline program required year-round use of 2.0% oxygen in gasoline in nine cities that failed to meet ozone standards. These areas were designated as RFG areas, and most used MtBE to meet the oxygenate requirement, with 87% of the country's reformulated gasoline being blended with MtBE [3]. However, there is considerable overlap in OXI and RFG areas, and some RFG areas used ethanol to meet oxygenate requirements. For the purposes of this discussion, RFG will be used to designate any gasoline that contains MtBE.

The demand for MtBE soared with the implementation of the RFG program. In the early 1990s, MtBE was one of the highest volume end-use chemicals manufactured in the United States. MtBE also showed the highest growth rate of all major chemicals during this period [151]. Production peaked in the late 1990s when MtBE was in use in 32% of the gasoline sold in America.

THE UNINTENDED CONSEQUENCE OF MtBE USE

MtBE was recognized as an environmental pollutant even during the Congressional debates. It had been included in a list of 189 hazardous air pollutants (HAP) in the 1990 CAAA. The EPA is therefore required to regulate MtBE. However, its use was still seen as overall beneficial. Since the introduction of RFG, ozone levels had decreased by 17% and carbon monoxide levels by as much as 13% [3]. Unfortunately, this was not its only effect. MtBE use also had consequences for the environment and public health.

HEALTH EFFECTS OF MtBE EXPOSURE

Soon after the introduction of MtBE into the gasoline pool, individuals who came into contact with it began complaining of headaches, dizziness, nausea and general malaise. This quickly led to public protest with widespread media coverage.

1993	Grass roots movements sprang up that were determined to remove MtBE from gasoline. One of the earliest was Oxybusters in New Jersey. Similar organizations were quickly established in other states where MtBE was in use. The EPA and Centers for Disease Control (CDC) undertook studies of possible health effects associated with MtBE fumes.
1994	Alaska banned fuels containing MtBE.
1996	More than 100,000 citizens in California signed a petition demanding a statewide ban. In affected areas all across the nation, local governments called for removal of MtBE from gasoline. However, as a result of its studies, the EPA declared MtBE safe, stating that it was not an acute health risk at typical exposure levels, and moreover, was safer than conventional gasoline. On the other hand, the Centers for Disease Control (CDC) testified before Congress and authenticated the connection between MtBE levels in the blood and health effects, including headaches, dizziness, disorientation, nausea and malaise. Also, MtBE is known to

aggravate chronic conditions such as asthma and allergic reactions. The CDC postulated a link between MtBE and cancer in laboratory animals.

2002 Investigators in California found that MtBE ranked sixth in detection frequency for VOCs in drinking water. Because of the generally low concentration ranges when detected and comparatively low toxicity, MtBE was considered the least threat to water supplies of the six most frequently detected VOCs [152].

MtBE ENTERS THE NATION'S GROUNDWATER

Gasoline containing MtBE has spilled or leaked from the nation's gasoline distribution infrastructure on many occasions since its introduction in 1979. Groundwater specialists recognize MtBE as a particularly troublesome contaminant due to its high water solubility, extremely slow rate of natural biodegradation, and very low odor and taste thresholds in water.

Early 1980s Cases of groundwater contamination appeared shortly after EPA approved MtBE for use in fuel.

1980s The EPA estimated that 11 million gallons of gasoline leaks from leaking underground storage tanks each year [12]. Despite the widespread problem, almost no concern was raised about the potential for contamination of groundwater by MtBE in the 1990 CAAA debates or implementation of the resulting regulations.

REGULATORS RESPOND WITH ADVISORY LEVELS

1986 Maine established a health advisory level of 50 ppb in domestic water.

1988 The EPA established a 20-200 ppb lifetime drinking water health advisory, but failed to mention important elements of the perception of public risk associated with its extremely low taste and odor thresholds. Health advisories are not legally enforceable, and the scattered indications that MtBE posed a threat to groundwater supplies were not enough to force changes in regulation of reformulated fuels.

1997 Santa Monica, CA. The situation changed when MtBE tainted seven of this city's eleven drinking water supplies, representing 50% of the total supply. The wells were closed and city engineers were faced with the challenge of providing alternative water supplies to this already water resource limited area. Widespread publicity pressured the government to conduct a statewide study.

1998 The study uncovered 10,000 MtBE contaminated sites in California, which led to increased public awareness and a renewed demand for action. Senate Bill (SB) 521 called for an outright ban on MtBE. However, air regulators, environmentalists and oil companies joined together to oppose an outright ban. Instead they advocated remediation of contaminated areas and improved spill prevention techniques, while still allowing the use of MtBE.

1998 A University of California study determined that MtBE use is placing the state's limited water resources at risk. The study recommended phasing out MtBE over several years.

March 1999 Governor Gray Davis declared MtBE a significant risk to California's environment and issued an executive order for the removal of MtBE from the state's gasoline by December 31, 2002 [153], although a one year moratorium was granted.

LAWSUITS

Perhaps more importantly, lawsuits over MtBE are legion in RFG areas. Just one example:

August 1997 CONOCO lost a $9.5 million lawsuit, plus undisclosed punitive damages, in North Carolina to residents of a trailer park who claimed CONOCO was negligent in contaminating their water wells with MtBE and benzene. Oil refiners began to announce they would eliminate MtBE from their gasolines.

HOW DO WE REPLACE MtBE?

In retrospect, it is clear that MtBE was an expensive solution to our transportation fuel induced air pollution problems [11]. Nevertheless, oxygenates are still considered the best blend components for reformulated gasoline. Under current law, methanol and ethanol are too volatile* for use in RFG [64, 67, 154, 155]. However, the debate is back in Congress to allow ethanol use by raising the Reid vapor pressure limit on RFG.

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* Actually, both methanol and ethanol have lower vapor pressures than gasoline. However, when these alcohols are blended in gasoline, they tend to displace the highly volatile butane/butylene fraction, with the consequence that the vapor pressure of the resulting mixture exceeds the limit imposed by law. There is so much controversy surrounding the formulation of reformulated gasoline that even the physical properties of alcohol/gasoline mixtures have been the subject of debate. At least one author [156] disagrees with the references cited above, insisting that “methanol does not make gasoline more volatile and does not lead to evaporation”.

HIGHER CARBON ETHERS

Other suitable oxygenates include higher carbon ethers, which are being developed for use as replacements for MtBE [6, 7]. The higher carbon ethers can be prepared by alkanolation of olefins [64]. Suitable olefins are present in Fluid Catalytic Cracking (FCC) gasolines [106]. The olefins can be alkanolated without being removed from the gasoline. This is very appealing to refiners as it avoids the cost of olefin removal [73]. There has been some research effort directed towards studying the process of olefin alkanolation in gasoline [81]. However, gasoline contains a limited quantity of olefins of sufficient carbon number for alkanolation to higher carbon ethers with readily available low molecular weight alcohols [70]. Moreover, since the higher carbon ethers contain proportionately less oxygen than MtBE, they must be present in gasoline at proportionately higher concentrations in order to provide the same octane enhancing effect. Therefore, an outside source of a higher carbon olefin would be desirable. Olefins of carbon numbers C_6 and C_8 would be suitable for alkanolation to higher carbon ethers with low molecular weight alcohols. Olefins of carbon numbers C_6 and C_8 are easily prepared from smaller olefins, namely propylene and isobutylene, which are present in large quantities in refinery cracking process streams.

PROPYLENE AND ISOBUTYLENE

Both thermal cracking and fluid catalytic cracking processes lead to olefins, C_nH_{2n}, notably propylene and isobutylene, $H_2C = CH\text{-}CH_3$ and $(CH_3)_2C = CH_2$, respectively. These olefins readily dimerize to 2,3-dimethylbutenes (C_6-olefins) [107] and 2,4,4-trimethylpentenes (C_8-olefins) [66], respectively. The C_6- and C_8-olefins are the starting point for alkanolation reactions that lead to the higher carbon ethers. These reactions are discussed in greater detail in Appendix C.

Should the demand for higher ethers ever exceed the supply of propylene and isobutylene available from refinery cracking streams, then an alternate source of these olefins would have to be found. C_3- and C_4-olefins olefins are readily prepared from synthesis gas by a modification of the Fischer-Tropsch reaction known as the Hydrocol process. With the proper choice of catalyst and reaction conditions, this reaction can be tailored to produce a gasoline/diesel fuel blend comprised of greater than 70% olefins. The C_3 and C_4 cut consists of over 80% olefins [156, 157]. The preparation of MtBE entirely from synthesis gas has been demonstrated [56-58]. The alkanolation of synthesis gas derived C_6- and C_8-olefins with synthesis gas derived alcohols could provide a completely non-petroleum based route to the higher carbon ethers. Thus, the current study is important not only from an environmental perspective, but also for its potential contribution to national energy independence.

ETHERIFICATION REACTIONS

The etherification reactions of interest proceed according to the following equations:

C_6-olefins + R-OH $\rightarrow$ C_6-alkoxy ethers, C_8-olefins + R-OH $\rightarrow$ C_8-alkoxy ethers,

where ROH = C_1- to C_4-alcohols.

The alcohols in turn can be derived from synthesis gas. For example, in the presence of a methanol synthesis catalyst:

$$CO + 2\ H_2 \rightarrow CH_3OH$$

Higher alcohols are prepared with a modified version of the methanol synthesis catalyst [90]. It should be possible, by introducing an olefin with the synthesis gas and both an etherification catalyst and an alcohol synthesis catalyst, to prepare higher ethers without removing the intermediate alcohol. The author termed this process the single-step etherification reaction.

APPENDIX B

RESEARCH PLAN

HIGHER CARBON ETHERS FROM OLEFINS AND SYNTHESIS GAS - THE RATIONALE BEHIND THE RESEARCH

Winter, 1998

In an effort to exploit America's coal resources, the DOE solicited proposals to fund C1 Chemistry Research. C1 chemistry refers to the conversion of simple carbon-containing materials that have one carbon atom per molecule into valuable products [8]. One of the major feedstocks for C1 chemistry is synthesis gas. Synthesis gas is readily prepared from coal, and its production is a current commercial reality. The DOE's target was value-added chemicals from synthesis gas. The focus was eventually narrowed to the production of motor fuel oxygenates, particularly MtBE, from syngas. The EPA was skeptical but DOE still supported MtBE use and further research.

Methanol is frequently an intermediate in the preparation of chemicals from synthesis gas:

$$CO + 2\ H_2 \rightarrow CH_3OH$$

Physical removal of the intermediate methanol, such as by distillation, is both costly and inefficient, and constitutes perhaps the major impediment to the industrial use of syngas. However, physical removal can be avoided by removing the methanol chemically in a value-added chemical. For example, the single-step dimethyl ether (DME) synthesis employs both a methanol synthesis catalyst and a dehydration catalyst to convert synthesis gas directly to DME:

$$2\,CO + 4\,H_2 \rightarrow 2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

Alternatively, an olefin could be introduced with the synthesis gas, and by employing both a methanol synthesis catalyst and an etherification catalyst, an ether could be prepared in a single step. For example, in the case of isobutylene:

$$\underset{\text{isobutylene}}{(CH_3)_2C = CH_2} + CO + 2\,H_2 \rightarrow \underset{\text{MtBE}}{(CH_3)_3\text{-}C\text{-}OCH_3}$$

Summer, 1999

Environmental pressure against MtBE continued to mount. The DOE discontinued funding of MtBE research in favor of higher carbon ethers that are thought to be more environmentally friendly.

The ethers selected to be produced for this study are in the C_7 to C_{12} range. The new DOE directive adds an enormous complexity to the current work. Consequently, the study is divided into two parts:

Part One	Determine the optimum conditions for the etherification of C_6- and C_8-olefins with pre-formed C_1- to C_4-alcohols in a series of batch reactions.
Part Two	Using the optimum conditions as determined in Part One, develop a continuous process for the preparation of higher carbon ethers from olefins and synthesis gas in a single-step etherification reactor. This constitutes future work, and is discussed in more detail in Chapter VI.

The research presented in Chapter III is concerned with Part One above.

A goal of this research is to determine, by a systematic evaluation of the relevant reaction parameters in a batch reactor system, the optimum conditions for the preparation of higher carbon ethers from C_6- and C_8-olefins and pre-formed methanol, ethanol and 2-butanol. These parameters include: temperature, pressure, reaction time, molar ratio of olefin to alcohol, effect of the reaction medium, and the effect of the presence of the methanol synthesis catalyst.

In all, 235 tubing bomb microreactor batch reactions were conducted using the technique described in Appendix D. This experimental technique was developed using isobutylene and methanol to first form MtBE, since a great deal is known about the preparation of MtBE, whereas very little is known about the synthesis of higher carbon ethers. In this investigation,

1) the catalytic activity of Amberlyst 15® wet and Amberlyst 15® dry will be compared.

2) thermal stability tests of 1-heptene and 1-octene will be conducted.

3) catalytic stability tests of 1-heptene and 1-octene will be conducted.

4) an attempt to etherify 1-heptene and 1-octene will be made.

5) the catalysts will be crushed to insure the reactions aren't diffusion limited.

6) C_6- and C_8-olefins will be etherified with methanol under varying reaction conditions as follows:

    a) The temperature will be varied (mindful of the constraints set by the methanol synthesis technology to be employed in Part Two of this project) to determine the optimum temperature for etherification reactions.

    b) The reaction time will be varied to determine the minimum time required to insure maximum ether production.

    c) The pressure will be varied to determine the effect on etherification, since Part Two of this project may require elevated pressures to drive the methanol synthesis reaction.

    d) An inert diluent (decalin) will be employed to determine whether there would be any effect on etherification yields, as Part Two may employ an inert hydrocarbon to dissipate the heat from the methanol synthesis reaction.

    e) A methanol synthesis catalyst will be introduced to determine

        i) if the methanol synthesis catalyst has any etherification activity of its own, and

        ii) if the methanol synthesis catalyst inhibits the etherification reaction. This will insure that the dual catalyst system proposed for use in Part Two is not composed of incompatible or antagonistic catalysts.

f) An acetone extraction technique using 2,2,4-trimethylpentane as an internal standard for quantitative gas chromatographic (GC) determination of reactants and products in reaction mixtures will be developed. The undiluted reaction mixtures have been found to flood the flame ionization detector.

g) The work will be extended to ethanol and 2-butanol. 2-propanol was masked by the acetone used in the extractive analytical procedure and could not be detected by GC. For this reason, no ethers of carbon number C_{11} were prepared. Developing an additional extractive analytical procedure with another solvent did not seem warranted.

Environmental Aspects

Potential environmental issues arising from replacing MtBE in gasoline with methyl tertiary hexyl ether or methyl tertiary octyl ether will also be addressed. There are two main sources of environmental contamination with gasoline oxygenates; one is direct emissions from automobiles to ambient air and the second is releases from leaking underground fuel tanks and subsequent migration into aquifers. Therefore, two models are required to simulate oxygenate behavior in the environment; an atmospheric contaminant transport model and a groundwater contaminant transport model.

Atmospheric Contaminant Transport Model

Since releases of gasoline constituents from automobiles are highly dispersed and diffuse, their fate is well modeled by the regional equilibrium compartmentalization type models. A simple box airshed model [112] for estimating MtBE concentrations in ambient air, which has been field validated, will be used to predict the expected atmospheric concentrations of methyl tertiary hexyl ether and methyl tertiary octyl ether. The air concentrations will also be assessed using the European Union System for the Evaluation of Substances version 2.0 multimedia fate model, which simultaneously predicts the expected concentrations of contaminants in the various environmental media of air, water, soil and sediment. The predicted environmental concentrations will then be compared to the concentrations that might be expected to cause adverse effects to humans or ecosystems, thereby giving an indication of risk.

Groundwater Contaminant Transport Model

MtHxE and MtOcE may also pose a threat to the environment if they are released from leaking underground fuel tanks (LUFT). The principal danger here is the contamination of groundwater supplies. As was the case with MtBE, this will constitute a highly localized issue and, as such, is not well modeled by the regional equilibrium compartmentalization type models. A physicochemical model is more suitable for this type of contaminant modeling. A model for use in the current study was selected from the recent literature [136] based on its ability to adequately predict concentrations of MtBE in well water near a leaking underground fuel tank release site. The model parameters will be adjusted to reflect the differing physicochemical properties of the higher carbon ethers and the expected increased release loadings. The predicted well water concentrations will then be compared to the concentrations that might be expected to cause adverse effects from consumption, or cause odor and taste problems, thereby giving an indication of risk.

APPENDIX C

ADDITION REACTIONS OF OLEFINS

The characteristic reaction of olefins is electrophilic addition to the carbon-carbon double bond [159]:

$$C{=}C + X\text{-}Y \rightarrow X\text{-}C\text{-}C\text{-}Y$$

In the single-step etherification of synthesis gas with olefins, methanol is added to the double bond according to the following reaction:

$$C{=}C + CH_3OH \rightarrow CH_3O\text{-}C\text{-}C\text{-}H$$

However, other molecular species present in the synthesis gas product mixture may also add to the double bond. Thus, unreacted hydrogen may add:

$$C{=}C + H_2 \rightarrow H\text{-}C\text{-}C\text{-}H$$

This reaction requires the presence of a suitable catalyst, usually finely divided Pt, Pd or Ni, and so should not proceed under etherification conditions. Olefins may also dimerize in the presence of an acidic catalyst:

$$C{=}C + C{=}C \rightarrow C\text{-}C\text{-}C\text{-}C$$

While this reaction is critical to the preparation of higher olefins from propylene and isobutylene, it is not desirable here. Dimerization has been shown to take place under etherification conditions [86]. In fact, di-isobutylene is the main byproduct of MtBE manufacture. However, the authors also point out that di-isobutylene is only formed at start-up. Given the lower reactivities of the C_6- and C_8-olefins, the buildup of dimerization products to detectable levels is not likely in the syntheses proposed here.

The acidic catalyst also promotes alkylation of olefins:

$$C{=}C + C\text{-}H \rightarrow C\text{-}C\text{-}C\text{-}H$$

through the formation of an intermediate hydride ion. Once formed, the alkyl portion of an ether may add to an olefin in this manner. This reaction is not observed in isobutylene methanolation, and is not likely here either.

Of particular concern to this discussion is the hydration of olefins to alcohols. As water will likely be present in the product mixture, the following reaction will occur to some extent:

$$C{=}C + HOH \rightarrow H\text{-}C\text{-}C\text{-}OH$$

A long range goal of this research is to develop a catalytic reaction system that enhances the addition of alcohols to olefins to the exclusion of the other addition reactions.

Competing Reactions and Catalyst Compatibility

In the single-step etherification of synthesis gas with olefins, the equilibrium

$$CO + 2H_2 \rightarrow CH_3OH$$

is shifted to the right by reacting the methanol with an olefin according to the reaction:

$$CH_3OH + C_nH_{2n} \rightarrow CH_3OC_nH_{2n+1}$$

The methanol synthesis step proceeds, ideally, according to the following reaction:

$$CO + 2H_2 \rightarrow CH_3OH$$

However, the methanol synthesis catalyst also possesses water gas shift activity, and if any CO_2 is present, which would be very likely in an industrial application, water is produced according to the reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Furthermore, experiments have shown that CO_2 has a stabilizing effect on monovalent copper, Cu^+ or CuO_2, which is thought to be the active form of copper in the $CuO/ZnO/Al_2O_3$ catalyst [160]. Even in the absence of CO_2, which could be attained for laboratory purposes, a number of competing reactions result in water being present in the product mixture, e.g., reactions leading to higher alcohols plus water, hydrocarbons plus water, dimethyl ether plus water, and ketones plus water. In other words, water is a very likely component of the product mixture. There exists the possibility that the water thus produced will hydrate the olefin as it is introduced, rendering it unavailable for the etherification step. To what extent this will occur is not currently known. There may be operational parameter adjustments that may minimize this reaction. It should also be noted that the formation of small amounts of alcohols by the hydration of olefins will not have a very deleterious effect on the overall process, as these higher alcohols are also quite suitable for use as oxygenates in reformulated gasolines and cleaner-burning diesel fuels.

APPENDIX D

EXPERIMENTAL METHODOLOGY

The initial experimentation for this project was concerned with the preparation of MtBE from methanol and isobutylene. The purpose for conducting these experiments was fourfold. The experiments were conducted

1) as a feasibility demonstration;
2) to establish a baseline for the production of ethers from olefins and alcohols;
3) to familiarize the author with the preparation of ethers from olefins and alcohols; and
4) to develop an analytical procedure for the quantitative determination of ethers and unreacted reactants in the product mixture.

The preliminary syntheses were conducted because, at the time, the goal of this research was to prepare MtBE. When the focus of this research changed from MtBE to the higher carbon ethers, the investigations with MtBE provided a good framework from which to proceed to the syntheses of higher carbon ethers, as the preparation and characterization of MtBE is well known, whereas very little is known about the higher carbon ethers.

Apparatus - Use and Operation of the Tubing Bomb Microreactor System

All of the reactions studied in this research were conducted in 25 cm^3 stainless steel batch tubing bomb microreactors (TBMR). A schematic diagram of the tubing bomb microreactor is presented in Figure D-1. The reactors were constructed of thick-walled 316 stainless steel tubes and Swagelok tube fittings: a stainless steel tube of 3" length x 3/4" outside diameter (O.D.) x 0.065" wall thickness with a 3/4" Swagelok fitting (SS-1210-6-12W) used as a threaded seal. A copper anti-seize compound is applied to the threads of the reactor and cap, the reactants and catalyst are charged, and the cap is tightened. The use of the anti-seize compound greatly facilitates removal of the cap after reaction, as the high temperature reaction conditions promote galling of the threads. The TBMR is then pressured up to reaction pressure by introducing a gas through a metering valve. The valve is then closed and the connection for gas entry is plugged to insure protection against leakage. The TBMR is held underwater to check for leaks. The tubing bomb is thoroughly dried to reduce caking of sand from the sandbath on the outside of the reactor and particularly in the threads. The reactor is then ready for the sandbath.

The batch reactor system consists of a variable temperature fluidized sandbath (Tecam SBL-2D), a temperature controller (Techne TC4D), a variable speed agitator equipped with a tachometer, and a temperature monitor (Omega 199 Digital Recorder). A schematic of the reactor system is presented in Figure D-2. Two reactors are simultaneously attached to the agitator shaft in the horizontal position. The motion of the agitator is also horizontal. This geometry has been shown to give much better mixing of the reactor contents than a vertical geometry. The rate of agitation in this work was

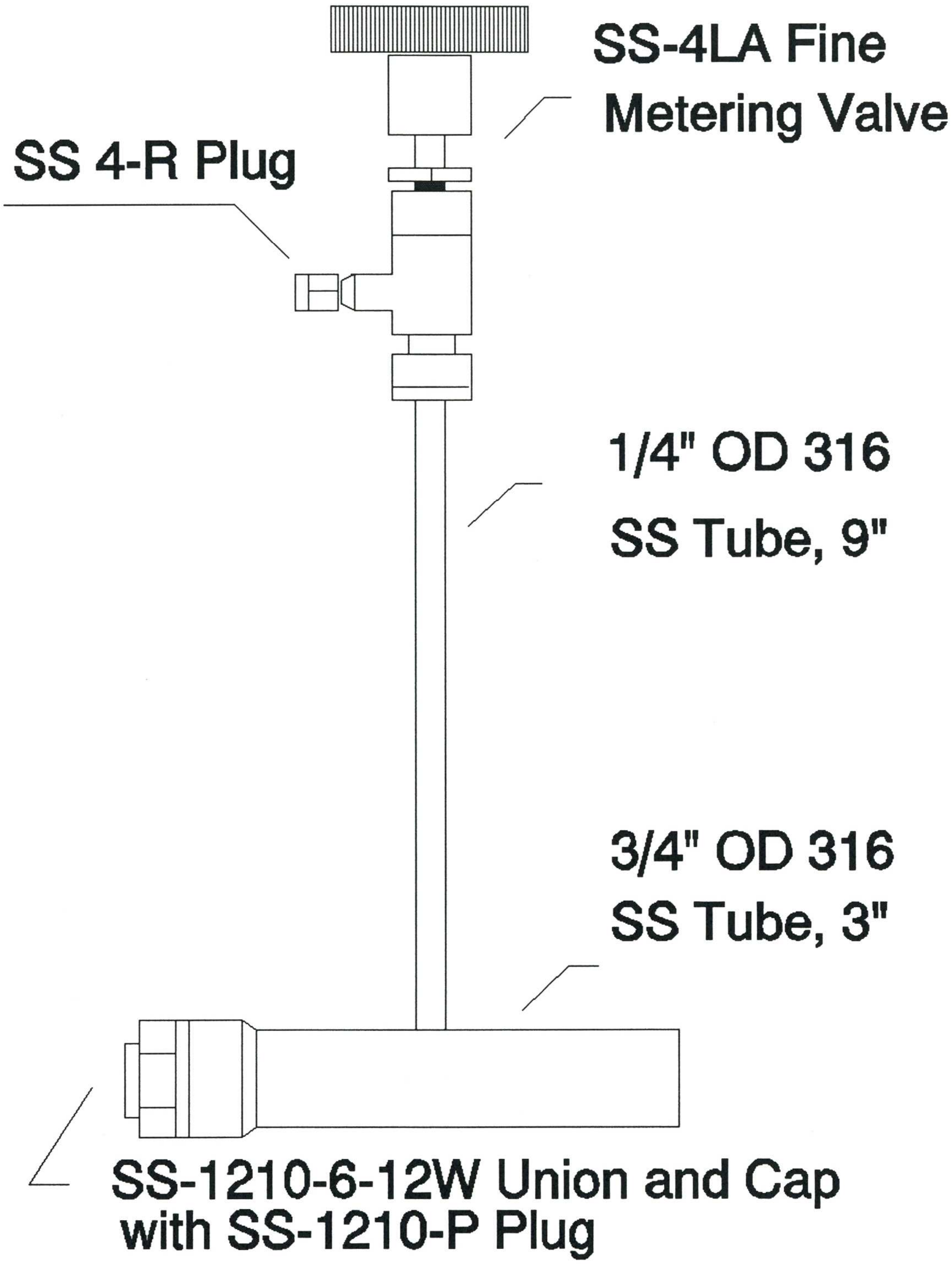


Figure D-1

Schematic Diagram of a Tubular Microreactor

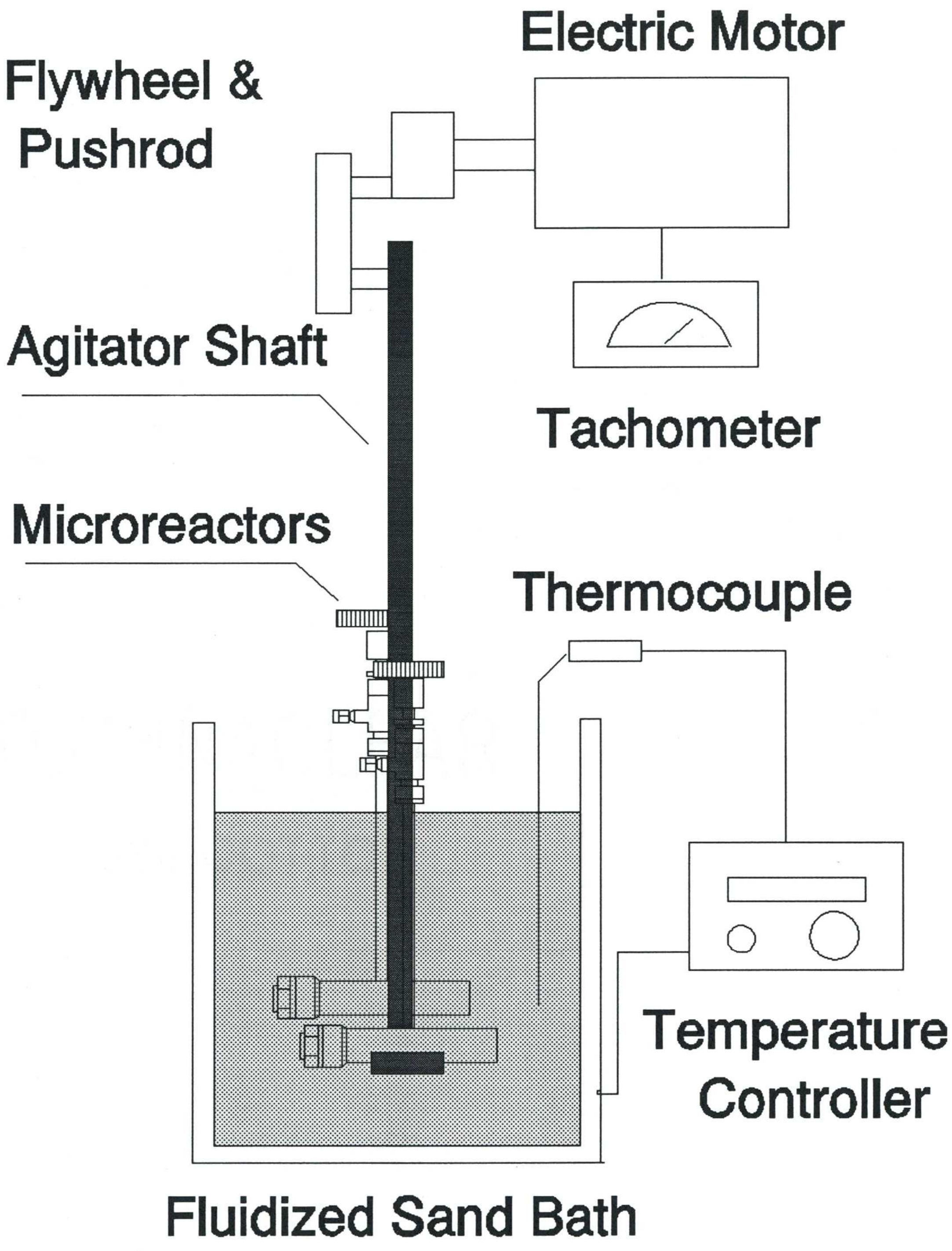


Figure D-2

Schematic Diagram of the Batch Reactor System

100 cycles/minute. The sandbath is preheated to the desired operating temperature and the reactors are lowered into the sand. The thermal shock from the introduction of the cold reactors into the hot sand is only about 2 ^{o}C of temperature loss, which persists for about one minute. The reactors are left to agitate in the sandbath for the specified length of time and then raised from the sandbath. The reactors are then allowed to cool to room temperature, as quenching the reactors made no difference in the product distribution.

Each reactor is then degassed through the metering valve into a foil bag under water in a completely full bucket. The water displaced from the bucket by the expansion of the gas into the submerged foil bag is weighed. This gives a rough approximation of the amount of inert gas in the tubing bomb after the reaction was over. Since no gases are generated or consumed in the preparation of higher ethers from preformed alcohols, it should be the same as the amount charged. This is a check against leakage, as these reactors are prone to leak, especially as they age. In theory, the collected gas could be subjected to analysis by GC. However, under the conditions of 200 psig pressure and room temperature, only trace amounts of the higher ethers enter the vapor phase [73], and GC analysis of the gaseous products was not performed. The cap is then removed from the reactor and the liquid and solid phases are removed and separated. The scheme liquid recovery is determined from the initial charge weight and the reactor liquid products weight. The catalyst is allowed to air dry and the percent catalyst recovery is likewise determined. The product liquids are now ready for GC analysis.

Dual (side-by-side) reactors are employed to produce replicate data sets. For any given test, the analytical results presented are an average of the results obtained from the individual reactors. As a general rule, the reactor charges and conditions are identical. The only exception to this rule is when the effect on ether production of changing one variable, for example pressure, is to be determined, all other parameters being held constant.

MtBE Syntheses

For the preparation of MtBE, 0.1 gram of Amberlyst® 15 dry is placed in the reactor along with one gram of methanol. The tube is pressurized to 20 psig with isobutylene, the saturation vapor pressure of isobutylene at room temperature. The isobutylene (99.0% purity) was obtained from BOC gases. Assuming isobutylene to behave as an ideal gas, which is a pretty safe assumption under the conditions of room temperature and 20 psig pressure, the amount of isobutylene in the tube is only about 0.12 grams. When the goal of this project was the preparation of MtBE, the plan was to increase the pressure of isobutylene to the 200 to 400 psig range or even higher. This would provide a more nearly equal molar ratio of methanol to isobutylene. For the purpose under discussion, all that was necessary was to provide enough isobutylene so that MtBE could be detected in the product mixture by GC analysis.

Reactions were conducted in the temperature range from 75 to 100 ^{o}C for one hour using the method described above. GC analyses confirmed the preparation of MtBE.

Synthesis of Ethers of Higher Carbon Number

In the study of the preparation of higher carbon ethers, a series of four reactions were performed to determine the efficacy of ether production from the reactions of olefins with methanol. Those reactions were thermal with olefin only (to demonstrate olefin stability); thermal with olefin and methanol; catalytic with olefin only (again, to demonstrate olefin stability) and catalytic with olefin and methanol. The first and third sets of reactions were conducted to establish baseline reactivity of the system without methanol, that is, to investigate any rearrangement of the olefinic structure. The reactions were performed using 25 cm^3 stainless steel batch reactors, which were immersed and agitated at 100 cpm in a temperature controlled sandbath. The reactions were performed at temperatures of 60 to 100 ^oC and reaction times from 15 minutes to 24 hours using a pressure of 200 psig hydrogen. Hydrogen was chosen as a blanketing gas as it represents a less toxic alternative to synthesis gas. The high-purity hydrogen (Grade 5.0) was obtained from BOC gases. One experiment was performed at an elevated pressure of 800 psig hydrogen to investigate the effect of pressure on etherification.

Materials

The olefins used in the preparation of higher ethers were the straight-chain olefins 1-hexene, 1-heptene and 1-octene, and the branched olefins 2,3-dimethyl-1-butene (23DM1B), 2,3-dimethyl-2-butene (23DM2B), 2,4,4-trimethyl-1-pentene (244TM1P) and 2,4,4-trimethyl-2-pentene (244TM2P). The reactions with the straight chain olefins were conducted at 100 ^oC while the reactions with the branched olefins were conducted at temperatures ranging from 60 to 100 ^{o}C, with most of the experiments being conducted at 70 ^{o}C. Reactions were initially performed at a 2:1 molar ratio of olefin (C_6 = 1.40 g; C_8 = 1.44 g) to methanol (for C_6 = 0.26 g; C_8 = 0.20 g) and then the molar ratio was changed to a 1:8 ratio of olefins (C_6 = 0.48 g; C_8 = 0.53 g) to methanol (for C_6 = 1.50 g; C_8 = 1.20 g) so that an excess of methanol would be present in the reactor. The olefins were obtained from Sigma Aldrich Chemical Company (97% purity) and the methanol was obtained from Fisher Scientific Company (OPTIMA® grade). The olefins were used as received. The methanol was dried over molecular sieves prior to use.

The etherification catalyst used in the reactions was Amberlyst® 15 (0.2 g) and was initially charged to the reactor at 10 wt% of the total charge. Catalyst studies were conducted in which dry Amberlyst® 15 was compared to wet Amberlyst® 15 and to crushed and extruded HZSM-5. Only the dry Amberlyst® 15 promoted any reactivity and hence was used for the rest of the experiments. Additional reactions using 23DM1B and 244TM1P were performed in which the amount of dry Amberlyst® 15 was halved to 5 wt%, doubled to 20 wt% and tripled to 30 wt% of the total charge; the Amberlyst® 15 was also crushed and charged at 10 wt%. Additionally, HZSM-5 was used alone and HZSM-5 and Amberlyst® 15 were used together to test the effect of the HZSM-5 on the etherification. Both dry and wet Amberlyst® 15 were obtained from Sigma-Aldrich Chemical Company. The wet Amberlyst® 15 was used as received. The dry Amberlyst® 15 was subjected to a pretreatment that consisted of rinsing the catalyst with deionized water and then drying the catalyst in an oven at 97 ^{o}C for three hours. The HZSM-5 was obtained from United Catalysts, Inc., and activated prior to use. The pretreatment consisted of heating the HZSM-5 under a nitrogen flow for two hours at 200 ^oC, followed by two hours at 400 ^oC.

After the reaction temperature and reaction time had been optimized, the study was extended to include ethanol and 2-butanol. The absolute ethanol was obtained from Florida Distillers Company. The 2-butanol was obtained from Sigma Aldrich Chemical Company (99% purity). The 2-butanol was used as received. The ethanol was dried over molecular sieves prior to use. Experiments were also conducted with 2-propanol, but the isopropanol eluted from the gas chromatography column at the same time as did acetone. Acetone was used as a diluent in the analytical procedure as described below in the analytical section. Since isopropanol could not be quantified, the study of its reactivity towards higher olefins was abandoned. Consequently, no ethers of carbon number C_{11} could be prepared. However, ethers of carbon number C_7 through C_{10} and C_{12} could be prepared with these starting materials, and this was thought to be sufficiently representative of the higher carbon ethers. The development of an analytical technique with a solvent other than acetone did not seem warranted.

Analytical Procedure

It was necessary to develop an extractive analytical gas chromatographic procedure to quantify the components of the reaction product mixtures generated in this study. Reaction products were analyzed by gas chromatography (GC) using a Varian model 3400 chromatograph equipped with a J&W Scientific DB-5 phase capillary, 25m x 0.32 mm I.D. with 0.52 μm film thickness. The injector was maintained at 200 ^{o}C and the flame ionization detector was maintained at 210 ^{o}C. The initial column temperature was 50 ^{o}C and the column was maintained at that temperature. 2,2,4-trimethylpentane was used as an internal standard. Response factors were determined for all available reactants and products. Response factors for the olefins were all close to unity. Response factors for oxygenates were directly proportional to the compound's weight percent carbon and inversely proportional to the compound's weight percent oxygen. Response factors for those products that were not commercially available were estimated by obtaining the response factors for structurally similar available compounds. For this reason, some of the product distributions presented may not sum to 100%. The response factors were determined to an accuracy of two significant figures.

An Analytical Method for Determining Olefins and Oxygenates in Reaction Product Mixtures

The reaction product mixtures were analyzed according to the following procedure. The liquid product was poured from the reactor into a pre-weighed vial. The vial was weighed again to determine the mass of liquid product. The percent liquid recovery was then calculated from the pre-reaction and post-reaction liquid masses. The percent liquid recoveries were generally in the 65 to 75% range, with some as high as 85%. Losses were mostly attributable to adhesion of the liquid product to the catalyst and to the reactor walls. It is also likely that small amounts of liquid product volatilized during transfer from the reactor to the vial. Like the percent gas recovery, the percent liquid recovery was used as an indicator of the integrity of the experimental run. Liquid recoveries less than 50% usually indicated that a leak had developed during the course of the reaction or that the degassing procedure was so violent as to expel some of the liquid contents into the foil gas bag. In such cases, the products were discarded without being analyzed and the experiments were repeated.

When the liquid products were injected neat onto the GC column, the Flame Ionization Detector (FID) was flooded, so it was necessary to develop a solvent extraction technique. Alcohols, hydrocarbons and ethers were eliminated as possible solvents *a priori* because of their potential for interference in the chromatograms of reactants and products. Acetone was chosen as solvent because both hydrocarbons and oxygenates are readily soluble in it and it has a low boiling point. The low boiling point ensures rapid and total flashing in the injection chamber of the GC. Acetone emerged from the column well ahead of reactant, product, and internal standard peaks. 2,2,4-trimethylpentane was chosen as the internal standard because of its structural similarity to one of the reactants (di-isobutylene) and because of its ready availability in small volumes of ultra-high purity material.

Preparation of Reaction Products for Injection onto the GC

0.2 grams of reaction product and 0.2 grams of internal standard were added to 1.5 grams of acetone and shaken thoroughly. 0.5 microliters of the resulting solution was injected onto the GC for analysis. The dilute solutions gave accurate, reproducible analytical results. The results were accurate to within three percent, and often to within one or two percent.

The Extension to Ethanol and 2-Butanol

Since alcohols in the C_2 to C_4 range can be prepared from synthesis gas with the proper choice of catalyst and conditions [56, 90], this work was extended to the higher alcohols ethanol and 2-butanol, from which ethers of carbon number C_8, C_{10} and C_{12} can be prepared using the same starting olefins. After the reaction temperature and run time for methanolation were optimized, the work was extended to ethanol and 2-butanol. It should be noted that the optimum reaction time for etherification with higher alcohols is greater than that for methanol because the higher alcohols are less reactive in etherification. However, since one of the goals of this research is to compare the reactivities of alcohols in etherification, once the optimum reaction time of two hours had been established, it was used as a basis for comparison thereafter. The optimization of the reaction time is discussed in greater detail in Appendix E.

Procedure for Using an Inert Diluent

The effect of concentration on etherification reactions was investigated by employing an inert diluent. Decalin was added to the reactant mixtures at mass ratios of one-to-one and one-to-two combined reactants to decalin. The decalin (99% purity) was obtained from Sigma-Aldrich Chemical Company and consisted of a 50:50 mixture of cis- and trans-decalin. No other modifications of the reaction procedure were necessary.

However, a modification had to be made to the analytical procedure. Because of the presence of the decalin, the reaction product mixtures were only partially soluble in acetone, and phase separation was observed. There was concern that the reaction products might partition between the two phases, which is to say that the acetone might not extract all the olefins and oxygenates from the decalin. Therefore, a new solvent had to be found that would dissolve both the reaction product mixture and the decalin. A suitable solvent was found in isopropanol. Ironically, isopropanol had been eliminated as a potential reactant in this investigation because it eluted at the same time as acetone, but now it found favor as an extraction solvent because it eluted at the same time as acetone, and therefore would not interfere with the chromatograms of the olefins and oxygenates. No other modifications to the analytical procedure were necessary.

APPENDIX E

THE SYNTHESIS OF HIGHER CARBON ETHERS

In this study, the investigation of etherification reactions began with the preparation of methyl tertiary butyl ether from methanol and isobutylene, as described in Appendix D. GC analysis confirmed the preparation of MtBE. The experiments with isobutylene allowed the author to gain valuable experience in the operation of the tubing bomb microreactor system and to begin the process of developing an analytical procedure for the determination of olefins, alcohols and ethers in the reaction product mixtures. However, since the goal of this research changed to the preparation of ethers of higher carbon number, the results of the experimentation with isobutylene will not be dwelt upon any further.

Reactions of Higher Olefins

As noted in Chapter II, attempts by Kazi et al. [19] to etherify isobutylene with synthesis gas resulted predominantly in the hydrogenation of the isobutylene. The hydrogenation activity was most likely attributable to the presence of the palladium on alumina catalyst. No other citations of etherification reactions conducted under an atmosphere containing hydrogen were found in the literature. Therefore, it was necessary to demonstrate that the etherification catalyst, Amberlyst® 15, did not possess hydrogenation activity. This was accomplished by comparing the reactivity towards etherification of a six carbon olefin under an inert atmosphere of helium and under a potentially reducing atmosphere of pure hydrogen. 2,3-dimethyl-1-butene has been shown to be reactive under etherification conditions [73] and so was selected for this test. In side-by-side testing, GC analysis of the reaction product mixtures revealed no peak corresponding to the hydrogenation product of the olefin, namely 2,3-dimethylbutane. Moreover, the product distributions into unreacted starting materials and ether were virtually identical. It was clear that hydrogen had no effect on the etherification reaction, so hydrogen was used as a blanketing gas in all subsequent experimentation.

Parameters Affecting the Synthesis of Ethers of Higher Carbon Number

In etherification, there are a number of reaction variables that determine the extent of reaction and product distribution. In this study, reaction temperature, reaction time, amount of catalyst loading, molar ratio of olefin to methanol, and concentration of reactants were selected for investigation. In total, 235 individual reactions were performed. For convenience in comparing the reaction conditions and experimental results, the olefins will be broken into three groups, namely, straight-chain olefins, the 2,3-dimethylbutenes and the 2,4,4-trimethylpentenes.

Straight-Chain Olefins

Given the proper reaction conditions, olefins undergo both isomerization and etherification. Therefore, it was deemed necessary to investigate the isomerization reaction separately, that is, in the absence of any alcohol. It was also of interest to determine what effect the catalyst had on isomerization. This was accomplished by utilizing an experimental design consisting of four reaction sets. The reaction sets performed were thermal reaction conditions with olefin only, catalytic reaction with olefin only, and thermal and catalytic reactions with olefins and methanol.

Thermal Reactivity of Neat Straight-Chain Olefins

In reactions using 1-hexene, 1-heptene, and 1-octene, performed at 100 ^{o}C, no reactivity was observed under thermal conditions, i.e., in the absence of a catalyst. The length of time that the olefins were allowed to react was two hours. Table E-1 presents the reaction conditions employed in the investigation of the thermal reactivity of these olefins.

Catalytic Reactivity of Neat Straight-Chain Olefins

Using the same reaction conditions except now in the presence of Amberlyst® 15, rearrangement of the olefinic structures was observed. The Amberlyst® provides the acidic sites necessary for the formation of a carbocation. The carbocation undergoes rearrangement and then adds a hydrogen atom to yield a different olefin than the starting compound. For all three starting olefins, less than 3% of the 1-alkene existed in the

Table E-1

Thermal Reactivity of Neat Straight-Chain Olefins

Run Number	Olefin	Ratio O/A	Time	wt% catalyst
SC-1	1-hexene	∞	2 hours	0
SC-2	1-heptene	∞	2 hours	0
SC-3	1-octene	∞	2 hours	0

SC denotes Straight-Chain olefin runs.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
wt% catalyst denotes weight percent of catalyst to the total reactor charge.

product after two hours of reaction time. Table E-2 presents the reaction conditions employed in the investigation of the catalytic reactivity of neat straight-chain olefins.

This type of rearrangement is typical of carbocations and therefore of olefins under these conditions [73], and shows that the 1-alkene, or alpha-olefin, is thermodynamically the least stable olefin. The terminal carbon atoms are only attached to one other carbon atom, whereas each carbon atom in the interior of the chain is attached to two other carbon atoms. Carbon atoms with two neighboring carbon atoms can better accommodate the positive charge of the carbocation. Therefore, migration of the carbocation to a beta, gamma or delta position takes place, yielding a mixture of isomers. As isomers, they have different boiling points and affinities for the packing material in the GC column, and therefore, different elution times. The isomers are readily identified as separate compounds by the gas chromatographic method employed in this research.

Table E-2

Catalytic Reactivity of Neat Straight-Chain Olefins

Run Number	Olefin	Ratio O/A	Time	wt% catalyst
SC-4	1-hexene	∞	2 hours	10
SC-5	1-heptene	∞	2 hours	10
SC-6	1-octene	∞	2 hours	10

SC denotes Straight-Chain olefin runs.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
wt% catalyst denotes weight percent of catalyst to the total reactor charge.

Thermal Reactivity of Straight-Chain Olefins towards Methanol

Using the same starting olefins, in reactions performed at 100 ^{o}C in the absence of any catalyst, no reactivity towards methanol was observed. The length of time that the olefins and methanol were allowed to react was two hours. Table E-3 presents the reaction conditions employed in the investigation of the thermal reactivity of these olefins towards methanol.

Catalytic Reactivity of Straight-Chain Olefins towards Methanol

The reactivity of 1-hexene, 1-heptene and 1-octene under etherification conditions could now be investigated. While a temperature of 100 ^{o}C was maintained for all the reactions, the time of reaction was varied from 15 minutes to two hours. Three molar ratios of olefin to methanol were employed, namely 2:1, 1:1 and 1:2. Also, the catalyst loading was doubled from the original 10 wt% to 20 wt% in the hopes of encouraging the reaction. However, no ethers were observed in the product mixtures. Table E-4 presents

Table E-3

Thermal Reactivity of Straight-Chain Olefins towards Methanol

Run Number	Olefin	Ratio O/A	Time	wt% catalyst
SC-7	1-hexene	2:1	2 hours	0
SC-8	1-heptene	2:1	2 hours	0
SC-9	1-octene	2:1	2 hours	0

SC denotes Straight-Chain olefin runs.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
wt% catalyst denotes weight percent of catalyst to the total reactor charge.

Table E-4

Catalytic Reactivity of Straight-Chain Olefins towards Methanol

Run Number	Olefin	Ratio O/A	Time	wt% catalyst
SC-10	1-hexene	2:1	2 hours	10
SC-11	1-heptene	2:1	2 hours	10
SC-12	1-heptene	1:2	2 hours	10
SC-13	1-octene	1:1	15 minutes	10
SC-14	1-octene	1:1	30 minutes	10
SC-15	1-octene	1:1	45 minutes	10
SC-16	1-octene	1:1	60 minutes	10
SC-17	1-octene	2:1	30 minutes	10
SC-18	1-octene	2:1	60 minutes	10
SC-19	1-octene	2:1	90 minutes	10
SC-20	1-octene	2:1	2 hours	10
SC-21	1-octene	1:2	2 hours	10
SC-22	1-octene	1:1	60 minutes	20
SC-23	1-octene	2:1	60 minutes	20

SC denotes Straight-Chain olefin runs.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
wt% catalyst denotes weight percent of catalyst to the total reactor charge.

the reaction conditions for the attempted etherifications. As was the case with the catalytic reactions without methanol, rearrangement of the olefins was observed in the presence of methanol. While in the presence of methanol, a small amount of unidentified higher boiling material was produced, but no ethers were observed in the product mixture. The higher boiling material was most likely a dimerization product of the starting olefins.

Branched Olefins

The next phase of the experimental work involved reactions of branched C_6- (2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) and C_8- (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) olefins. These olefins were subjected to the same set of four basic reaction conditions as were the straight-chain olefins, namely, thermal reaction conditions with olefin only, catalytic reaction with olefin only, and thermal and catalytic reactions with olefins and methanol. The work with C_6- and C_8-olefins was extended to ethanol and 2-butanol. Additionally, the reactivity towards etherification of mixtures of C_6- and C_8-olefins towards methanol, ethanol and 2-butanol was investigated. The reactivity of C_6-olefins and C_8-olefins towards mixtures of methanol and ethanol was also studied. Finally, the reactivity of mixtures of C_6-olefins and C_8-olefins towards mixtures of methanol and ethanol was investigated.

The effect on etherification of several other process parameters was also determined. These parameters include reaction temperature, pressure, run time, catalyst loading, molar ratio of olefin to alcohol, and concentration of reactants. The concentration of the reactants was varied by dilution in an inert hydrocarbon solvent, namely decalin. Additionally, the effect of crushing the etherification catalyst was also determined. Finally, the effect of the presence of a methanol synthesis catalyst, both pelletized and crushed, was investigated.

Thermal Reactivity of Neat 2,3-Dimethylbutenes

The 2,3-dimethylbutenes were found to be thermally stable when heated to 80 °C and allowed to react for two hours in the absence of any catalyst or other reactant.

Thermal Reactivity of 2,3-Dimethylbutenes towards Methanol

Under the same conditions, the 2,3-dimethylbutenes did not react with methanol in the absence of a catalyst.

Catalytic Reactivity of Neat 2,3-Dimethylbutenes

Under the same conditions, both 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene isomerize in the presence of Amberlyst® 15 to give a mixture containing approximately 10% 2,3-dimethyl-1-butene and 90% 2,3-dimethyl-2-butene.

Etherification of 2,3-Dimethylbutenes with Methanol

Having established the baseline reactivities of the 2,3-dimethylbutenes, a systematic evaluation of their reactivities towards etherification in methanol was performed. In these reactions, the temperature was varied from 60 °C to 100 °C. The run times varied from two hours to 24 hours. Two molar ratios of olefin to methanol were employed, namely 2:1 and 1:8. Figure E-1 presents the reaction schemes for these etherifications.

It was noticed in the literature that some investigators chose to pretreat their Amberlyst® 15 before attempting etherifications. It was decided to determine whether such a pretreatment would have any effect on the etherifications under study here. The pretreatment consisted of rinsing the Amberlyst® 15 with deionized water and then drying in an oven at 97 °C for three hours. The activity in etherification of the pretreated Amberlyst® 15 was then compared to the activity of Amberlyst® 15 as received in side-by-side testing. 2,3-Dimethyl-1-butene was etherified with methanol at 100 °C for two hours. Table E-5 presents the reaction conditions and product distributions for this experimentation. All of the product distributions presented in this dissertation are reported on a methanol free basis. It can be seen from the product distributions that the pretreatment had little or no effect on the etherification reaction, with both the pretreated catalyst and the as received catalyst yielding twenty-three percent ether with an overall conversion of ninety percent. Similarly, no differences were noted in the etherification of 2,4,4-trimethyl-1-pentene. The practice of pretreating the catalyst was therefore not adopted.

Effect of Temperature on the Synthesis of Methyl Tertiary Hexyl Ether

The effect of temperature on the reactivity of 2,3-dimethyl-1-butene towards etherification with methanol was determined in the temperature range from 60 °C to

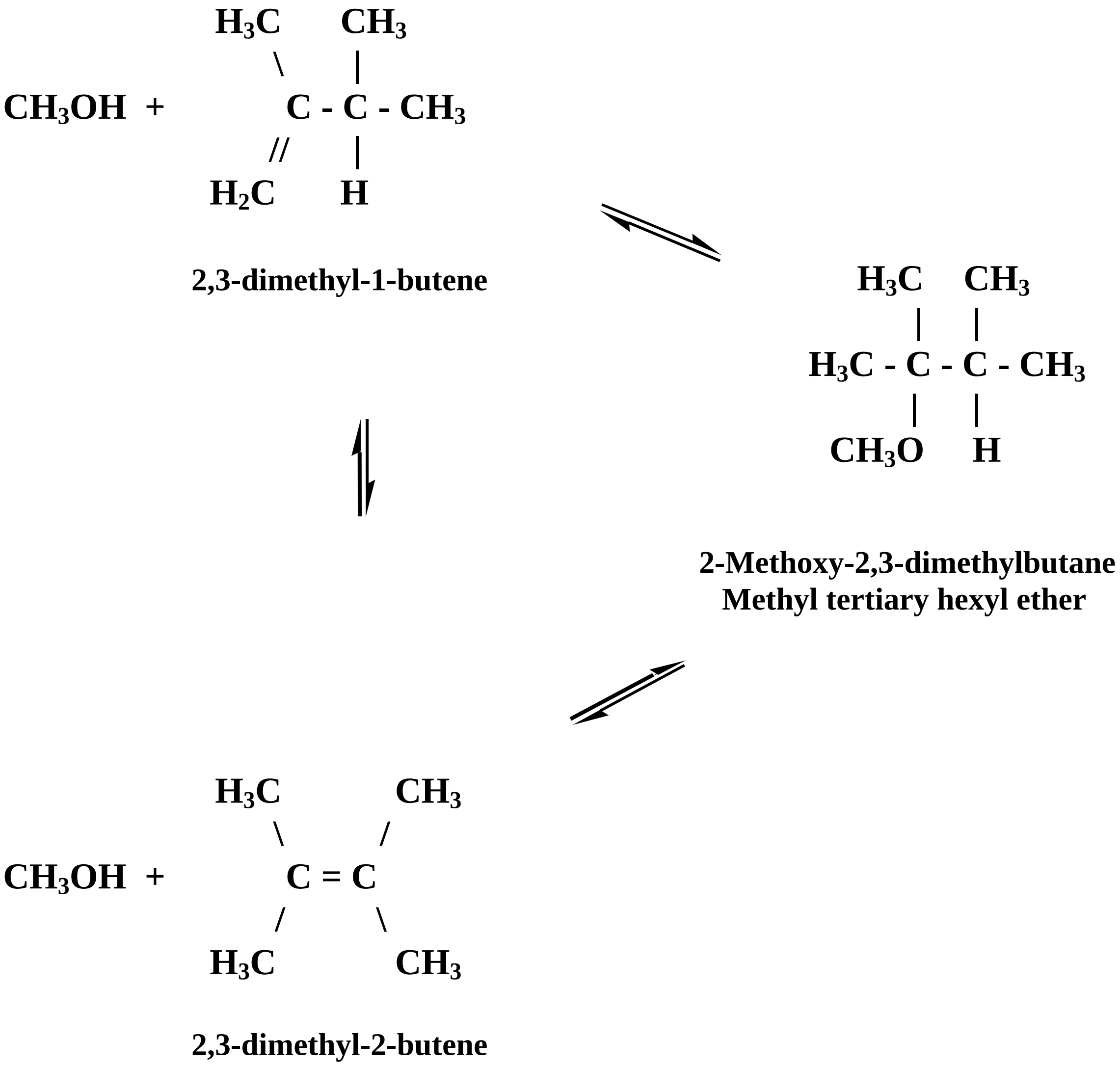


Figure E-1

Reaction Scheme for the Etherification of the 2,3-Dimethylbutenes with Methanol

Table E-5

Comparison of the Catalytic Activity of Pretreated Amberlyst® and Amberlyst® Used as Received

Run #	Olefin	Ratio O/A	Catalyst Condition	Product Distribution (mole %)			ε
				DM1B	DM2B	MtHxE	
DB-1	DM1B	2:1	Pretreated	10	67	23	90
DB-2	DM1B	2:1	As received	10	68	23	90

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
ε denotes the extent of reaction, or percent overall conversion of starting olefin.

100 ^{o}C. The molar ratio of olefin to alcohol employed was two to one. Table E-6 presents the reaction conditions and product distributions for this experimentation.

In this synthesis, the selectivity is defined as the molar ratio of the desired product, the ether, to the undesired product, or 2-alkene. At 60 ^{o}C, the selectivity was the highest, at 0.84, but the overall conversion was only 39%. This result most likely indicates that reaction kinetics are limiting at this low of a temperature. Raising the temperature to 70 ^{o}C more than doubled the overall conversion, to 86%, but the selectivity dropped to 0.63. Increasing the temperature to 80 ^{o}C raised the overall conversion slightly, to 91%, but the selectivity to ether production was reduced to 0.43.

Table E-6

Effect of Temperature on the Etherification of 2,3-Dimethyl-1-butene with Methanol

Run #	Starting Olefin	Temp (^oC)	Time	Product Distribution (mole %)				ε	S
				DM1B	DM2B	MtHxE	tHxA		
DB-3	DM1B	60	2 hr	61	19	16	4.3	36	0.84
DB-4	DM1B	70	2 hr	14	53	33	1.2	86	0.63
DB-5	DM1B	80	2 hr	8.5	63	27	1.5	91	0.43
DB-2	DM1B	100	2 hr	9.0	68	23	—	90	0.34

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.
ε denotes the extent of reaction, or percent overall conversion of starting olefin.
S denotes the selectivity to ether production, or molar ratio of ether to DM2B.

A further increase in temperature to 100 ^oC did not affect the overall conversion, but an additional decrease in selectivity to ether production to only 0.34 was observed. At temperatures between 60 ^oC and 80 ^oC, a small amount of an unidentified material was also produced. The identity of this material was determined by Gas Chromatography-Mass Spectrometry (GC/MS). The unknown compound turned out to be the hydration product of the olefins, namely 2-hydroxy-2,3-dimethylbutane, one of the three tertiary hexyl alcohols (tHxA). Evidently, there were traces of moisture present in the reactor, as olefins hydrate readily under etherification conditions. The reaction scheme for the hydration of the 2,3-dimethylbutenes is presented in Figure E-2.

The conclusion to be drawn here is that while temperatures of 80 ^{o}C and above enhance the overall conversion of the starting olefin, they do so to the deficit of ether production. Therefore, the optimum temperature for synthesizing methyl tertiary hexyl ether appears to be about 70 ^{o}C. Figure E-3 presents a plot of overall conversion and selectivity to ether production versus temperature for these reactions.

Since the etherification reaction is reversible, 2-methoxy-2,3-dimethylbutane can be cleaved to yield methanol and either of the 2,3-dimethylbutenes. It is therefore of interest to compare the relative reactivity in etherification of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

Comparison of the Reactivity in Etherification of the 2,3-Dimethylbutenes

The reactivities of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene were compared in two hour tests at 70 ^{o}C. Table E-7 presents the reaction conditions and product distributions for this comparison.

The most striking result is that the 1-butene isomer produces three times more ether than the 2-butene isomer. It should also be noted that the overall conversion for the 2-butene isomer is only 16%, whereas that for the 1-butene isomer is 86%. This result compares favorably with the result from the catalytic activity study of neat olefins, namely that the 2-butene isomer is by far the preferred isomer. Both of these results, the higher overall conversion for the 1-butene isomer and the greater ether production for the

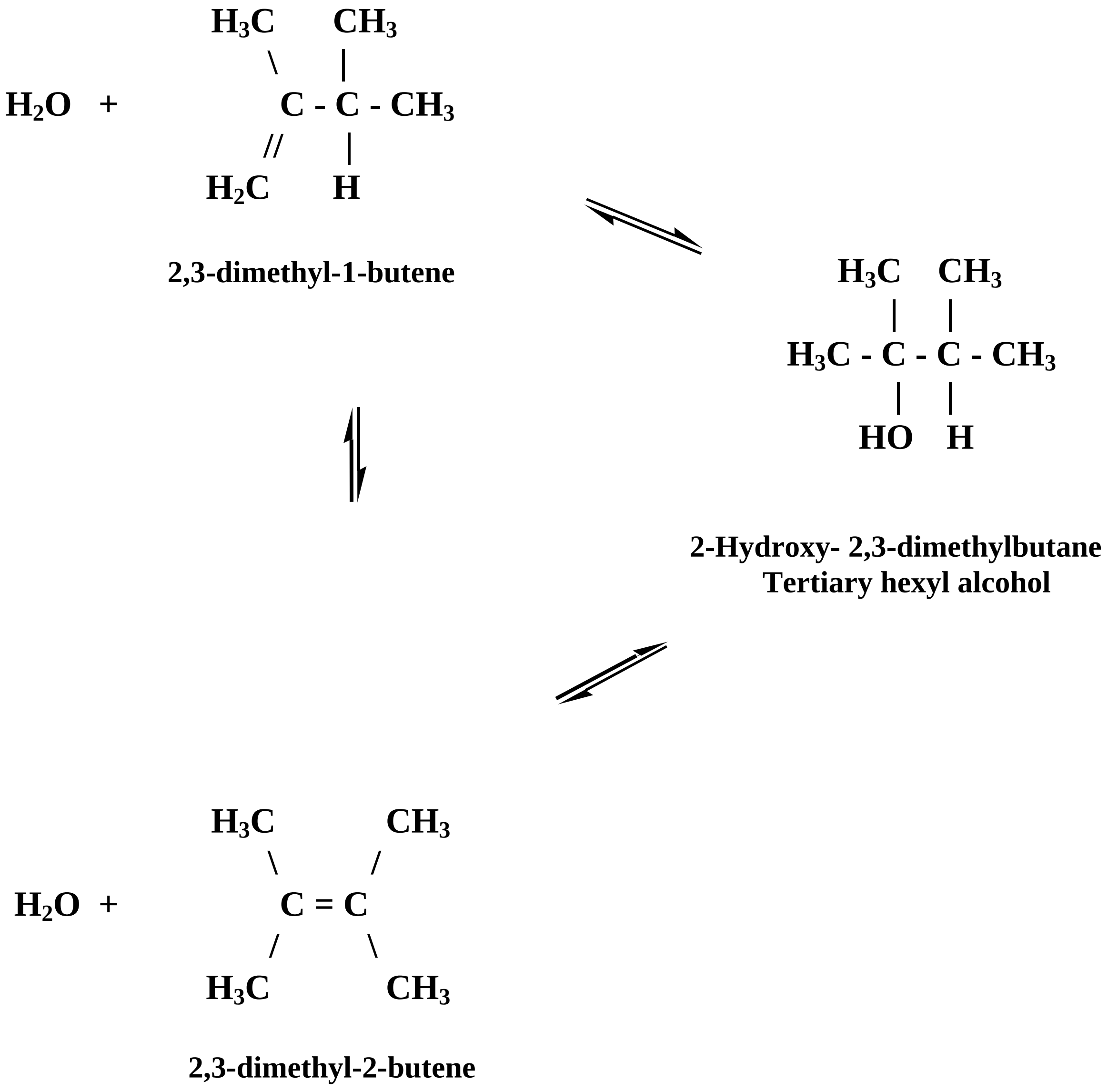


Figure E-2

Reaction Scheme for the Hydration of the 2,3-Dimethylbutenes

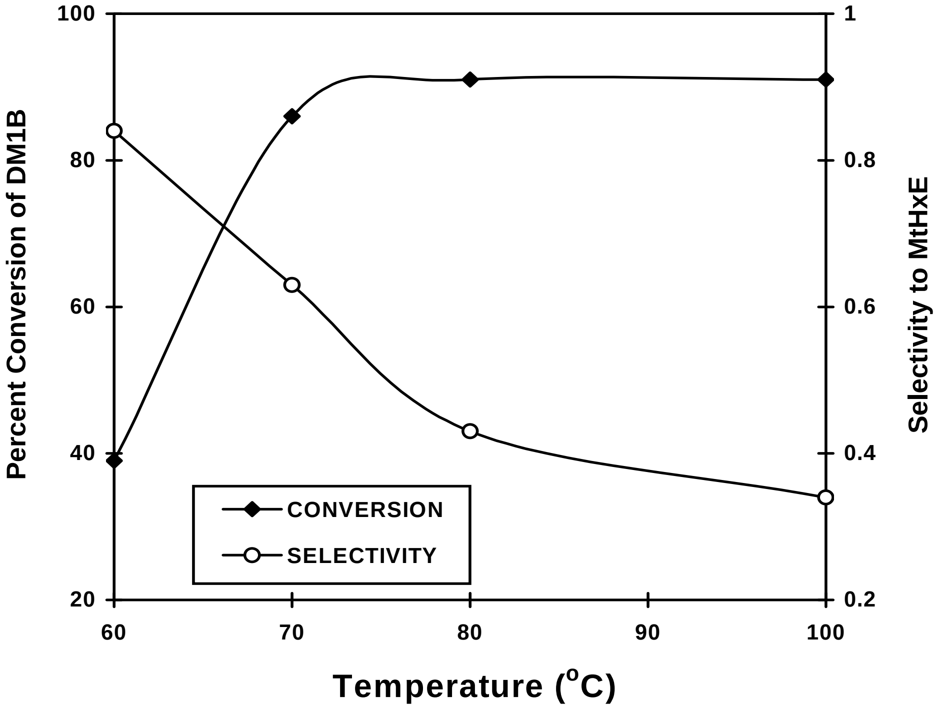


Figure E-3

Plot of Overall Conversion and Selectivity versus Temperature

for Etherification of 2,3-Dimethyl-1-butene

1-butene isomer, are in good agreement with the results of previous researchers [73, 76-78].

The implications to this study are twofold. First, it is clear that the 1-butene isomer would be much preferred as a feedstock for the methyl tertiary hexyl ether synthesis reaction. Secondly, since the methyl tertiary hexyl ether, once formed, is in equilibrium with methanol and the 2,3-dimethylbutenes, it will cleave, most likely yielding the thermodynamically preferred, more stable and less reactive 2-butene isomer.

Table E-7

Comparison of the Reactivities of the 2,3-Dimethylbutenes

Run #	Olefin	Ratio O/A	Temp	Time	Product Distribution (mole %)				ε
					DM1B	DM2B	MtHxE	tHxA	
DB-4	DM1B	2:1	70 ^{o}C	2 hrs	14	53	33	1.2	86
DB-6	DM2B	2:1	70 ^{o}C	2 hrs	3.0	84	11	2.6	16

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.
ε denotes the extent of reaction, or percent overall conversion of starting olefin.

It is therefore of interest to investigate the effect of the length of the reaction time on ether production from 2,3-dimethyl-1-butene. The simultaneous reaction equilibria involving olefin isomerization and etherification are discussed in greater detail in Appendix F.

Effect of the Reaction Time on Ether Production from 2,3-Dimethyl-1-butene

The effect of the reaction time on the production of methyl tertiary hexyl ether from 2,3-dimethyl-1-butene at 70 ^{o}C was determined for reaction times varying from two hours to 24 hours. Table E-8 presents the reaction conditions and product distributions for these runs. The lengthened reaction times had little effect on the yield of methyl tertiary hexyl ether, with all of the yields lying between 30 and 36%. It was concluded that the reactions had reached equilibrium, or at the very least, had stopped proceeding,

Table E-8

Effect of the Reaction Time on Ether Production from 2,3-Dimethyl-1-butene

Run #	Olefin	Ratio O/A	Time	Product Distribution (mole %)			
				DM1B	DM2B	MtHxE	tHxA
DB-4	DM1B	2:1	2 hrs	14	52	33	1.2
DB-7	DM1B	2:1	4 hrs	6.4	58	34	1.3
DB-8	DM1B	2:1	6 hrs	6.3	59	34	0.79
DB-9	DM1B	2:1	8 hrs	4.9	58	36	0.88
DB-10	DM1B	2:1	24 hrs	6.8	59	30	4.6

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

after two hours had elapsed. It was clear that lengthening the run times beyond two hours was not necessary. However, the isomerization was not complete after two hours, as the ratio of beta-olefin to alpha-olefin was not nine to one. It is seen that the presence of the methanol inhibits the kinetics of the isomerization but has little or no effect on the position of the isomerization equilibrium. By the time four hours had elapsed, the distribution of isomers was ten percent alpha- and ninety percent beta-olefin, the same as found for the equilibrium partitioning in the absence of any methanol. This result indicates that the etherification is fast compared to the isomerization. Consequently, long reaction times hinder ether production, and it would not be desirable to run an etherification reactor at equilibrium. The choice of the optimum reaction time is discussed further in the section on etherification of the 2,4,4-trimethylpentenes, below.

Effect of Changing the Olefin to Alcohol Ratio

Despite having varied the reaction parameters as delineated above, the maximum yields of ether were only about 30%, which was considered to be low. In an effort to increase the yield of ether, it was decided to employ an excess of methanol in the reaction. An excess of methanol would help shift the reaction equilibrium in favor of ether production. The molar ratio of olefin to methanol chosen was one to eight. The reactions were conducted at 70 ^{o}C for two hours. Table E-9 presents the reaction conditions and product distributions for this experimentation.

Table E-9

Effect of Changing the Molar Ratio of Olefin to Alcohol on Ether Production from 2,3-Dimethyl-1-butene

Run #	Olefin	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
					DM1B	DM2B	MtHxE	tHxA
DB-4	DM1B	2:1	70 ^{o}C	2 hrs	14	52	33	1.2
DB-11	DM1B	1:8	70 ^{o}C	2 hrs	5.9	36	54	4.0

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Changing the molar ratio of olefin to alcohol from 2:1 to 1:8 increased the ether production from 33% to 54%, a 1.6 fold increase. It was recognized that employing an excess of methanol to drive the ether synthesis conflicts with the constraint of removing the methanol to help drive the methanol synthesis reaction, but at the time the emphasis was on increasing ether production. These conflicting thermodynamic constraints are discussed further in Chapters III and VI.

Effect of Changing the Catalyst Loading

It was deemed necessary to insure that the ether yields were not limited by the amount of catalyst employed in the batch reactions. Therefore, the catalyst loading was halved to 5 wt%, doubled to 20 wt% and tripled to 30 wt% to determine if there would be any effect on ether production from 2,3-dimethyl-1-butene. The tests were conducted at 70 °C for two hours. Table E-10 presents the reaction conditions and product distributions for these runs.

Table E-10

Effect of Changing the Catalyst Loading

on Ether Production from 2,3-Dimethyl-1-butene

Run #	Catalyst wt%	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
					DM1B	DM2B	MtHxE	tHxA
DB-12	5	1:8	70 °C	2 hrs	11	31	57	1.7
DB-11	10	1:8	70 °C	2 hrs	5.9	36	54	4.0
DB-13	20	1:8	70 °C	2 hrs	2.2	29	66	2.6
DB-14	30	1:8	70 °C	2 hrs	1.1	27	66	5.8

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Halving the catalyst loading had little effect on ether production. Doubling the catalyst loading increased ether production from 59% to 66%, for a relative increase of just over ten percent. Tripling the catalyst loading did not increase ether production above that obtained by doubling the catalyst loading. Since the maintenance of the catalyst in an industrial catalytic reactor is both a major challenge and a major expense, doubling the amount of catalyst to increase the ether yield by ten percent does not seem justified. The effect of catalyst loading on ether production is discussed further in the section on etherification of the 2,4,4-trimethylpentenes, below.

Effect of Crushing the Etherification Catalyst

It was also deemed necessary to ensure that the etherification reaction was not diffusion limited, that is to say, to show that the pores in the Amberlyst® 15 were of sufficient size to not restrict access of the reactants to the active sites. This was accomplished by comparing the activity in etherification of crushed Amberlyst® to Amberlyst® as received. Table E-11 presents the reaction conditions and product distributions for this testing.

Crushing the Amberlyst® had an almost identical effect on ether production as did doubling the catalyst loading. The slight increase in ether production of just over ten percent indicates that there may be a slight diffusion limitation involved in these reactions. The effect was even more pronounced in reactions with C_8-olefins, as discussed below. However, the difficulties inherent in utilizing a catalyst in pulverized

Table E-11

Effect of Crushing the Catalyst on Ether Production from 2,3-Dimethyl-1-butene

Run #	Catalyst condition	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
					DM1B	DM2B	MtHxE	tHxA
DB-11	as received	1:8	70 ^{o}C	2 hrs	5.9	36	54	4.0
DB-15	Crushed	1:8	70 ^{o}C	2 hrs	2.8	29	65	3.2

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

form, as opposed to as a bead, in a slurry reactor probably would not be justified by an increase in ether production of only ten percent.

Effect of the Presence of a Methanol Synthesis Catalyst on Etherification of 2,3-Dimethyl-1-butene

Since the continuous etherification reactor being proposed here will employ a dual catalyst system consisting of both an etherification catalyst and a methanol synthesis catalyst, it was necessary to determine what effect, if any, the methanol synthesis catalyst might have on the etherification. The methanol synthesis catalyst consists of copper oxide and zinc oxide precipitated on alumina. The methanol synthesis catalyst, employed by itself, whether crushed or used as received, showed no etherification or isomerization activity. The task remaining was to determine if it had an inhibitory effect on etherification when both catalysts were used together. The catalyst composition employed was 7.5 wt% methanol synthesis catalyst and 10 wt% Amberlyst®. Table E-12 presents the reaction conditions and product distributions for this test. For ease of comparison, the product distribution for the test with 10 wt% Amberlyst® without the methanol synthesis catalyst is also presented. The methanol synthesis catalyst appears to have enhanced ether production slightly, and inhibited the isomerization slightly. This is an important result, with implications to the design of a continuous single-step etherification reactor. It shows that, at the very least, the methanol synthesis catalyst is not antagonistic towards the etherification, and thus may be a suitable candidate for use in the dual catalyst system.

Table E-12

Effect of the Presence of a Methanol Synthesis Catalyst on Ether Production from 2,3-Dimethyl-1-butene

Run #	Amberlyst wt%	MeOH synth. wt%	Temp	Time	Product Distribution (mole %)			
					DM1B	DM2B	MtHxE	tHxA
DB-11	10	—	70 ^{o}C	2 hrs	5.9	36	54	4.0
DB-16	10	7.5	70 ^{o}C	2 hrs	5.5	33	58	3.2

DB denotes 2,3-Dimethylbutene runs.
MeOH synth. wt% denotes weight percent of the methanol synthesis catalyst.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Effect of Pressure on Etherification

Since the single-step etherification reactor will likely employ high pressures to drive the methanol synthesis reaction, the effect of pressure on etherification was investigated. The pressure chosen for this investigation was 800 psig. In side-by-side testing, the reactivity of 2,3-dimethyl-1-butene towards etherification with methanol at 200 psig and 800 psig was compared, all other conditions being identical. Table E-13 presents the reaction conditions and product distributions for these runs. Comparison of the product distributions from these runs shows that the elevated pressure had little effect on the etherification.

Table E-13

Effect of Pressure on Ether Production from 2,3-Dimethyl-1-butene

Run #	Pressure (psig)	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
					DM1B	DM2B	MtHxE	tHxA
DB-17	200	2:1	70 °C	2 hrs	4.9	59	35	0.4
DB-18	800	2:1	70 °C	2 hrs	7.2	59	33	3.3

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Thermal Reactivity of Neat 2,4,4-Trimethylpentenes

The 2,4,4-trimethylpentenes were found to be thermally stable when heated to 80 °C and allowed to react for two hours in the absence of any catalyst or other reactant.

Thermal Reactivity of 2,4,4-Trimethylpentenes Towards Methanol

Under the same conditions, the 2,4,4-trimethylpentenes did not react with methanol in the absence of a catalyst.

Catalytic Reactivity of Neat 2,4,4-Trimethylpentenes

Under the same conditions, both 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene isomerize in the presence of Amberlyst® 15 to give a mixture containing approximately 80% 2,4,4-trimethyl-1-pentene and 20% 2,4,4-trimethyl-2-pentene. This result is in keeping with the results of other researchers [79, 158]. It should be noted here that the 1-alkene, 2,4,4-trimethyl-1-pentene, predominates at equilibrium, whereas for the 2,3-dimethylbutenes, the 2-alkene is the thermodynamically favored isomer. The position of equilibrium for the isomeric 2,3-dimethylbutenes and 2,4,4-trimethylpentenes is discussed in more detail in Appendix F.

Etherification of 2,4,4-Trimethylpentenes with Methanol

Having established the baseline reactivities of the 2,4,4-trimethylpentenes, a systematic evaluation of their reactivities towards etherification in methanol was performed. In these reactions, the temperature was varied from 60 ^{o}C to 100 ^{o}C. The run times varied from fifteen minutes to twenty-four hours. Two molar ratios of olefin to methanol were employed, namely 2:1 and 1:8. Figure E-4 presents the reaction scheme for these etherifications.

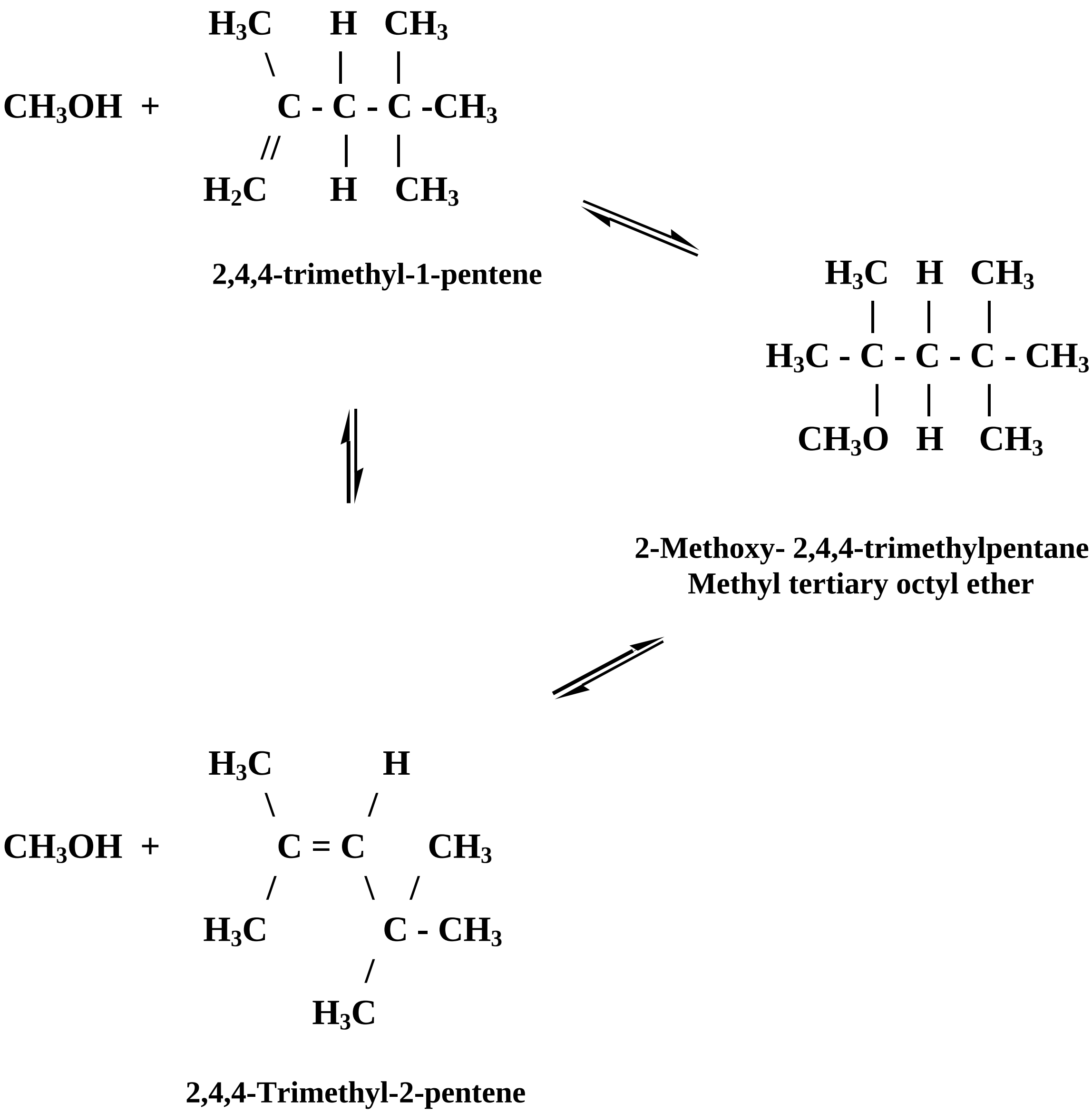


Figure E-4

Reaction Scheme for Etherification of the 2,4,4-Trimethylpentenes with Methanol

Comparison of the Reactivity in Etherification of the 2,4,4-Trimethylpentenes

The reactivities of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene were compared in two hour tests at 70 ^{o}C. The molar ratio of olefin to alcohol employed was 2:1. Table E-14 presents the reaction conditions and product distributions for this comparison.

Table E-14

Comparison of the Reactivities of the 2,4,4-Trimethylpentenes

Run #	Olefin	Ratio O/A	Temp.	Time	Product Distribution (mole %)		
					TM1P	TM2P	MtOcE
TP-1	TM1P	2:1	70 ^{o}C	2 hrs	91	3.4	5.1
TP-2	TM2P	2:1	70 ^{o}C	2 hrs	5.1	92	3.0

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

2,4,4-trimethyl-2-pentene proved to be about seventy percent as reactive in etherification as 2,4,4-trimethyl-1-pentene. As was the case with the 2,3-dimethyl-1-butenes, the 1-alkene is the more reactive isomer, although the difference in relative reactivities is considerably less dramatic. Since the simultaneous isomerization favors the production of the more reactive isomer, the role of an isomerization unit is greatly diminished. Moreover, since the ultimate goal of this project is to develop a commercial-scale etherification reactor, and since the di-isobutylene of commerce consists of a mixture of eighty percent 2,4,4-trimethyl-1-pentene and twenty percent 2,4,4-trimethyl-2-pentene, it was decided to focus attention on studying the reactivity of 2,4,4-trimethyl-1-pentene.

Effect of Reaction Time on the Synthesis of Methyl Tertiary Octyl Ether

The effect of reaction time on the production of methyl tertiary octyl ether from 2,4,4-trimethyl-1-pentene in the temperature range from 70 ^{o}C to 100 ^{o}C was determined for reaction times varying from fifteen minutes to twenty-four hours. The molar ratio of olefin to alcohol employed was two to one. Table E-15 presents the reaction conditions and product distributions for these runs.

Comparison of Runs TP-3 through TP-7 shows that the reaction time had little effect on ether production at 100 ^{o}C. Yields of ether were fairly consistent at around five to six percent. Evidently, the reaction takes place very quickly at this temperature. The reaction was considerably slower at 80 ^{o}C. Comparison of runs TP-8 through TP-14 shows that ether production reached a maximum of 7.8% after one hour. After four hours of reaction time, the ether production was nearly the same, at 7.6%. However, the isomerization to the less reactive 2-pentene isomer nearly doubled from its value after one hour. The reaction was even slower at 70 ^{o}C, requiring four hours to reach a similar ether yield of 7.5%. However, the isomerization to the 2-pentene isomer was reduced by two-thirds from its value after four hours at 80 ^{o}C. Because of the competing isomerization reaction, the reaction time and temperature could not be optimized

Table E-15

Effect of Reaction Time on Ether Production from 2,4,4-Trimethyl-1-Pentene

Run #	Temp	Time	Product Distribution (mole %)		
			TM1P	TM2P	MtOcE
TP-3	100 ^oC	15 mins	81	14	5.4
TP-4	100 ^oC	30 mins	76	18	5.6
TP-5	100 ^oC	60 mins	76	18	6.2
TP-6	100 ^oC	90 mins	73	22	4.7
TP-7	100 ^oC	2 hrs	79	16	5.1
TP-8	80 ^oC	15 mins	93	3.3	3.7
TP-9	80 ^oC	30 mins	91	4.3	5.0
TP-10	80 ^oC	45 mins	92	3.8	4.3
TP-11	80 ^oC	60 mins	84	8.5	7.8
TP-12	80 ^oC	90 mins	83	9.8	7.2
TP-13	80 ^oC	2 hrs	88	5.7	6.4
TP-14	80 ^oC	4 hrs	77	16	7.6
TP-15	70 ^oC	1 hr	95	2.2	2.5
TP-1	70 ^oC	2 hrs	91	3.4	5.1
TP-16	70 ^oC	4 hrs	87	5.5	7.5
TP-17	70 ^oC	8 hrs	82	9.3	9.0
TP-18	70 ^oC	24 hrs	70	20	9.6

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

independently. The choice of an optimum reaction time will be discussed further after the effect of temperature on the simultaneous etherification and isomerization reactions is discussed.

Effect of Temperature on the Synthesis of Methyl Tertiary Octyl Ether

The effect of temperature on the reactivity of 2,4,4-trimethyl-1-pentene towards etherification with methanol was determined in the temperature range from 60 ^oC to 100 ^oC. Table E-16 presents the reaction conditions and product distributions for this experimentation.

Table E-16

Effect of Temperature on the Etherification of 2,4,4-Trimethyl-1-Pentene with Methanol

Run #	Ratio O/A	Temp	Time	Product Distribution (mole %)			ε	S
				TM1P	TM2P	MtOcE		
TP-19	2:1	60 ^oC	2 hrs	81	14	5.4	19	0.39
TP-1	2:1	70 ^oC	2 hrs	91	3.4	5.1	9.0	1.5
TP-13	2:1	80 ^oC	2 hrs	88	5.7	6.4	12	1.1
TP-7	2:1	100 ^oC	2 hrs	79	16	5.1	21	0.32

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

Ether production remained fairly constant, at five to six mole percent, over the temperature range from 60 ^oC to 100 ^oC. However, selectivity to ether production proved to be a strong function of temperature, with a definite maximum around 70 ^oC. For this reason, and in light of the fact that 70 ^oC had proven to be the optimum temperature at which to conduct C_6-olefin etherifications, 70 ^oC was the temperature of choice in all subsequent etherifications in this study. Figure E-5 presents a plot of overall conversion and selectivity to ether production versus temperature for this experimentation.

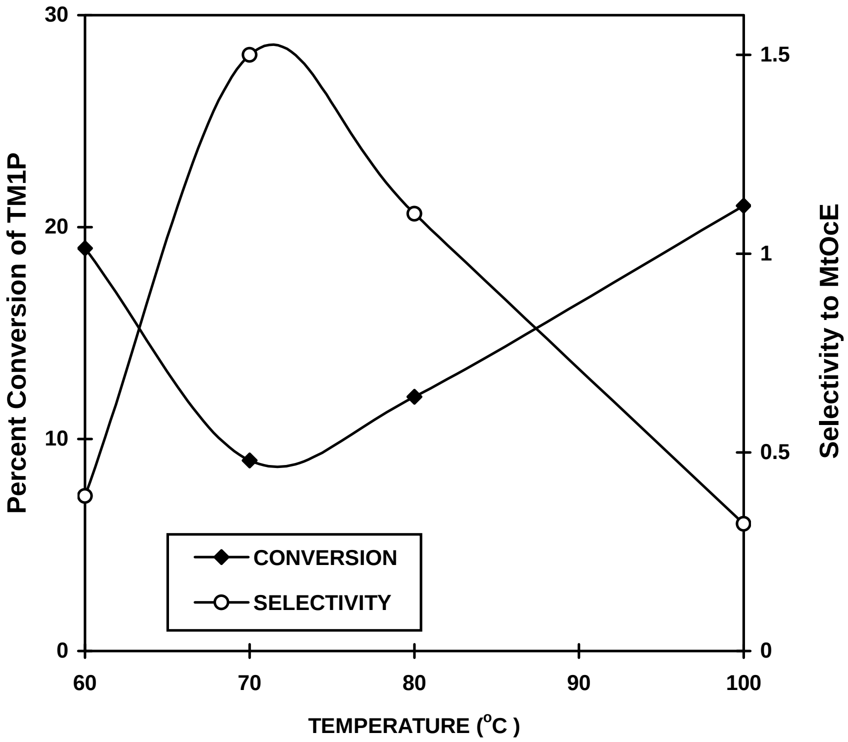


Figure E-5

Plot of Conversion and Selectivity versus Temperature for

Etherification of 2,4,4-Trimethyl-1-pentene

The choice of 70 °C as the optimum temperature meant that four hours would be required to achieve an ether production of 7.5% from 2,4,4-trimethyl-1-pentene.

However, there is an additional constraint on the optimum run time. That constraint is that it is one of the goals of this study is to directly compare the relative reactivities of C_6- and C_8-olefins. Therefore, the optimum run time would have to be the minimum run time necessary to achieve maximum ether production from the less reactive of the two ethers, that is, from 2,4,4-trimethyl-1-pentene. The choice of an optimum run time will be discussed further after the effect of the molar ratio of olefin to alcohol is discussed.

Effect of Changing the Olefin to Alcohol Ratio

Yields of ether of only six percent were considered to be low. As with the C_6-olefin experimentation, it was decided to employ an excess of methanol in the reaction to shift the equilibrium to the favor of ether production. The molar ratio of olefin to methanol chosen was one to eight. The reactions were conducted at 70 ^{o}C with run times of one, two and six hours. Table E-17 presents the reaction conditions and product distributions for this experimentation.

Changing the molar ratio of olefin to alcohol from 2:1 to 1:8 tripled the ether production, to seventeen percent, at a reaction time of two hours. Maximum ether production had not been reached after one hour had elapsed. Lengthening the reaction time to six hours had little effect on ether production. It did, however, nearly double the isomerization to the undesirable 2-pentene isomer. Therefore, an optimum run time of two hours was selected, and was used in most of the subsequent testing.

Table E-17

Effect of Changing the Molar Ratio of Olefin to Alcohol on Ether Production from 2,4,4-Trimethyl-1-Pentene

Run #	Ratio O/A	Temp.	Time	Product Distribution (mole %)		
				TM1P	TM2P	MtOcE
TP-1	2:1	70 °C	2 hrs	91	3.4	5.1
TP-20	1:8	70 °C	1 hr	82	5.3	13
TP-21	1:8	70 °C	2 hrs	73	9.2	17
TP-22	1:8	70 °C	6 hrs	65	17	18

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

Effect of Increasing the Catalyst Loading

As was the case with the C_6-olefins, it was necessary to insure that the ether yields were not limited by the amount of catalyst employed in the batch reactions. Therefore, the catalyst loading was doubled to 20 wt% and tripled to 30 wt% to determine the effect on ether production from 2,4,4-trimethyl-1-pentene. Table E-18 presents the reaction conditions and product distributions for these runs.

Doubling the catalyst loading increased ether production from 17% to 24%, an increase of over 1.4 fold. Tripling the catalyst loading did not increase ether production over that observed with the double loading of catalyst. An increase in ether production of forty percent is significant, and would indicate that the methyl tertiary octyl ether synthesis is much more limited for catalyst than the methyl tertiary hexyl ether synthesis

Table E-18

Effect of Changing the Catalyst Loading on Ether Production from 2,4,4-Trimethyl-1-Pentene

Run #	Ratio O/A	Catalyst wt%	Temp.	Time	Product Distribution (mole %)		
					TM1P	TM2P	MtOcE
TP-21	1:8	10	70 ^oC	2 hrs	73	9.2	17
TP-23	1:8	20	70 ^oC	2 hrs	63	13	24
TP-24	1:8	30	70 ^oC	2 hrs	61	16	23

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

was. In light of this fact, it is also of interest to determine the effect of crushing the Amberlyst® on methyl tertiary octyl ether production.

Effect of Crushing the Etherification Catalyst

Since 2,4,4-trimethyl-1-pentene is bulkier than 2,3-dimethyl-1-butene, it is more likely to exhibit diffusion limitations in etherification. To verify this effect, the activity in etherification of crushed Amberlyst® was compared to Amberlyst® as received. Table E-19 presents the reaction conditions and product distributions for this testing.

As was the case with 2.3-dimethyl-1-butene, crushing the Amberlyst® had the same effect on etherification yields from 2,4,4-trimethyl-1-pentene as did doubling the Amberlyst®, an increase of about forty percent. From a practical standpoint, increasing

Table E-19

Effect of Crushing the Catalyst on Ether Production from 2,4,4-Trimethyl-1-Pentene

Run #	Ratio O/A	Catalyst condition	Temp	Time	Product Distribution (mole %)		
					TM1P	TM2P	MtOcE
TP-21	1:8	as received	70 ^oC	2 hrs	73	9.2	17
TP-25	1:8	Crushed	70 ^oC	2 hrs	61	16	23

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
As was the case with 2,3-dimethyl-1-butene, crushing the Amberlyst® had the the

the catalyst loading in a reactor would be much simpler than trying to maintain the catalyst in a powder form in a slurry reactor. Just how much of an increase in ether production would be necessary to justify an addition to the catalyst loading constitutes an interesting avenue for future research.

Effect of the Presence of a Methanol Synthesis Catalyst on Etherification of 2,4,4-Trimethyl-1-Pentene

The effect of the presence of a methanol synthesis catalyst on etherification of 2,4,4-trimethyl-1-pentene was also determined. The methanol synthesis catalyst had little effect on the etherification or the isomerization, whether employed by itself or in a mixture with Amberlyst® 15.

Etherification of Mixed Olefins with Methanol

The next phase of the experimental work involved the methanolation of a mixture of C_6- and C_8-olefins. Since the 1-alkene isomers, or alpha-olefins, have been shown to be more reactive in etherification than the 2-alkene isomers, or beta-olefins, they were used exclusively for this portion of the study. In this investigation, the effect of varying three process parameters was determined. These parameters were the olefins to methanol ratio, amount of catalyst loading, and the run time.

Effect of Varying the Olefin to Alcohol Ratio

Two ratios of mixed olefins to methanol were selected for study, namely 1:1:16 and 1:1:23 for 2,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene and methanol, respectively. The experiments were conducted at 70 ^{o}C for two hours. Table E-20 presents the reaction conditions and product distributions for these runs.

The product distributions from these two runs were virtually identical. This shows that the etherification is not limited by the availability of methanol. Interestingly, the presence of the C_8-olefin suppressed the formation of tertiary hexyl alcohol.

Effect of Changing the Catalyst Loading on the Production of Mixed Methyl Ethers

Since doubling the catalyst loading produced a significant increase of over 40% in C_9-ether production, but only a slight increase, of 10% in C_7-ether production, it was of interest to see what effect doubling the catalyst loading would have on the production of mixed methyl ethers from alpha-olefins. In these reactions, the C_6-olefin and the

Table E-20

Effect of Changing the Molar Ratio of Olefin to Alcohol on Methyl Ether Production from Mixed Alpha-Olefins

Run #	Ratio O/A	Product Distribution (mole %)					
		DM1B	DM2B	MtHxE	TM1P	TM2P	MtOcE
MO-1	1:1:16	3.6	18	29	38	5.0	6.9
MO-2	1:1:23	3.2	17	30	38	5.0	7.2

MO denotes Mixed alpha-Olefin runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

C_8-olefin must compete for the reactive sites on the catalyst. The tests were conducted at 70 °C for two hours. The molar ratio of mixed alpha-olefins to methanol employed was 1:1:16 for 2,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene and methanol, respectively. Table E-21 presents the reaction conditions and product distributions for these runs.

Comparison of Runs MO-1 and MO-3 shows that doubling the catalyst loading increased methyl tertiary hexyl ether production by a little over ten percent, while methyl tertiary octyl ether production increased by over forty percent. The percent increase in ether production were much the same as those observed when the olefins were etherified separately.

Table E-21

Effect of Changing the Catalyst Loading on Ether Production from Mixed Alpha-Olefins

Run #	Amberlyst wt%	Product Distribution (mole %)					
		DM1B	DM2B	MtHxE	TM1P	TM2P	MtOcE
MO-1	10	3.6	18	29	38	5.0	6.9
MO-3	20	1.5	16	32	32	8.0	10

MO denotes Mixed alpha-Olefin runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

Effect of the Reaction Time on Ether Production from Mixed Alpha-Olefins

The effect of lengthening the reaction time from two hours to four hours on the production of methyl tertiary hexyl ether and methyl tertiary octyl ether was also determined. The temperature of the reactions for this comparison was 70 ^{o}C. The molar ratio of mixed alpha-olefins to methanol employed was 1:1:16 for 2,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene and methanol, respectively. The catalyst loading was 20 wt% Amberlyst®. That is to say that both the catalyst loading and the reaction time were doubled from their values in the established practice, in the hope of increasing ether production. Table E-22 presents the reaction conditions and product distributions for these runs. The reaction conditions and product distributions for the single and double loading, two hour tests are also presented for ease of comparison.

Table E-22

Effect of the Reaction Time on Ether Production from Mixed Alpha-Olefins

Run #	Amberlyst wt%	Time	Product Distribution (mole %)					
			DM1B	DM2B	MtHxE	TM1P	TM2P	MtOcE
MO-1	10	2 hrs	3.6	18	29	38	5.0	6.9
MO-3	20	2 hrs	1.5	16	32	32	8.0	10
MO-4	20	4 hrs	0.9	14	35	30	7.4	13

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.

Lengthening the reaction time to four hours increased the production of methyl tertiary octyl ether by thirty percent, while production of methyl tertiary hexyl ether increased by about ten percent. If a continuous etherification reactor is to be designed to convert mixed olefin feedstocks, careful attention will have to be paid to the optimum catalyst contact time. Given the wide difference in reactivities, it may be best to design separate units for C_6- and C_8-olefin etherification. The great variation found in the reactivities of the C_6- and C_8-olefins is in agreement with the results of other researchers [63].

The Extension to Ethanol and 2-Butanol

Because higher alcohols are also available from synthesis gas conversion processes [56, 90], this work was extended to ethanol and 2-butanol. Since ethanol is also available from biomass and renewable resources, ethanolation of higher olefins has received more attention in the literature [74, 75, 80] than etherification with any other alcohol except methanol.

Etherification of 2,3-Dimethyl-1-butene with Ethanol

2,3-dimethyl-1-butene was etherified with ethanol using the process parameters as optimized above, that is, a temperature of 70 ^{o}C, a two hour run time, a catalyst loading of ten weight percent of the total reactor charge, and an olefin to alcohol ratio of one to eight. Table E-23 presents the product distribution for this experimentation (Run # DB-19). The product distribution for the etherification of 2,3-dimethyl-1-butene with methanol under identical conditions (Run # DB-11) are also presented so that a comparison of the reactivity of the two alcohols towards etherification can be made. The product distributions are reported on a methanol and ethanol free basis. Figure E-6 presents the reaction scheme for the etherification of 2,3-dimethyl-1-butene with ethanol.

Comparison of ether production for ethanol and methanol shows that ethanol is about half as reactive as methanol in etherification. It is of interest to note that almost ten mole percent of the product from the etherification with ethanol was tertiary hexyl alcohol, the hydration product of the olefin. Hydration occurred even though absolute ethanol, dried over molecular sieves, was employed in these reactions. The affinity of ethanol for water is so great that it evidently absorbed enough moisture from the air during the charging of the reactor to hydrate the olefin during the course of the reaction to the extent of ten percent. Since the hydration reaction competes with the etherification,

Table E-23

Reactivity of Ethanol in Etherification of 2,3-Dimethyl-1-Butene

Run #	Product Distribution (mole %)				
	DM1B	DM2B	MtHxE	EtHxE	tHxA
DB-11	5.9	36	54	—	4.0
DB-19	8.5	55	—	27	9.8

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

the ether production is limited. It might be interesting to see if the ether production could be increased by performing the reactor loading in a dry box.

Etherification of 2,3-Dimethyl-1-butene with a Mixture of Methanol and Ethanol

2,3-dimethyl-1-butene was etherified with a mixture of methanol and ethanol using the same process parameters. The ratio of olefin to alcohols was 1:4:4, for 2,3-dimethyl-1-butene, methanol and ethanol, respectively, for a total olefin to alcohol ratio of one to eight. Table E-24 presents the product distribution for this experimentation (Run # DB-20). The product distributions for the etherification of 2,3-dimethyl-1-butene with methanol (Run # DB-11), and separately with ethanol (Run # DB-19), under identical conditions, and at an olefin to alcohol ratio of one to eight, are also presented for ease of comparison.

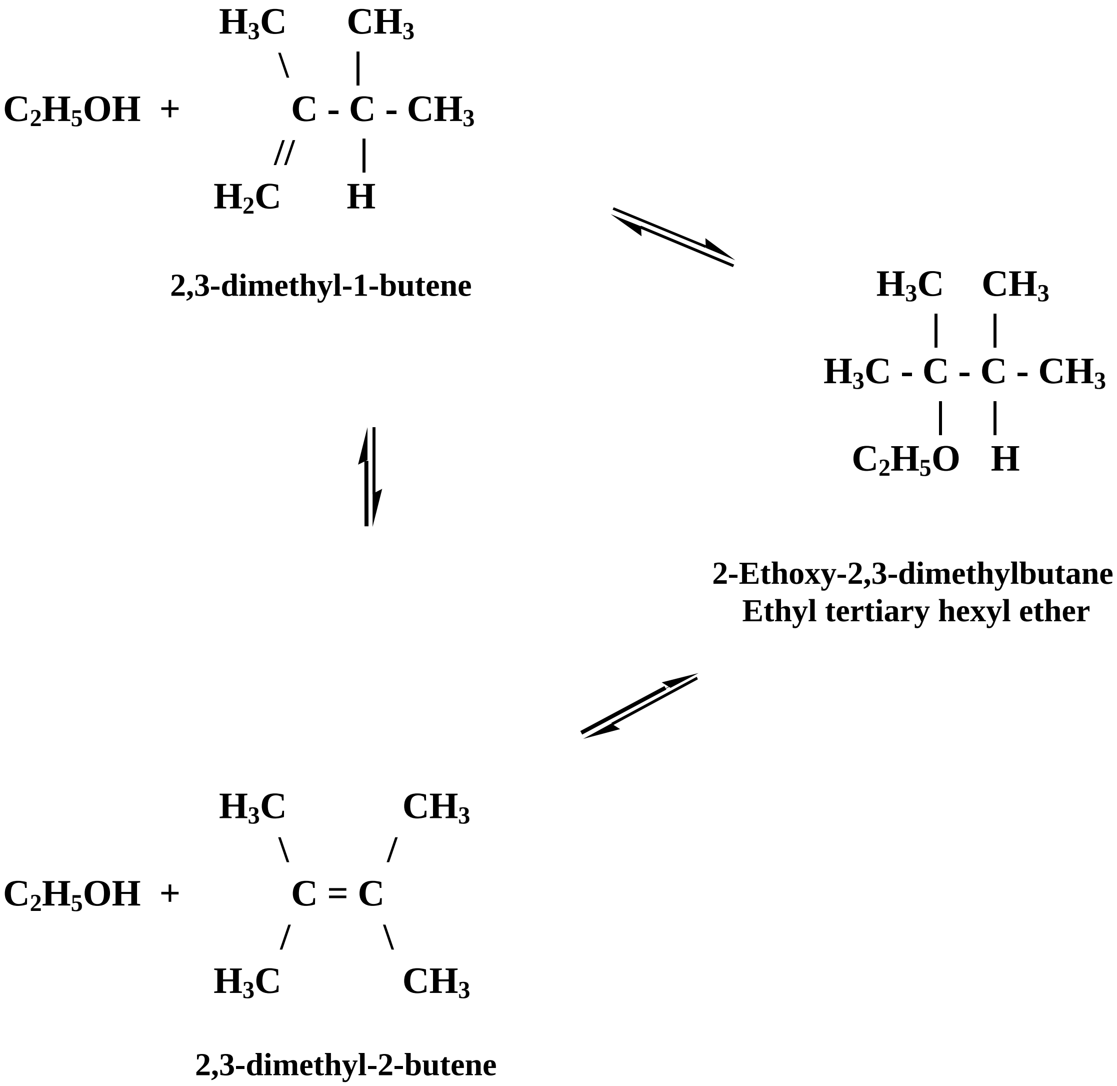


Figure E-6

Reaction Scheme for the Etherification of the 2,3-Dimethylbutenes with Ethanol

Table E-24

Reactivity of a Mixture of Methanol and Ethanol in Etherification of 2,3-Dimethyl-1-butene

Run #	Alcohol	Product Distribution (mole %)				
		DM1B	DM2B	MtHxE	EtHxE	tHxA
DB-11	MeOH	5.9	36	54	—	4.0
DB-19	EtOH	8.5	55	—	27	9.8
DB-20	Mixture	8.7	43	27	14	7.5

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Production of methyl tertiary hexyl ether and ethyl tertiary hexyl ether was about half of what it was when the alcohols were tested separately, which is to be expected since there was only half as much of either alcohol available for reaction with the olefin. By the same reasoning, the production of tertiary hexyl alcohol should be an average of the values obtained with the individual alcohols, or around seven percent. The actual production of this alcohol was 7.5%, in keeping with expectations. Since it is difficult to prepare and maintain dry ethanol, the hydrated olefin will very likely be a component of the product mixture from a continuous etherification reactor if ethanol is used as a feedstock. Fortunately, tertiary hexyl alcohol is also a useful oxygenate for blending in gasoline.

Effect of Increasing the Catalyst Loading on the Production of Methyl and Ethyl Ethers from 2,3-Dimethyl-1-butene

The amount of catalyst loaded was doubled from ten weight percent to twenty weight percent to determine what effect it would have on the production of methyl and ethyl ethers from 2,3-dimethyl-1-butene. Table E-25 presents the product distributions for these runs.

Table E-25

Effect of Increasing the Catalyst Loading on the Production of Methyl and Ethyl Ethers from 2,3-Dimethyl-1-butene

Run #	Catalyst wt%	Product Distribution (mole %)				
		DM1B	DM2B	MtHxE	EtHxE	tHxA
DB-20	10	8.7	43	27	14	7.5
DB-21	20	4.0	39	38	8.8	9.5

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
tHxA denotes tertiary hexyl alcohol, 2-hydroxy-2,3-dimethylbutane.

Doubling the catalyst loading resulted in a twenty-five percent increase in the hydration of the olefin. More interestingly, the production of methyl tertiary hexyl ether increased by over forty percent, while the production of ethyl tertiary hexyl ether decreased by sixty percent. Since methanol is more reactive than ethanol in etherification, the additional catalyst causes more rapid consumption of the olefin by methanolation, leaving less of it available for ethanolation.

Etherification of 2,4,4-Trimethyl-1-pentene with Ethanol

2,4,4-trimethyl-1-pentene was etherified with ethanol using the process parameters as optimized above, that is, a temperature of 70 ^{o}C, a two hour run time, a catalyst loading of ten weight percent of the total reactor charge, and an olefin to alcohol ratio of one to eight. Table E-26 presents the product distribution for this experimentation (Run # TP-26). The product distributions for the etherification of 2,4,4-trimethyl-1-pentene with methanol under identical conditions (Run # TP-21) are also presented so that a comparison of the reactivity of the two alcohols towards etherification can be made. The product distributions are reported on an ethanol free basis. Figure E-7 presents the reaction scheme for the etherification of 2,2,4-trimethyl-1-pentene with ethanol.

Table E-26

Reactivity of Ethanol in Etherification of 2,4,4-Trimethyl-1-pentene

Run #	Product Distribution (mole %)				
	TM1P	TM2P	MtOcE	EtOcE	tOcA
TP-21	73	9.2	17	—	—
TP-26	80	12	—	7.5	0.52

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane
tOcA denotes tertiary Octyl Alcohol, 2-hydroxy-2,4,4-trimethylpentane.

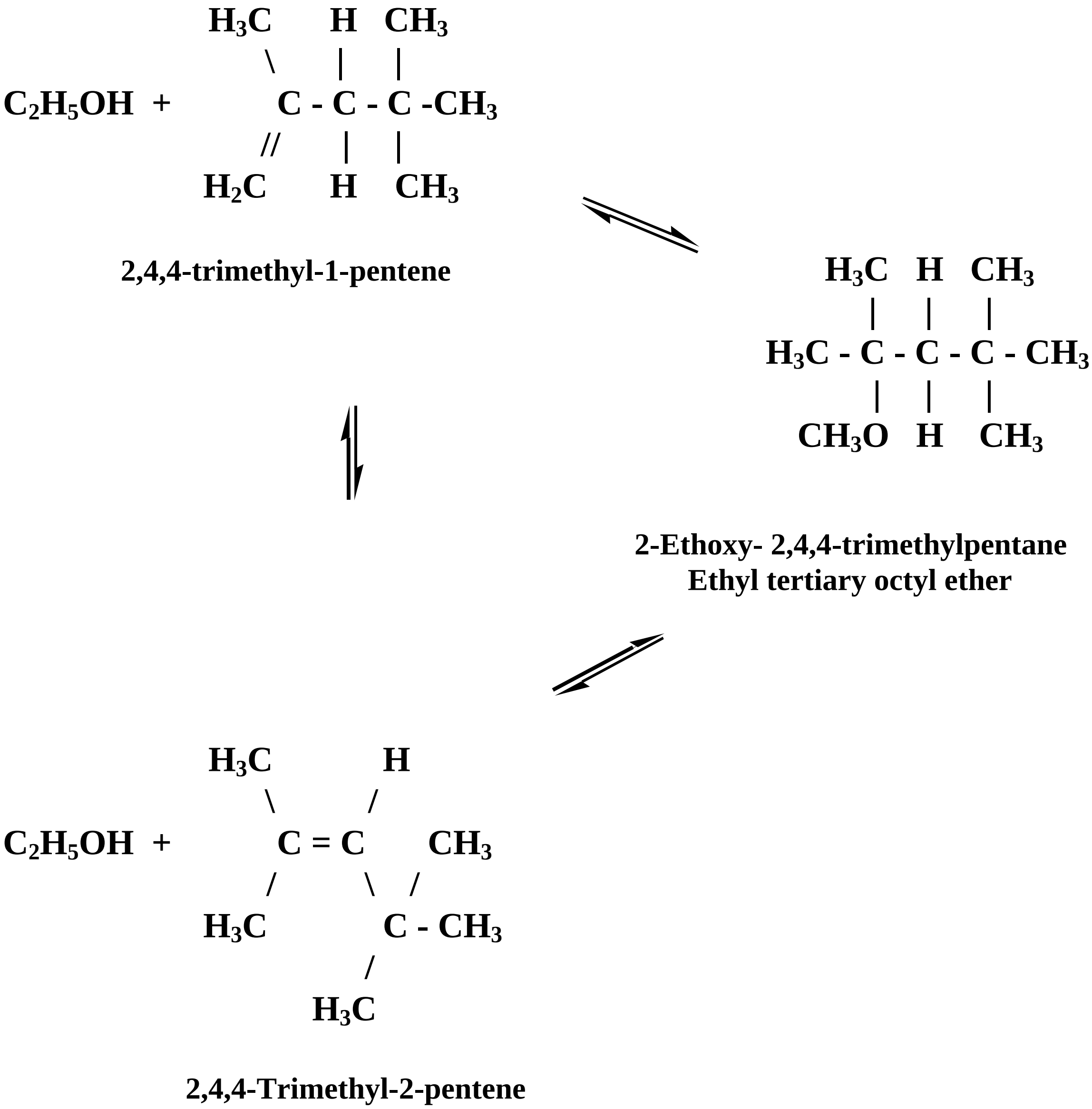


Figure E-7

Reaction Scheme for Etherification of 2,4,4-Trimethyl-1-pentene with Ethanol

Comparison of ether production for ethanol and methanol shows that ethanol is a little less than half as reactive as methanol in this etherification. A similar result was obtained for the etherification of the C_6-alpha-olefin. The C_8-alpha-olefin is much less reactive towards hydration than is the C_6-alpha-olefin, with only one half of one percent of tertiary octyl alcohol being formed, as opposed to ten percent for tertiary hexyl alcohol. Again, alcohols of higher carbon number are suitable oxygenates for use in gasoline blends. Figure E-8 presents the reaction scheme for the hydration of 2,4,4-trimethyl-1-pentene.

Etherification of 2,4,4-Trimethyl-1-pentene with a Mixture of Methanol and Ethanol

2,4,4-trimethyl-1-pentene was etherified with a mixture of methanol and ethanol using the same process parameters. The ratio of olefin to alcohols was 1:4:4, for 2,4,4-trimethyl-1-pentene, methanol and ethanol, respectively, for a total olefin to alcohol ratio of one to eight. Table E-27 presents the product distribution for this experimentation (Run # TP-27). The product distributions for the etherification of 2,4,4-trimethyl-1-pentene with methanol (Run # TP-21), and separately with ethanol (Run # TP-26), under identical conditions, and at an olefin to alcohol ratio of one to eight, are also presented here for ease of comparison.

Production of methyl tertiary octyl ether and ethyl tertiary octyl ether was about half of what it was when the alcohols were tested separately, which is to be expected

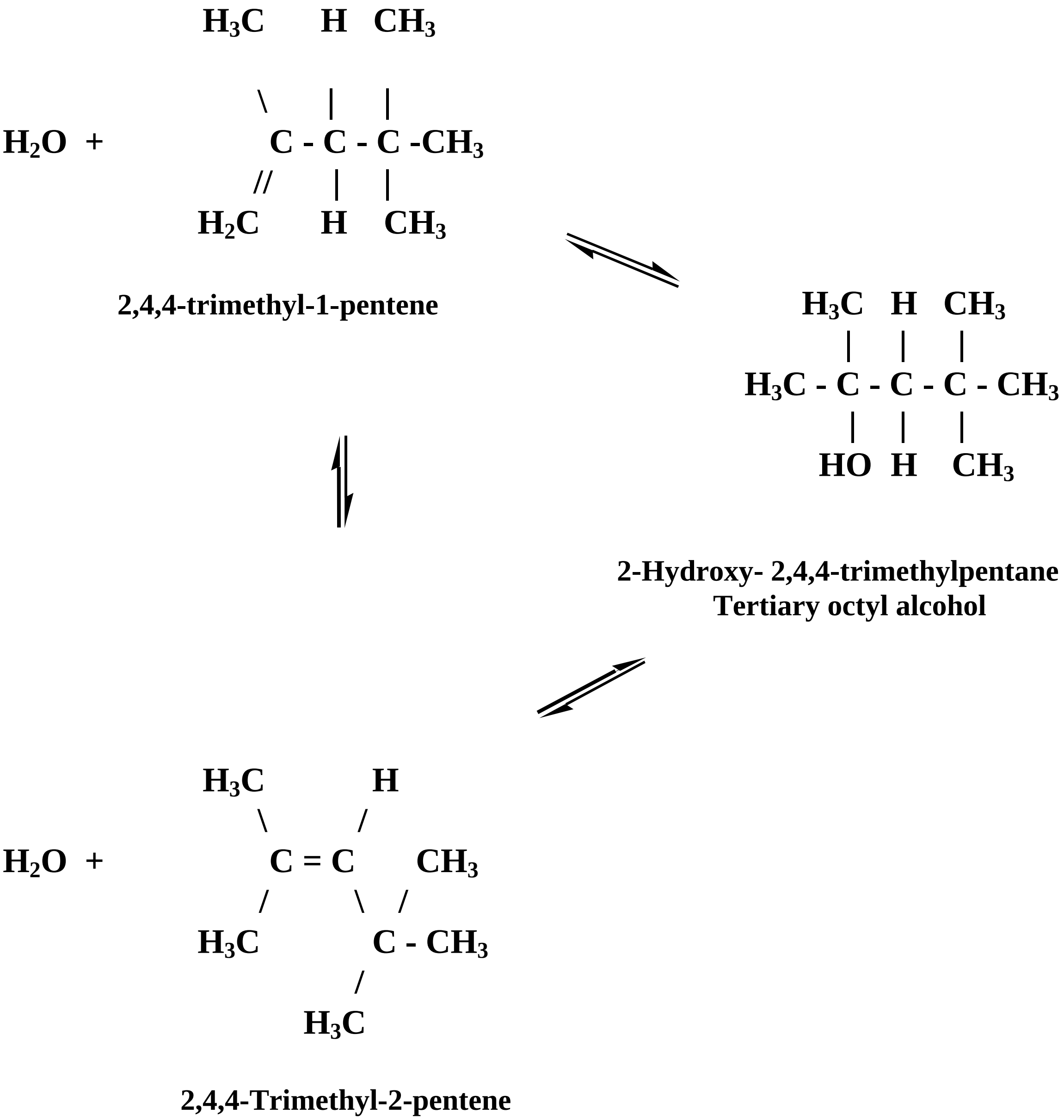


Figure E-8

Reaction Scheme for the Hydration of the 2,4,4-Trimethylpentenes

Table E-27

Reactivity of a Mixture of Methanol and Ethanol in Etherification of 2,4,4-Trimethyl-1-pentene

Run #	Ratio O/M	Ratio O/E	Ratio O/M/E	Product Distribution (mole %)				
				TM1P	TM2P	MtOcE	EtOcE	tOcA
TP-21	1:8	—	—	73	9.2	17	—	—
TP-26	—	1:8	—	80	12	—	7.5	0.52
TP-27	—	—	1:4:4	73	14	9.0	3.5	—

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/M denotes the molar ratio of olefin to methanol.
Ratio O/E denotes the molar ratio of olefin to ethanol.
Ratio O/M/E denotes the molar ratio of olefin to methanol to ethanol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane
tOcA denotes tertiary Octyl Alcohol, 2-hydroxy-2,4,4-trimethylpentane.

since there was only half as much of either alcohol available for reaction with the olefin. No tertiary octyl alcohol was observed in the reaction product mixtures.

Effect of Increasing the Catalyst Loading on the Production of Methyl and Ethyl Ethers from 2,4,4-Trimethyl-1-pentene

The amount of catalyst loaded was doubled from ten weight percent to twenty weight percent to determine what effect it would have on the production of methyl and ethyl ethers from 2,4,4-trimethyl-1-pentene. Table E-28 presents the product distributions for these runs.

Table E-28

Effect of Increasing the Catalyst Loading on the Production of Methyl and Ethyl Ethers from 2,4,4-Trimethyl-1-pentene

Run #	Catalyst wt%	Product Distribution (mole %)			
		TM1P	TM2P	MtOcE	EtOcE
TP-27	10	73	14	9.0	3.5
TP-28	20	71	15	12	2.5

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane.

Doubling the catalyst loading caused an increase in the production of methyl tertiary octyl ether of over thirty percent, while the production of ethyl tertiary hexyl ether decreased by forty percent. The increase in methanolation is somewhat less than it was in the case of the C_6-alpha-olefin, but the decrease in ethanolation is quite a bit less than in the case of the C_6-alpha-olefin. It should be noted that no tertiary octyl alcohol was formed, whereas hydration of the C_6-olefin was significant, with more tertiary hexyl alcohol being formed than was ethyl tertiary hexyl ether. It could be that since none of the C_8-olefin was converted into an alcohol, more was available for ethanolation.

Etherification of a Mixture of 2,3-Dimethyl-1-butene and 2,4,4-Trimethyl-1-pentene with Ethanol

An equimolar mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was etherified with ethanol using the process parameters as optimized above and a ratio of olefin to alcohol of one to eight, that is, a molar ratio of 1: 1: 16 for 2,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene and ethanol, respectively. Table E-29 presents the product distribution for this experimentation (Run # MO-5) .The product distributions for the etherification of a mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene with methanol under identical conditions (Run # MO-1) are also presented so that a comparison of the reactivity of the two alcohols towards etherification can be made. The product distributions are reported on a methanol and ethanol free basis. Ethanol proved to be about one-half as reactive as methanol towards etherification of the 2,3 -dimethyl-1-butene and a little less than half as reactive towards etherification of the 2,4,4-trimethyl-1-pentene. The result is in keeping with the results above for the ethanolation of the two olefins separately. 2.8 mole percent of tertiary hexyl alcohol was also formed, which is equivalent to the amount of ethyl tertiary hexyl ether produced. No tertiary octyl alcohol was detected in the product mixture.

Etherification of a Mixture of 2,3-Dimethyl-1-butene and 2,4,4-Trimethyl-1-pentene with a Mixture of Methanol and Ethanol

An equimolar mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was etherified with an equimolar mixture of methanol and ethanol using the process

Table E-29

Reactivity of Ethanol in Etherification of a Mixture of 2,3-Dimethyl-1-butene and 2,4,4-Trimethyl-1-pentene

Run #	Product Distribution (mole %)							
	DM1B	DM2B	MtHxE	EtHxE	TM1P	TM2P	MtOcE	EtOcE
MO-1	3.6	18	29	—	38	5.0	6.9	—
MO-5	5.2	30	—	15	43	4.2	—	2.6

MO denotes Mixed alpha-Olefin runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane.

parameters as optimized above and a ratio of total olefins to alcohols of one to eight, that is, a molar ratio of 1:1:8:8 for 2,3-dimethyl-1-butene, 2,4,4-trimethyl-1-pentene, methanol and ethanol, respectively. Table E-30 presents the product distribution for this testing (Run # MO-6). The product distributions for the etherification of a mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene with methanol (Run # MO-1) and separately with ethanol (Run # MO-5) under identical conditions are also presented for ease of comparison.

Ethyl tertiary octyl ether production was reduced by about one half, which would be expected from the dilution. Production of the methyl ethers was decreased a little less than half, while the formation of ethyl tertiary hexyl ether was decreased a little more

Table E-30

Reactivity of a Mixture of Methanol and Ethanol in Etherification of a Mixture of 2,3-Dimethyl-1-butene and 2,4,4-Trimethyl-1-pentene

Run #	Product Distribution (mole %)							
	DM1B	DM2B	MtHxE	EtHxE	TM1P	TM2P	MtOcE	EtOcE
MO-1	3.6	18	29	—	38	5.0	6.9	—
MO-5	5.2	30	—	15	43	4.2	—	2.6
MO-6	3.2	24	18	5.8	38	6.7	4.0	1.3

MO denotes Mixed alpha-Olefin runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane.

than half. The results are in good keeping with the results above, the production of methyl ethers being more favorable when there is competition between ethanol and methanol for the olefins. 1.9 mole percent of tertiary hexyl alcohol was also formed, which means thatin this case, the production of tertiary hexyl alcohol actually exceeded the production of ethyl tertiary octyl ether.

Effect of Concentration on the Etherification of C_6- and C_8-Olefins

As noted above, it may be necessary for heat dissipation purposes, to employ a diluent in the design of the continuous single-step etherification reactor. Therefore, the effect of concentration on the etherification of C_6- and C_8-olefins was determined by diluting the starting reaction mixtures with an inert hydrocarbon diluent, namely decalin. Two initial starting concentrations were employed in this testing, namely a one to one mass ratio of reactants to decalin and a one to two mass ratio of reactants to decalin. Other reaction parameters varied in this experimentation were the amount of catalyst loaded and the length of the reaction run time. 2,3-dimethyl-1-butene was etherified with methanol and then with an equimolar mixture of methanol and ethanol. Likewise, 2,4,4-trimethyl-1-pentene was etherified with methanol and then with an equimolar mixture of methanol and ethanol. In addition, an equimolar mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was etherified with methanol and separately with ethanol.

Effect of Concentration on the Etherification of 2,3-Dimethyl-1-butene with Methanol

The reactivity of 2,3-dimethyl-1-butene in etherification with methanol was determined at the two concentrations noted above. The experiments were conducted at 70 ^{o}C and the length of the reaction run time was two hours. The amount of catalyst employed was the same as the single loading of catalyst above. Table E-31 presents the reaction conditions and product distributions for this testing. The results of testing in the absence of any diluent, but under otherwise identical conditions are also presented here for ease of comparison (Run # DB-11).

Halving the concentration of the reactants resulted in a decrease in ether production of a little over twenty-five percent. The overall conversion also suffered, with

Table E-31

Effect of Concentration on Ether Production from 2,3-Dimethyl-1-butene and Methanol

Run #	Ratio R/D	Ratio O/A	Product Distribution (mole %)				ε	S
			DM1B	DM2B	MtHxE	tHxA		
DB-11	∞	1:8	5.9	36	54	4.0	94	1.5
DB-22	1:1	1:8	16	37	45	2.0	84	1.2
DB-23	1:2	1:8	41	27	30	1.7	58	1.1

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.
ε denotes the extent of reaction, or percent conversion of DM1B.
S denotes the selectivity to ether production, or the molar ratio of ether to DM2B.

almost three times as much unreacted starting material left. The selectivity to ether production dropped from near two to about 1.2. When the concentration was reduced to one-third of the neat concentration, ether production dropped to about half of its previous value. The overall conversion went way down, to only 58 percent, while selectivity to ether production fell to about 1.1.

Effect of Catalyst Loading on Etherification of Dilute 2,3-Dimethyl-1-butene with Methanol

Because the presence of an inert diluent may hinder the migration of reactants to the active sites on the catalyst, it is also of interest to the design of a slurry phase reactor to determine if the yields could be enhanced by using additional catalyst. The amount of catalyst employed was the double catalyst loading. The concentrations of reactants employed in this testing were as above, that is, a one to one and a one to two mass ratio of reactants to decalin. Table E-32 presents the reaction conditions and product distributions for these runs. The product distributions for the single loading of Amberlyst® are also presented here for ease of comparison (Runs # DB-22 and DB-23).

Doubling the catalyst loading significantly enhanced the overall conversion of 2,3-dimethyl-1-butene, with only about half as much unreacted starting material left in each case. The selectivity to ether production remained close to unity for both dilutions.

Effect of Reaction Time on Etherification of Dilute 2,3-Dimethyl-1-butene with Methanol

The effect of the length of the reaction run time on etherification of a dilute mixture of 2,3-dimethyl-1-butene was determined. The reaction run time was lengthened from two hours to four hours to see if any further reaction would take place. The dilution rate was one to one by weight of reactants to decalin. A single loading of Amberlyst® 15 was employed. Table E-33 presents the reaction conditions and product distributions for this testing, along with the results of the identical test at a run time of two hours.

Table E-32

Effect of Catalyst Loading on Ether Production from Dilute 2,3-Dimethyl-1-butene and Methanol

Run #	Ratio R/D	Ratio O/A	wt % catalyst	Product Distribution (mole %)			
				DM1B	DM2B	MtHxE	tHxA
DB-22	1:1	1:8	5	16	37	45	2.0
DB-24	1:1	1:8	10	8.3	43	47	2.0
DB-23	1:2	1:8	5	41	27	30	1.7
DB-25	1:2	1:8	10	22	38	38	2.0

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
wt % catalyst denotes weight percent of Amberlyst® to the total reactor charge.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Lengthening the reaction time had no effect on ether production, with both the two and four hour tests yielding 45 percent ether in the reaction product mixture. However, the overall conversion increased significantly, with the amount of unreacted alpha-olefin being reduced by over 30 percent. Unfortunately, the increase in conversion only led to the production of additional beta-olefin. A similar result was obtained with the neat reactants. Therefore, lengthening the reaction time to four hours is probably not advisable.

Table E-33

Effect of Reaction Time on Etherification of Dilute 2,3-Dimethyl-1-butene with Methanol

Run #	Ratio R/D	Ratio O/A	Run Time	Product Distribution (mole %)			
				DM1B	DM2B	MtHxE	tHxA
DB-22	1:1	1:8	2 hrs	16	37	45	2.0
DB-26	1:1	1:8	4 hrs	11	42	45	2.1

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

Simultaneous Etherification of Dilute 2,3-Dimethyl-1-butene with Methanol and Ethanol

The effect of concentration on the etherification of 2,3-dimethyl-1-butene was determined using an equimolar mixture of methanol and ethanol. Equal weights of combined reactants and decalin were used. The single loading of Amberlyst® 15 was employed and the time of the reaction was two hours. Table E-34 presents the reaction conditions and product distribution for these runs. The product distributions for the testing of the neat reactants under identical conditions are reproduced here for ease of comparison (Run # DB-20).

Table E-34

Effect of Concentration on Ether Production from 2,3-Dimethyl-1-butene with Methanol and Ethanol

Run #	Ratio R/D	Ratio O/M/E	Product Distribution (mole %)					ε
			DM1B	DM2B	MtHxE	EtHxE	tHxA	
DB-20	∞	1:4:4	8.7	43	27	14	7.5	91
DB-27	1:1	1:4:4	24	38	29	4.8	4.1	76

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
Ratio O/M/E denotes the molar ratio of Olefin to Methanol to Ethanol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.
ε denotes the extent of reaction, or percent overall conversion of DM1B.

The product distribution from these runs is rather interesting. The overall conversion decreased from 91 to 76 percent, which means that the amount of unreacted alpha-olefin almost tripled. The same result was observed in the etherification of dilute 2,3-dimethyl-1-butene with methanol alone. The production of tertiary hexyl alcohol was a little more than half, while ethyl tertiary hexyl ether production was only about a third of that obtained with the neat reactants. However, production of methyl tertiary hexyl ether actually increased slightly. This product distribution cannot be explained on the basis of dilution alone. The presence of the non-polar decalin is very likely affecting the activity of the catalyst in these reactions, as the nature of ion-exchange resin catalysts has been shown to be sensitive to the polarity of the reaction medium [82, 83]. Therefore, if an inert diluent is to be employed in a continuous etherification reactor, careful consideration will have to be given to not only the quantity of diluent employed, but also to its interaction with the catalyst and reactants.

Effect of Concentration on the Etherification of 2,4,4-Trimethyl-1-pentene with Methanol

The reactivity of 2,4,4-trimethyl-1-pentene in etherification with methanol was determined at the same two concentrations as noted above for 2,3-dimethyl-1-butene. The experiments were conducted at 70 ^{o}C and the length of the reaction run time was two hours. The amount of catalyst employed was the single catalyst loading. Table E-35 presents the reaction conditions and product distributions for this testing. The results of testing in the absence of any diluent, but under otherwise identical conditions are also presented here for ease of comparison (Run # TP-21).

In contrast to the results for the experimentation with 2,3-dimethyl-1-butene, the product distributions from this testing are what would be expected on the basis of dilution chemistry. In the one to one dilution, only about half as much ether was produced, whereas in the one to two dilution, only about one-third as much ether was produced. It should be noted that in all three cases, the selectivity to ether production consistently remained in the 1.8 to 2.2 range.

Table E-35

Effect of Concentration on Ether Production from 2,4,4-Trimethyl-1-pentene and Methanol

Run #	Ratio R/D	Ratio O/A	Product Distribution (mole %)			Selectivity
			TM1P	TM2P	MtOcE	
TP-21	∞	1:8	73	9.2	17	1.8
TP-29	1:1	1:8	89	3.6	7.9	2.2
TP-30	1:2	1:8	93	2.5	4.8	1.9

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
Selectivity denotes the molar ratio of ether to beta-olefin.

Effect of Catalyst Loading on Etherification of Dilute 2,4,4-Trimethyl-1-pentene with Methanol

The effect of catalyst loading on etherification of dilute 2,4,4-trimethyl-1-pentene was also determined. The catalyst loadings tested were the single and double loadings. The mass ratios of reactants to decalin employed were one to one and one to two. Table E-36 presents the reaction conditions and product distributions for this experimentation.

For both the one to one and one to two dilutions, doubling the amount of Amberlyst® increased the overall conversion by over fifty percent. For the one to one dilution, ether production increased by about forty percent, while that for the one to two

Table E-36

Effect of Catalyst Loading on Ether Production from Dilute 2,4,4-Trimethyl-1-pentene and Methanol

Run #	Ratio R/D	Ratio O/A	wt % catalyst	Product Distribution (mole %)			Selectivity
				TM1P	TM2P	MtOcE	
TP-29	1:1	1:8	5	89	3.6	7.9	2.2
TP-31	1:1	1:8	10	83	5.4	11	2.0
TP-30	1:2	1:8	5	93	2.5	4.8	1.9
TP-32	1:2	1:8	10	89	3.5	7.2	2.1

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
Selectivity denotes the molar ratio of ether to beta-olefin.

dilution increased by fifty percent. As was the case with 2,3-dimethyl-1-butene, the etherification of 2,4,4-trimethyl-1-pentene is limited for catalyst under these conditions. Again, it should be noted that the selectivity was consistently around two.

Effect of Reaction Time on Etherification of Dilute 2,4,4-Trimethyl-1-pentene with Methanol

The effect of the length of the reaction run time on etherification of a dilute mixture of 2,4,4-trimethyl-1-pentene was determined. The reaction run time was lengthened from two hours to four hours to see if any further reaction would take place. The dilution rate was one to one by weight of reactants to decalin. A single loading of

Amberlyst® 15 was employed. Table E-37 presents the reaction conditions and product distributions for this testing, along with the results of the identical test at a run time of two hours.

Table E-37

Effect of Reaction Time on Etherification of Dilute 2,4,4-Trimethyl-1-pentene with Methanol

Run #	Ratio R/D	Ratio O/A	Run Time	Product Distribution (mole %)			Selectivity
				TM1P	TM2P	MtOcE	
TP-29	1:1	1:8	2 hr	89	3.6	7.9	2.2
TP-33	1:1	1:8	4 hr	84	5.5	11	2.0

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
Selectivity denotes the molar ratio of ether to beta-olefin.

Lengthening the reaction time from two hours to four hours resulted in a fifty percent increase in overall conversion and a forty percent increase in ether production, while the selectivity remained near two. This result is in keeping with the previous results for the etherification of neat 2,4,4-trimethyl-1-pentene. That is to say, in neither case did the reaction reach completion after two hours.

Simultaneous Etherification of Dilute 2,4,4-Trimethyl-1-pentene with Methanol and Ethanol

The effect of concentration on the etherification of 2,4,4-trimethyl-1-pentene was determined using an equimolar mixture of methanol and ethanol. Equal weights of combined reactants and decalin were used. The single loading of Amberlyst® 15 was employed and the time of the reaction was two hours. Table E-38 presents the reaction conditions and product distribution for these runs. The product distributions for the testing of the neat reactants under identical conditions are reproduced here for ease of comparison (Run # TP-27).

Table E-38

Effect of Concentration on Etherification of

2,4,4-Trimethyl-1-pentene with Methanol and Ethanol

Run #	Ratio R/D	Ratio O/M/E	Product Distribution (mole %)			
			TM1P	TM2P	MtOcE	EtOcE
TP-27	∞	1:4:4	73	14	9.0	3.5
TP-34	1:1	1:4:4	92	3.1	3.7	1.1

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
Ratio O/M/E denotes the molar ratio of olefin to methanol to ethanol.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane.

As was the case with the simultaneous etherification of 2,3-dimethyl-1-butene with methanol and ethanol, the overall conversion of alpha-olefin was reduced by a factor of about three. Here again, some preference for methanolation over ethanolation was observed in that the yield of ethyl tertiary octyl ether was reduced over threefold, whereas the yield of ethyl tertiary octyl ether was reduced by just under 2.5 fold.

Effect of Concentration on Etherification of Mixed Alpha-Olefins with Methanol

The effect of concentration on etherification with methanol of an equimolar mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was determined. The catalyst loading employed was ten weight percent of the reactants. The molar ratio of olefin mixture to methanol was 1:8, and the dilution ratio was one to one of combined reactants to decalin by weight. Table E-39 presents the reaction conditions and product distributions for this testing. The results for the etherification of the olefin mixture with methanol in the absence of any diluent but under otherwise identical conditions are also presented here for ease of comparison (Run # MO-1).

In the etherification of the dilute olefin mixture, the overall conversion for both 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was about nine-tenths of the conversion obtained in the absence of any diluent. Production of methyl tertiary hexyl ether declined to about seventy percent of its value for the neat olefin mixture, whereas production of methyl tertiary octyl ether fell to less than sixty percent of its value for the neat olefin mixture.

Table E-39

Effect of Concentration on Etherification of Mixed Alpha-Olefins with Methanol

Run #	Ratio R/D	Product Distribution (mole %)					
		DM1B	DM2B	MtHxE	TM1P	TM2P	MtOcE
MO-1	∞	3.6	18	29	38	5.0	6.9
MO-7	1:1	13	17	20	43	2.4	4.2

MO denotes Mixed alpha-Olefin runs.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether, 2-methoxy-2,4,4-trimethylpentane.

Effect of Concentration on Etherification of Mixed Alpha-Olefins with Ethanol

The effect of concentration on etherification with ethanol of an equimolar mixture of 2,3-dimethyl-1-butene and 2,4,4-trimethyl-1-pentene was determined. The catalyst loading employed was ten weight percent of the reactants. The molar ratio of olefin mixture to ethanol was 1:8, and the dilution ratio was one to one of combined reactants to decalin by weight. Table E-40 presents the reaction conditions and product distributions for this testing. The results for the etherification of the olefin mixture with ethanol in the absence of any diluent but under otherwise identical conditions are also presented here for ease of comparison (Run # MO-5).

Table E-40

Effect of Concentration on Etherification of Mixed Alpha-Olefins with Ethanol

Run #	Ratio R/D	Product Distribution (mole %)					
		DM1B	DM2B	EtHxE	TM1P	TM2P	EtOcE
MO-5	∞	5.2	30	15	43	4.2	2.6
MO-8	1:1	13	23	9.4	46	2.2	1.3

MO denotes Mixed alpha-Olefin runs.
Ratio R/D denotes the mass ratio of Reactants to Decalin.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
EtHxE denotes Ethyl tertiary Hexyl Ether, 2-ethoxy-2,3-dimethylbutane.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
TM2P denotes 2,4,4-Trimethyl-2-Pentene.
EtOcE denotes Ethyl tertiary Octyl Ether, 2-ethoxy-2,4,4-trimethylpentane.

Unlike the case of etherification of the mixed olefins with methanol, the results here are more readily explained on the basis of a dilution effect. The overall conversion for the C_8-olefin decreased by about ten percent, but only about half as much ethyl tertiary octyl ether was produced in the dilute solution. Likewise for the C_6-olefin, the overall conversion was reduced by about ten percent, and about sixty percent as much methyl tertiary octyl ether was produced.

Reactions with 2-Butanol

2-Butanol did not react with either 2,3-dimethyl-1-butene or 2,4,4-trimethyl-1-pentene under etherification conditions, that is, 70 ^{o}C , a single catalyst loading, and two hours run time. Therefore, 2-butanol is not a likely candidate for an alcohol to use in preparing higher carbon ethers. The choice of olefins, alcohols and reaction conditions to employ in the development of a continuous etherification reactor is discussed further in Chapter VI.

APPENDIX F

REACTION EQUILIBRIA IN THE SYNTHESIS OF HIGHER CARBON ETHERS

As noted in Appendix E, because the acidic catalyst promotes both etherification and isomerization, it is not possible to study the etherification of olefins independently of the competing isomerization reaction. However, it is possible to investigate the isomerization reaction in the absence of an added alcohol.

Reaction Equilibria in the Isomerization of the 2,3-Dimethylbutenes

In this study, the equilibrium composition of the 2,3-dimethylbutenes at 80 ^{o}C has been determined to be ten percent 2,3-dimethyl-1-butene (DM1B) and ninety percent 2,3-dimethyl-2-butene (DM2B). For the reversible reaction:

$$\text{DM1B} \rightleftarrows \text{DM2B},$$

the equilibrium constant based on mole fraction of components in solution is defined as

$$K_{eq} = x_{products}/x_{reactants}, \text{ or}$$

$$K_{eq} = x_{DM2B}/x_{DM1B},$$

where x_{DM1B} = the mole fraction of 2,3-dimethyl-1-butene and

x_{DM2B} = the mole fraction of 2,3-dimethyl-2-butene. Inserting the appropriate experimental values gives:

$$K_{eq} = x_{DM2B}/x_{DM1B} = 0.90/0.10 = 9.0$$

More formally, the equilibrium constant based on activities of the components in solution is defined as

$$K_a = a_{products}/a_{reactants}, \text{ or}$$

$$K_a = a_{DM2B}/a_{DM1B},$$

where a_{DM1B} = the activity of 2,3-dimethyl-1-butene and

a_{DM2B} = the activity of 2,3-dimethyl-2-butene. The activity is defined as the product of the mole fraction and the activity coefficient for each component *i* in solution:

$$a_i = \gamma_i x_i,$$

where the activity coefficient, γ_i, is an indicator of the non-ideality of component *i* in solution [161]. Because the mixture here is composed of two isomers, the solution formed is quite ideal, and the activity coefficients are very close to unity. For this reason,

$$K_a \approx K_{eq},$$

and K_{eq} is adequate for the purposes of this discussion.

The change in the Gibb's Free Energy for a chemical reaction is defined as

$$\Delta G = -RT \ln K,$$

where R = the universal gas constant, and

T = the temperature in Kelvins. Substituting the appropriate values,

$$\Delta G = -RT \ln K = -(8.314 \text{ J/g-mol K})(343 \text{ K}) \ln 9.0$$

$$\Delta G = -6.3 \text{ kJ/mol.}$$

The negative value for ΔG indicates that the reaction proceeds spontaneously as written, yielding the less reactive beta-olefin.

Reaction Equilibria in the Isomerization of the 2,3-Dimethylbutenes under Etherification Conditions

The presence of methanol and product ether has little or no effect on the equilibrium partitioning of the 2,3-dimethylbutenes. That is to say that the value of K_{eq} for the reaction

$$\text{DM1B} \rightleftarrows \text{DM2B},$$

is only minimally affected by the presence of the oxygenates. Table F-1 presents a comparison of the equilibrium partitioning of the 2,3-dimethylbutenes after reacting for two hours at 80 ^{o}C under etherification conditions and in the absence of any added methanol.

Comparison of the product distributions on an oxygenate free basis shows only a two percent difference in the equilibrium partitionings, which is within the experimental error for this testing. The result is in good agreement with the results of previous

Table F-1

Equilibrium Partitioning of the 2,3-Dimethylbutenes in Isomerization With and Without Methanol

Run #	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
				DM1B	DM2B	MtHxE	tHxA
DB-5	2:1	80 ^oC	2 hrs	8.5	63	27	1.5
DB-5	2:1	80 ^oC	2 hrs	12	88	Oxygenate free	Oxygenate free
ISO	∞	80 ^oC	2 hrs	10	90	—	—

DB denotes 2,3-Dimethylbutene runs.
ISO denotes isomerization runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

researchers [76]. As discussed below, this result is important to the calculation of equilibrium constants for the simultaneous etherification and isomerization reactions.

Temperature Dependence of Reaction Equilibria in the Isomerization of the 2,3-Dimethylbutenes under Etherification Conditions

The temperature dependence of the olefin isomerization under etherification conditions has been determined in the temperature range from 70 ^oC to 100 ^oC. Table

F-2 presents the reaction conditions and product distributions used in this determination. The reaction at 70 °C required four hours to reach equilibrium, whereas the reactions at 80 °C and 100 °C were complete in two hours.

Table F-2

Equilibrium Partitioning of the 2,3-Dimethylbutenes in Isomerization under Etherification Conditions

Run #	Ratio O/A	Temp.	Time	Product Distribution (mole %)			
				DM1B	DM2B	MtHxE	tHxA
DB-7	2:1	70 °C	4 hrs	6.4	58	34	1.3
DB-5	2:1	80 °C	2 hrs	8.5	63	27	1.5
DB-2	2:1	100 °C	2 hrs	10	68	23	—

DB denotes 2,3-Dimethylbutene runs.
ISO denotes isomerization runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.
Ratio O/A denotes the molar ratio of Olefin to Alcohol.
MtHxE denotes Methyl tertiary Hexyl Ether, 2-methoxy-2,3-dimethylbutane.
tHxA denotes tertiary Hexyl Alcohol, 2-hydroxy-2,3-dimethylbutane.

The data in Table F-2 can be used to determine the equilibrium constants, the reaction enthalpy, the reaction entropy, and the temperature dependence of the Gibb's free energy function for the isomerization. The procedure used for this determination is

Table F-3

Equilibrium Constants for the Isomerization of 2,3-Dimethyl-1-butene under Etherification Conditions

Run #	Temp.	Temp. (kelvins)	Product Distribution (mole %)		K_{eq}	1/T $(\text{kelvins})^{-1}$	ln K
			DM1B	DM2B			
DB-7	70 °C	343	6.4	58	9.06	0.00292	2.20
DB-5	80 °C	353	8.5	63	7.41	0.00283	2.00
DB-2	100 °C	373	10	68	6.8	0.00268	1.92

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
DM2B denotes 2,3-Dimethyl-2-Butene.

as follows. A Van't Hoff plot is constructed from the temperatures and their corresponding equilibrium constants. The data for this construction are compiled in Table F-3.

The change in the Gibb's free energy for a chemical reaction is defined as

$$\Delta G = \Delta H - T\Delta S$$

where ΔH = the enthalpy change for the reaction,

T = the temperature in kelvins and

ΔS = the entropy change for the reaction.

From above,

$$\Delta G = -RT \ln K.$$

Combining these equations gives

$$-RT \ln K = \Delta H - T\Delta S.$$

Rearranging gives

$$\ln K = -\Delta H/RT + \Delta S/R.$$

This equation expresses ΔG, or more formally, ln K, as a function of temperature, in slope-intercept form, that is, $y = mx + b$. A Van’t Hoff plot is created by plotting the independent or y-variable, ln K, versus the dependent or x-variable, 1/T. The slope, m, of the line gives the enthalpy of reaction in terms of $-\Delta H/R$, and the y-intercept, b, gives the entropy of reaction in terms of $\Delta S/R$. Figure F-1 provides a Van’t Hoff plot of the data in Table F-3.

The value determined for the enthalpy of the isomerization reaction compares very well with the only experimentally determined value found in the literature, which was -9.0 kJ/mol [76].

By regression analysis, m was found to be 1141 kelvins. Therefore,

$$\Delta H = -mR = -1141 \text{ K} * 8.314 \text{ J/mol K}$$

$$\Delta H = -9.5 \text{ kJ/mol}.$$

Similarly, b was determined to be -1.164, therefore

$$\Delta S = bR = -1.164 * 8.314 \text{ J/mol K}$$

$$\Delta S = -9.7 \text{ J/mol K}$$

Agreement with the literature value of -9.5 J/mol K was considered to be very good [76].

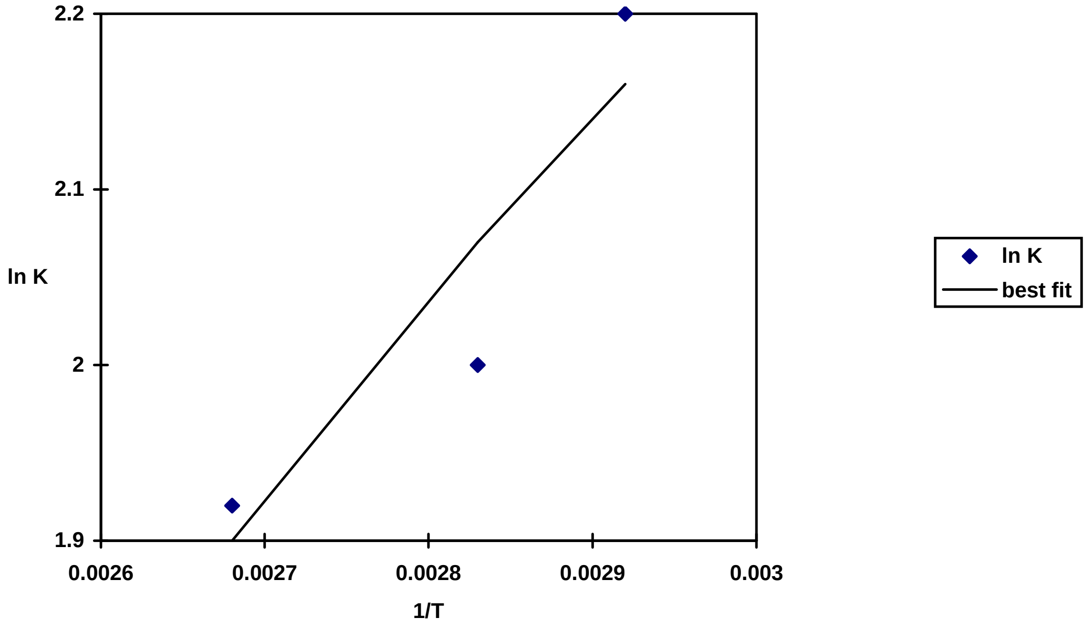


Figure F-1

Van't Hoff Plot for the Isomerization of 2,3-Dimethyl-1-butene

It follows that

$$\ln K = 1140 \text{ kelvins } (1/T) - 1.16.$$

Since the equilibrium constant decreases with increasing temperature, the enthalpy of reaction is negative, which means that the isomerization is an exothermic reaction.

It is always of interest to compare the magnitudes of the contributions of ΔH and TΔS to the Gibb's free energy function for a reaction, that is, to demonstrate enthalpic versus entropic control using the definition of the Gibb's free energy function:

$$\Delta G = \Delta H - T\Delta S.$$

At 70 °C,

$$\Delta G = -9.5 \text{ kJ/mol} - (343 \text{ K})*(- 9.7 \text{ J/mol K})$$

$$\Delta G = -9.5 \text{ kJ/mol} + 3.3 \text{ kJ/mol}$$

The magnitude of ΔH is 9.5 kJ/mol, while that of TΔS is 3.3 kJ/mol, so that ΔH is approximately three times the size of TΔS, and the reaction will be largely under enthalpic control.

Simultaneous Reaction Equilibria in the Synthesis of Methyl Tertiary Hexyl Ether

The simultaneous isomerization and etherification reaction equilibria can be represented by three equations as follows:

$$\text{DM1B} \rightleftarrows \text{DM2B} \qquad \text{(F-1)}$$

$$\text{DM1B} + \text{MeOH} \rightleftarrows \text{MtHxE} \qquad \text{(F-2)}$$

$$\text{DM2B} + \text{MeOH} \rightleftarrows \text{MtHxE} \qquad \text{(F-3)}$$

Only two of the three equations are independent, as Equation F-2 minus Equation F-3 gives Equation F-1. Working with the first two equations and assuming ideal liquids in solution, K_1 for the isomerization is as defined as above, and K_2 for the etherification is

$$K_2 = x_{MtHxE}/(x_{DM1B}\, x_{MeOH}),$$

where x_{MtHxE} = the mole fraction of methyl tertiary hexyl ether in solution, and

x_{MeOH} = the mole fraction of methanol in solution.

In order to calculate equilibrium constants, the product distributions have to be converted to mole fractions. Substituting the appropriate normalized values for the mole fractions of reactants and products at 70 ^{o}C gives

$$K_2 = x_{MtHxE}/(x_{DM1B}\, x_{MeOH}) = 0.299/((0.0563)(0.134))$$

$$K_2 = 39.6.$$

Similar calculations with the values for 80 ^{o}C and 100 ^{o}C provide the data necessary for the determination of the reaction enthalpy and entropy for the etherification. These data are tabulated in Table F-4. Figure F-2 provides a Van’t Hoff plot of the data in Table F-4.

Table F-4

Equilibrium Constants for the Etherification of

2,3-Dimethyl-1-butene With Methanol

Run #	Temp.	1/T (kelvins)$^{-1}$	Product Distribution (mole fraction)			K_{eq}	ln K
			DM1B	MeOH	MtHxE		
DB-7	70 ^{o}C	0.00292	0.0563	0.134	0.299	39.6	3.68
DB-5	80 ^{o}C	0.00283	0.0704	0.184	0.224	17.2	2.85
DB-2	100 ^{o}C	0.00268	0.0778	0.214	0.179	10.8	2.38

DB denotes 2,3-Dimethylbutene runs.
DM1B denotes 2,3-Dimethyl-1-Butene.
MtHxE denotes Methyl tertiary Hexyl Ether.

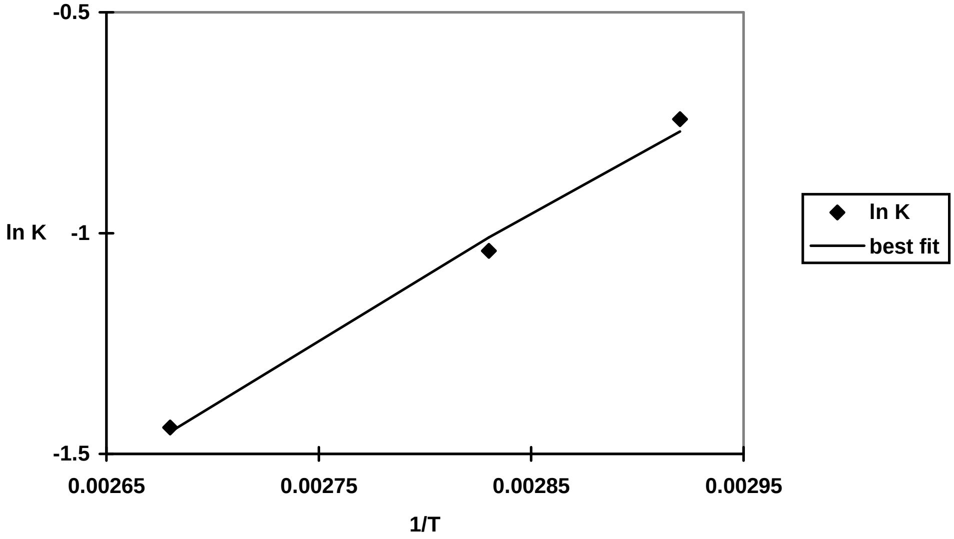


Figure F-2

Van’t Hoff Plot for the Etherification of 2,3-Dimethyl-1-butene

By regression analysis, ΔH = - 43 kJ/mol and ΔS = - 100 J/mol K. The etherification reaction is much more exothermic than the isomerization. The experimental value determined here for the enthalpy change of reaction compares reasonably well with the literature value of -34.4 kJ/mol. The value determined for the entropy change of reaction compares very well with the literature value of -104 kJ/mol. Comparing the magnitudes of ΔH and TΔS of 43 kJ/mol and 34.3 kJ/mol at 70 ^{o}C, respectively, indicates that entropy factors play a much more significant role in etherification than they do in isomerization.

It cannot be overemphasized that since the etherification reaction proceeds more readily than the isomerization, the equilibrium product distribution is not the most favorable distribution for ether production from 2,3-dimethyl-1-butene and methanol. The matter will be discussed in more detail in Appendix G.

Reaction Equilibria in the Isomerization of the 2,4,4-Trimethylpentenes

In this study, the equilibrium composition of the neat 2,4,4-trimethylpentenes at 80 °C has been determined to be seventy-eight percent 2,4,4-trimethyl-1-pentene (TM1P) and twenty-two percent 2,4,4-trimethyl-2-pentene (TM2P). The result is in excellent agreement with the results of other researchers [79]. Again, this is in contrast to the distribution for the 2,3-dimethyl-butenes, where the beta-olefin is the thermodynamically preferred isomer.

For the reaction:

$$\text{TM1P} \rightleftharpoons \text{TM2P},$$

the equilibrium constant based on mole fraction of components in solution is defined as

$$K_{eq} = x_{products}/x_{reactants}$$

$$K_{eq} = x_{TM2P}/x_{TM1P}$$

where x_{TM1P} = the mole fraction of 2,4,4-trimethyl-1-pentene, and

x_{TM2P} = the mole fraction of 2,4,4-trimethyl-2-pentene.

The activity coefficients for 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene have been determined to be 1.03 and 1.01, respectively, in the temperature range of interest to this study [79]. Therefore, the error introduced by the approximation

$$K_a \approx K_{eq},$$

is within the limits of experimental error. Substituting the appropriate values,

$$K_{eq} = x_{TM2P}/x_{TM1P} = 0.22/0.78 = 0.28.$$

The result is in excellent agreement with the results of other researchers [79], who provide the following equation for ln K for this isomerization:

$$\ln K = - 421.67(1/T) - 0.056.$$

At 80 ^{o}C, this equation gives

$$\ln K = -1.25$$

$$K = \exp(-1.25) = 0.286.$$

Since

$$K = x_{TM2P}/x_{TM1P}$$

$$x_{TM2P} + x_{TM1P} = 1$$

it follows that $x_{TM2P} = 0.222$ and $x_{TM1P} = 0.778$, or $x_{TM2P} = 0.22$ and $x_{TM1P} = 0.78$, within the experimental error limits for this testing. The change in the Gibb's Free Energy is given by

$$\Delta G = -RT \ln K = - (8.314 \text{ J/mol K})(353 \text{ K}) \ln 0.28$$

$$\Delta G = 3.7 \text{ kJ/mol.}$$

The positive value of ΔG indicates that the reaction proceeds to the left as written, that is, the alpha-olefin is the thermodynamically preferred isomer. Again, this is in contrast to the isomerization of the 2,3-dimethylbutenes, where the beta-olefin is the preferred isomer.

Reaction Equilibria in the Synthesis of Methyl Tertiary Octyl Ether

The simultaneous isomerization and etherification reaction equilibria can be represented by three equations as follows:

$$\text{TM1P} \rightleftharpoons \text{TM2P} \qquad \text{(F-4)}$$

$$\text{TM1P} + \text{MeOH} \rightleftharpoons \text{MtOcE} \qquad \text{(F-5)}$$

$$\text{TM2P} + \text{MeOH} \rightleftharpoons \text{MtOcE} \qquad \text{(F-6)}$$

Only two of the three equations are independent, as Equation (F-5) minus Equation (F-6) gives Equation (F-4).

As discussed above, because the etherification proceeds more readily than the isomerization, maximum ether production is achieved before equilibrium is attained for the simultaneous isomerization and etherification of 2,3-dimethyl-1-butene. The same behavior was observed in the etherification of 2,4,4-trimethyl-1-pentene at temperatures of 80 ^{o}C and above. That is to say that as the isomerization continued, the ether production was reduced, which probably indicates that decomposition of the ether was taking place. For this reason, most of the reactions were stopped short of equilibrium. On the contrary, the maximum ether yield from 2,4,4-trimethyl-1-pentene at a temperature of 70 ^{o}C appears to occur at equilibrium. This research has also demonstrated that the equilibrium partitioning of olefins between alpha- and beta-isomers was nearly identical whether the isomers were allowed to react neat or the isomerization was conducted under etherification conditions. Moreover, previous researchers have used equilibrium constants for isomerization obtained with the neat reactants in developing kinetic models for etherification [60]. Therefore, it is possible to calculate equilibrium constants for this etherification by using experimental values for the methanol and ether concentrations, and calculating the alpha-olefin concentration from the experimental total olefin concentration and the known ratio of beta- to alpha-olefin at equilibrium. Table F-5 presents the data necessary for the calculation of the relevant thermodynamic parameters for the etherification of 2,4,4-trimethyl-1-pentene with methanol. Figure F-3 presents a Van't Hoff plot for the data in Table F-5.

From regression analysis,

$$\ln K = 2884 \text{ kelvins } (1/T) - 9.18.$$

It follows that $\Delta H = -24.0$ kJ/mol and $\Delta S = -76$ J/mol K. No directly comparable studies of this etherification were found in the literature. One study did investigate the reaction equilibria for this etherification in an inert diluent, namely iso-octane [60]. The authors provide the following equation for this etherification:

$$\ln K = 2268.6 \text{ kelvins } (1/T) - 8.60.$$

Table F-5

Equilibrium Constants for the Etherification of 2,4,4-Trimethyl-1-pentene With Methanol

Run #	Temp.	1/T (kelvins)$^{-1}$	Product Distribution (mole fraction)				K_{eq}	ln K
			TM1P (exp.)	TM1P (calc.)	MeOH	MtOcE		
TP-18	70 °C	0.00292	0.501	0.501	0.288	0.0687	0.476	-0.742
TP-14	80 °C	0.00283	0.537	0.505	0.298	0.0530	0.352	-1.04
TP-7	100 °C	0.00268	0.544	0.509	0.308	0.0372	0.237	-1.44

TP denotes 2,4,4-Trimethylpentene runs.
TM1P denotes 2,4,4-Trimethyl-1-Pentene.
MtOcE denotes Methyl tertiary Octyl Ether.

It follows that ΔH = - 18.9 kJ/mol and ΔS = - 72 J/mol K. The difference between the experimental and literature values for the enthalpies is over twenty percent. Activity coefficients, particularly of methanol, have been shown to be significant [60].

The contributions of enthalpic and entropic effects to the Gibb’s free energy function for this etherification can be demonstrated. For the literature study cited, in the presence of an inert diluent at 70 °C,

$$\Delta G = \Delta H - T\Delta S.$$

$$\Delta G = -19.3 \text{ kJ/mol} - (343 \text{ K})*(-73 \text{ J/mol K})$$

$$\Delta G = -19.3 \text{ kJ/mol} + 25.0 \text{ kJ/mol}.$$

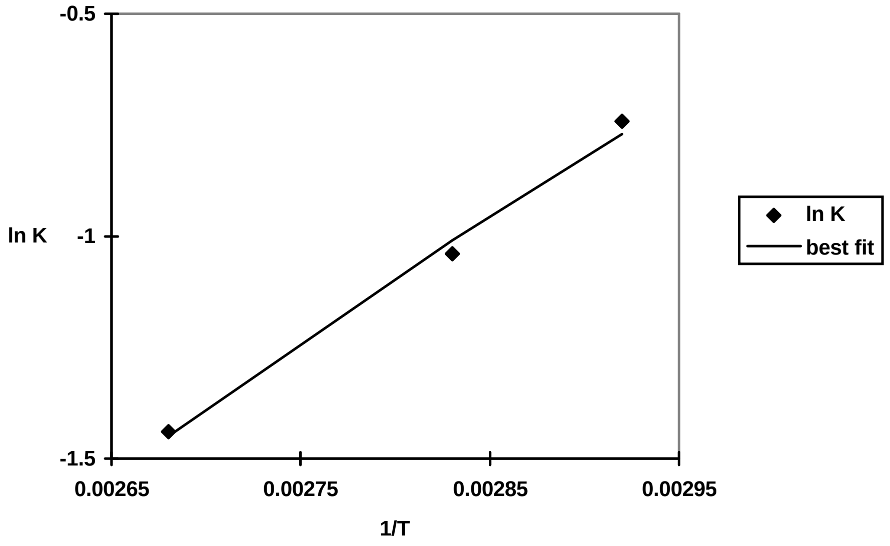


Figure F-3

Van’t Hoff Plot for the Etherification of 2,4,4-Trimethyl-1-pentene

Here the magnitude of $T\Delta S$ actually exceeds the magnitude of ΔH. Similarly, for the experimental values determined in this research

$$\Delta G = -23.4 \text{ kJ/mol} - (343 \text{ K})*(- 57 \text{ J/mol K})$$

$$\Delta G = -23.4 \text{ kJ/mol} + 17.2 \text{ kJ/mol.}$$

The magnitude of $T\Delta S$ is less than the magnitude of ΔH in the absence of a solvent, but is still quite significant. Therefore, considerable attention will have to be paid to entropic effects in the development of a continuous etherification reactor to convert C_8-olefins, perhaps even more so if an inert solvent is to be employed for heat dissipation purposes.

The matter of heat dissipation from the exothermic reactions is discussed further in Chapter VI.

APPENDIX G

REACTION KINETICS IN THE SYNTHESIS OF HIGHER CARBON ETHERS

It is one of the stated goals of the research presented here to compare the relative reactivities of C_6- and C_8-olefins towards etherification with low molecular weight alcohols, and also to compare the relative reactivities of low molecular weight alcohols towards alkanolation of C_6- and C_8-olefins. It is not the goal of the current research to develop a kinetic model for etherification. The development of such a model constitutes future work. However, the data collected in the C_8-olefins portion of this work are sufficiently accurate to develop a preliminary model for the simultaneous etherifications and isomerization. Since the outputs from this work constitute the inputs to the development of a continuous bench-top etherification reactor, it is of interest to extract as much information from the data as possible.

The comparison of the relative reactivities of C_6- and C_8-olefins towards etherification is based on the mole fraction of ether in the product after a certain reaction time at a given temperature with a specified catalyst loading and initial concentration of reactants. On the other hand, the determination of rate constants requires the evaluation of the mole fraction of products and unreacted reactants in the product mixture at a number of incremental reaction times over a range of temperatures. Since a goal of this research was to determine the optimum conditions for ether production, the range of temperatures and reaction times grew narrower as the work progressed.

Reaction Kinetics in the Synthesis of Methyl Tertiary Hexyl Ether

2,3-dimethyl-1-butene proved to be about three times more reactive in etherification with methanol than did 2,3-dimethyl-2-butene. That is to say that in testing for two hours at 70 ^{o}C, there was three times as much ether in the product mixture when the starting olefin was 2,3-dimethyl-1-butene, all other parameters being equal.

As discussed in Appendix E, the choice of the optimum run time, of two hours, was based on the reactivity of 2,4,4-trimethyl-1-pentene. Because 2,3-dimethyl-1-butene ultimately proved to be far more reactive than 2,4,4-trimethyl-1-pentene, this meant that equilibrium had been achieved in the two hour tests with 2,3-dimethyl-1-butene at 70 ^{o}C. Consequently, kinetic parameters cannot be determined from these data. The type of data that would be required to make such a determination is discussed below.

Reaction Kinetics in the Synthesis of Methyl Tertiary Octyl Ether

In the case of the 2,4,4-trimethylpentenes, 2,4,4-trimethyl-2-pentene proved to be about seventy percent as reactive in etherification with methanol as 2,4,4-trimethyl-1-pentene. That is to say that in testing for two hours at 70 ^{o}C, there was seventy percent as much ether in the product mixture when the starting olefin was 2,4,4-trimethyl-2-pentene, all other parameters being equal.

It should be noted that, unlike the case with methyl tertiary hexyl ether, the production of methyl tertiary octyl ether is equilibrium limited, at least at 70 ^{o}C. This is readily explained by the observation that in the etherification of 2,3-dimethyl-1-butene, the competing isomerization reaction leads to the formation of the three times less reactive 2,3-dimethyl-2-butene. Since the etherification is fast compared to the isomerization, maximum ether production is attained before the 2,3-dimethylbutenes equilibrate. Previous researchers arrived at the same conclusion [60]. In the case of the etherification of 2,4,4-trimethyl-1-pentene, while isomerization does lead to the less reactive beta-olefin, 2,4,4-trimethyl-2-pentene retains about seventy percent of the reactivity of 2,4,4-trimethyl-1-pentene. Moreover, the maximum amount of the less reactive beta-olefin formed is only twenty-two percent. The net result is that in contrast to the reaction with the C_6-olefins, the isomerization has little effect on the overall reactivity of the C_8-olefin mixture towards etherification. Mathematically, with pure alpha-olefin as starting material, at any time before equilibrium,

$$\text{reactivity}_{\text{mixture}} \geq 0.78*\text{reactivity}_{\alpha\text{-olefin}} + 0.22*\text{reactivity}_{\beta\text{-olefin}}$$

$$\text{reactivity}_{\text{mixture}} \geq 0.78*\text{reactivity}_{\alpha\text{-olefin}} + 0.22*0.70*\text{reactivity}_{\alpha\text{-olefin}}$$

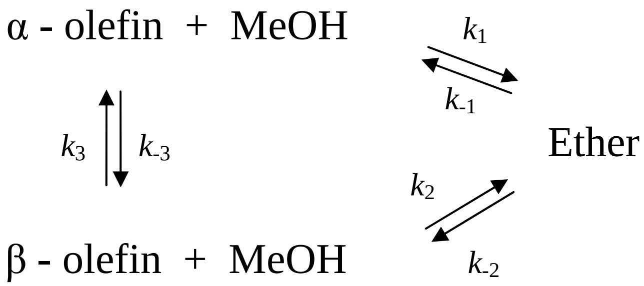
$$\text{reactivity}_{\text{mixture}} \geq 0.78*\text{reactivity}_{\alpha\text{-olefin}} + 0.15*\text{reactivity}_{\alpha\text{-olefin}}$$

$$\text{reactivity}_{\text{mixture}} \geq 0.93*\text{reactivity}_{\alpha\text{-olefin}}.$$

Therefore, equilibrium is limiting and the maximum ether production occurs at equilibrium. In other words, if the temporal distribution favors a maximum ether production before equilibrium is attained, it was not detected in the current work. This result is in good keeping with the results of other researchers [60]. The matter of kinetics versus equilibrium control of these reactions is discussed further below.

For the purposes of the current research, the similarity in reactivities of the C_8-olefins and the preponderance of the more reactive alpha-olefin at all times meant that only the study of the reactivity of 2,4,4-trimethyl-1-pentene would be necessary to optimize the relevant reaction parameters for maximum ether production. The data so generated were also sufficiently detailed to allow a preliminary kinetics analysis to be performed.

Modeling of simultaneous heterogeneous reactions where liquid phase reactants react on the surface of a solid phase catalyst can become quite complex. For simplicity, a pseudo-homogeneous model is assumed. The model applies equally well to the case of the C_6-olefins [76]. The simultaneous etherification and isomerization reactions can be represented by



where the apparent rate constants for each reaction are given by k_i (i = -3 to 3). In addition, thermodynamics provides another constraint for each reaction in the form of the equilibrium constants:

$$K_i = k_i / k_{-i}$$

where

$$K_1 = x_{\text{Ether}}/(x_{\alpha\text{-olefin}} * x_{\text{MeOH}})$$

$$K_2 = x_{\text{Ether}}/(x_{\beta\text{-olefin}} * x_{\text{MeOH}})$$

$$K_3 = x_{\beta\text{-olefin}} / x_{\alpha\text{-olefin}}$$

Only two of the equilibrium constants are independent, as

$$K_3 = K_1 / K_2.$$

Therefore, if two of the equilibrium constants are obtained experimentally, the third is known, and thus there are only three independent rate constants for the reactions in the above model. In practice however, it is best to determine all three equilibrium constants, and to use the mathematical relationship between the three as a check on the validity of the experimental technique.

Assuming first-order elementary reversible reactions, a material balance over the batch reactor provides the following differential equations:

Rate of accumulation = rate of formation - rate of consumption.

For the alpha-olefin,

$$d[\alpha\text{-olefin}]/dt = - k_1[\text{MeOH}][\alpha\text{-olefin}] + k_{-1}[\text{Ether}] - k_3[\alpha\text{-olefin}] + k_{-3}[\beta\text{-olefin}]$$

Invoking the thermodynamic constraints gives

$$d[\alpha\text{-olefin}]/dt = - k_1[\text{MeOH}][\alpha\text{-olefin}] + k_1[\text{Ether}]/K_1 - k_3[\alpha\text{-olefin}] + k_3[\beta\text{-olefin}]/K_3$$

Grouping like terms:

$$d[\alpha\text{-olefin}]/dt = -\,k_1([MeOH][\alpha\text{-olefin}] - [Ether]/K_1) - k_3([\alpha\text{-olefin}] - [\beta\text{-olefin}]/K_3)$$

Similarly for the beta-olefin,

$$d[\beta\text{-olefin}]/dt = -\,k_2([MeOH][\beta\text{-olefin}] - [Ether]/K_2) + k_3([\alpha\text{-olefin}] - [\beta\text{-olefin}]/K_3)$$

For the ether,

$$d[Ether]/dt = k_1([MeOH][\alpha\text{-olefin}] - [Ether]/K_1) + k_2([MeOH][\beta\text{-olefin}] - [Ether]/K_2)$$

Finally, for every mole of methanol consumed, one mole of ether is produced:

$$-d[MeOH]/dt = d[Ether]/dt$$

The model is thus reduced to a system of four equations and seven unknowns, namely k_1, k_2, k_3, [Ether], [α-olefin], [β-olefin] and [MeOH]. The integrated forms of these equations provide predicted concentration curves for the components in solution as a function of reaction time.

Perhaps the simplest way to perform this integration is with a numerical integration program such as Polymath©. The initial values for k_1, k_2 and k_3 have to be guessed. The k_i's are then adjusted to give the best possible fit of the generated curves for the concentration profiles of the components in solution to the experimental data curves. A detailed description of the process is provided by Fogler [162].

To generate the experimental concentration profile curves, careful determinations of the compositions of olefins, methanol and ether must be made at a number of different reactions run times. At least two, and preferably all three of the equilibrium constants must be obtained at at least three temperatures in the temperature range of interest. Starting with one (as in this case), or preferably both, of the pure olefin isomers, the temporal distribution of products and unreacted reactants as a function of time is determined at the same three temperatures. The reaction time intervals must be short enough so that a smooth plot of concentration versus reaction run time results. The spacing of the concentration sampling times will be much closer at the beginning of the reaction than they will as the reaction approaches equilibrium. The rate of reaction is dependent on the concentration, and since the concentration of olefin is highest initially, the rate of etherification slows down as the reaction proceeds. The proper sampling time can only be determined by trial and may have to be varied to accommodate temperature effects.

When sufficient data have been collected to generate a smooth curve on a plot of concentration versus time for the three temperatures of interest, the curves are ready for comparison with the predicted concentration curves from above. As mentioned above, the k_i's will have to be adjusted to give the best possible fit to the experimental data.

There will be nine k_i's determined by the Polymath© program, that is k_1, k_2 and k_3 for each of the three temperatures. The rate constants so determined are then used to determine activation energies for the etherifications and the isomerization by correlating with temperature according to the Arrhenius equation:

$$k = \mathrm{A}\exp(-\mathrm{E}_{\mathrm{act}}/\mathrm{RT})$$

where A = the pre-exponential factor and

$\mathrm{E}_{\mathrm{act}}$ = the activation energy.

In logarithmic form,

$$\ln k = \ln \mathrm{A} - (\mathrm{E}_{\mathrm{act}}/\mathrm{RT})\,.$$

In slope-intercept form,

$$\ln k = -(E_{act}/R)*1/T + \ln A\ .$$

The slope of the line in a plot of ln k versus 1/T provides the value of the activation energy in terms of $-E_{act}/R$.

Projected concentration curves generated by the Polymath© program are presented in Figures G-1 through G-3. The values for K_1 were determined experimentally, as shown in Appendix F. The values for K_3 were taken from the literature [79]. The values for K_2 were derived from the relationship

$$K_2 = K_1 / K_3.$$

The k_i's were adjusted to give the best fit of the projected curves to the experimental data before and up to the point where the maximum ether yield was obtained. As discussed below, after the maximum yield of ether was obtained, the reactions were no longer under kinetic control, and the curve-fitting model was not applicable. The maximum yield of ether was obtained at reaction times of eight hours, two hours, and fifteen minutes for the temperatures of 70 ^{o}C, 80 ^{o}C and 100 ^{o}C, respectively.

Good agreement was obtained between the calculated concentration profiles and the experimental concentration curves, particularly at temperatures of 70 ^{o}C and 80 ^{o}C. Unfortunately, at 100 ^{o}C, the reaction happened so quickly that only one sampling time occurred before the maximum concentration of ether was attained. Consequently, the rate constants determined at this temperature may not be the most reliable. No comparable rate constants for these reactions under these conditions were found in the literature.

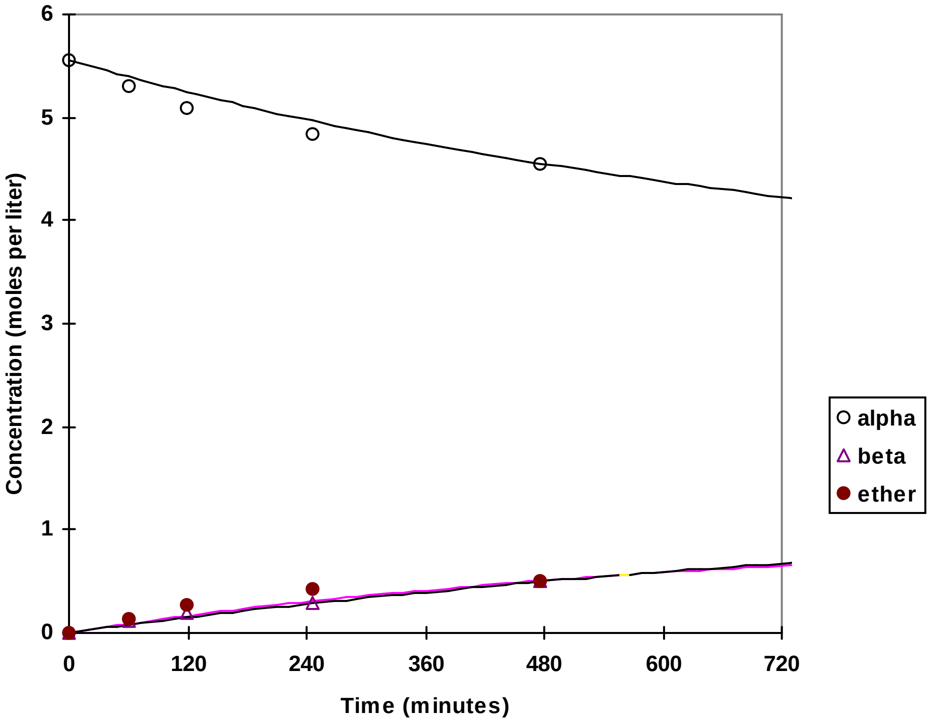


Figure G-1

Comparison of Experimental and Calculated Concentration Profiles at 70 °C

The values of the rate constants determined by the Polymath© program were used to determine the activation energies for both of the etherifications and the isomerization. Table G-1 presents the values of the k_i's at the three temperatures. Figure G-4 presents an Arrhenius plot for these reactions. Table G-2 presents the calculated activation energies for this experimentation, as well as comparable values from the literature.

The experimentally determined value for the activation energy for the etherification of 2,4,4-trimethyl-1-pentene with methanol is 95 (± 3) kJ/mol, which is close to the literature value of 86 to 94 kJ/mol. The experimentally determined value for

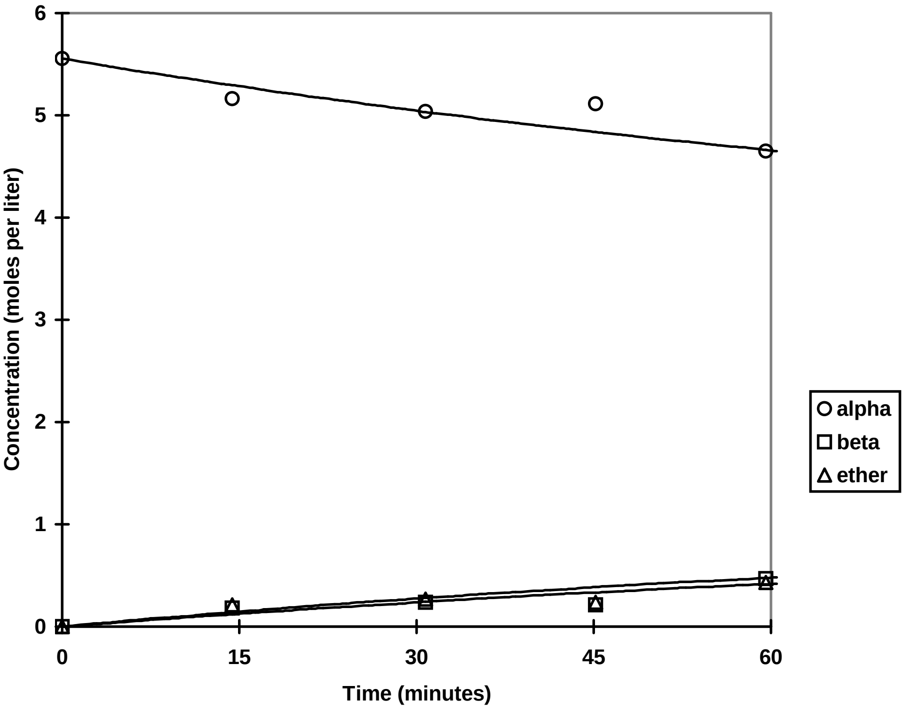


Figure G-2

Comparison of Experimental and Calculated Concentration Profiles at 80 ^{o}C

the activation energy for the etherification of 2,4,4-trimethyl-2-pentene with methanol is 87 (± 3) kJ/mol, which is in good agreement with the literature value of 80 to 90 kJ/mol.

The experimentally determined value for the activation energy for the isomerization of 2,4,4-trimethyl-1-pentene is 137 (± 3) kJ/mol, which is in the high range of the literature values, which vary from 99 to 137 kJ/mol. It should be pointed out that in the cited reference, the authors employed heterogeneous adsorption models that attempted to account for factors such as relative adsorptivities of the reacting components

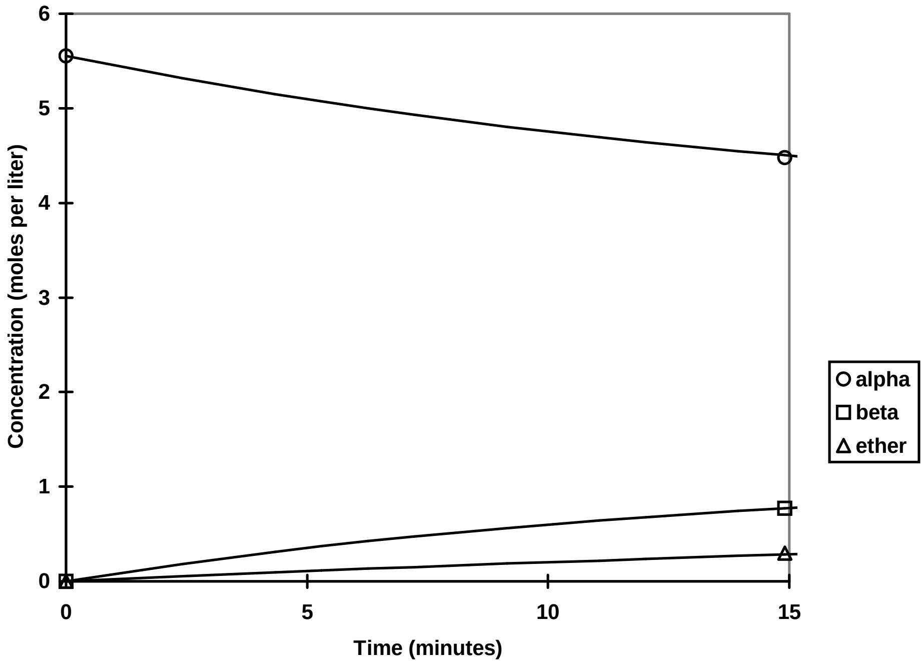


Figure G-3

Comparison of Experimental and Calculated Concentration Profiles at 100 ^{o}C

on the catalyst surface and the activities of the individual components in the bulk solution. The close agreement between their results and the activation energies determined here indicate that the simplified pseudo-homogeneous model is adequate to the present purpose.

More accurate values of the rate constants could be determined by increasing the sample frequency, that is, shortening the time between samples, in the 70 ^{o}C reaction. For reasons discussed below, this improvement would not be available to the 80 ^{o}C and 100 ^{o}C runs. The use of pure beta-olefin as starting material for these reactions could

Table G-1

Rate Constants in the Simultaneous Etherification and Isomerization of 2,4,4-Trimethyl-1-pentene

Temp	1/T (kelvins)$^{-1}$	k_1 (liters per mol*min)	k_2 (liters per mol*min)	k_3 (min^{-1})	ln k_1	ln k_2	ln k_3
70 ^{o}C	0.00292	0.000085	0.00003	0.00027	-9.37	-10.4	-8.22
80 ^{o}C	0.00283	0.00058	0.000072	0.0019	-7.45	-9.54	-6.27
100 ^{o}C	0.00268	0.0015	0.00038	0.0150	-6.50	-7.88	-4.20

lead to a more accurate determination of k_2 and k_{-3}. In addition, isolation, purification, and use of the product ether in decomposition reactions may lead to better values for k_{-1} and k_{-2}

The current modeling technique is equally applicable to the etherification and isomerization reactions of the 2,3-dimethylbutenes. However, the reactions of 2,3-dimethyl-1-butene have proven to be too fast to follow with the current experimental method. That is to say that in order to generate a smooth concentration versus time profile, the sampling interval would have to be reduced well below fifteen minutes. However, there is a process equipment limitation here. As noted in Appendix D, the introduction of the cold reactors into the sandbath produces a momentary cooling of the sand, which persists for a minute or two. This implies that the temperature of the reacting mixture is less than the setpoint temperature for at least two minutes, probably longer.

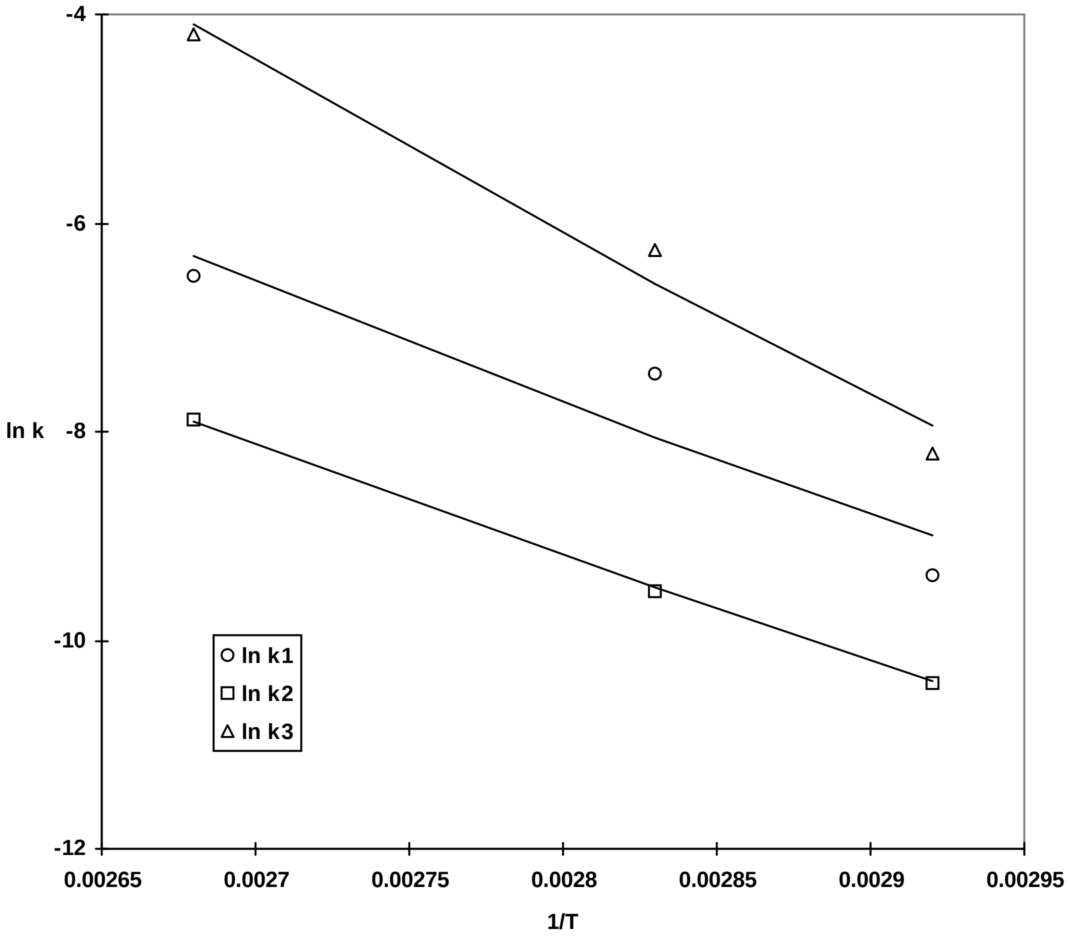


Figure G-4

Arrhenius Plot for the Etherification of 2,4,4-Trimethyl-1-pentene

If the sampling interval were to be shortened to, say ten minutes, then the warm-up period becomes a significant portion of the total reaction time. Therefore, fifteen minutes seems to be a practical lower bound on the sampling interval.

Table G-2

Activation Energies in the Simultaneous Etherification and Isomerization of 2,4,4-Trimethyl-1-pentene

Reaction	Experimental value	Literature value [60]
Etherification of TM1P	95 (± 3) kJ/mol	86 to 94 kJ/mol
Etherification of TM2P	87 (± 3) kJ/mol	80 to 90 kJ/mol
Isomerization of TM1P	137 (± 3) kJ/mol	99 to 137 kJ/mol

TM1P denotes 2,4,4-trimethyl-1-pentene.
TM2P denotes 2,4,4-trimethyl-2-pentene.

For the current experimental methodology to be used to investigate the kinetics of the etherification of the 2,4,4-trimethylpentenes at 100 ^{o}C or the etherification of the 2,3-dimethylbutenes in the temperature range from 70 ^{o}C to 100 ^{o}C, some way of slowing down the reactions would have to be found. Perhaps the simplest way would be to use less catalyst. An inert diluent might also be useful, as the rate of reaction is dependent on concentration. Caution is advised however, if an inert diluent is to be employed. This research has shown that the use of an inert diluent leads to results that cannot be explained on the basis of dilution effects alone. Moreover, previous investigators have shown that the diluent does more than just inhibit access of the reactants to the catalyst by occupying the reactive sites, but actually affects the nature of the polymeric resin matrix [82].

Perhaps the most advantageous approach would be to use the results of the current experimental work to develop a bench top CSTR for studying the etherifications. Continuous reactors lend themselves to determining kinetic parameters much more readily than do batch reactors. The development of such a continuous bench top reactor constitutes the next phase of future work.

It is also of interest to note that the activation energy for the etherification of 2,4,4-trimethyl-1-pentene is actually a little higher than that of 2,4,4-trimethyl-2-pentene, indicating that 2,4,4-trimethyl-2-pentene, the beta-olefin, is the more reactive isomer. That is to say that the thermodynamically preferred isomer is the less reactive isomer. This result is in keeping with that of previous researchers [60]. However, as indicated in Appendix E, under the conditions optimized in this testing (two hours at 70 ^{o}C), the alpha-olefin produced more ether and thus was thought to be the more reactive. It is clear that equilibrium is limiting even at a reaction time of two hours, whereas maximum ether production was not approached until eight hours. The implication to the design of a continuous reactor for the etherification of C_8-olefins is that, in contrast to the C_6-olefins, the reactivities of the alpha- and beta-olefins are so similar that it would probably not be necessary to employ an isomerizer. The matter of kinetic versus equilibrium control of these reactions is discussed further in Chapter VI.

APPENDIX H

NOMENCLATURE

a	thermodynamic activity function
A	pre-exponential factor
C_{air}	spatially averaged concentration of ether in the air in the box
$C_{air,\ in}$	spatially averaged concentration of ether in the air flowing into the box
$C_{air,\ steady\text{-}state}$	steady-state concentration of ether in the air in the box
E_{act}	Activation energy of a reaction
G	thermodynamic Gibb's free energy function
H	thermodynamic enthalpy function
k_i	rate constant for the reaction of species *i*
k_i	rate constant for the reaction of hydroxyl radical
K_a	thermodynamic equilibrium constant based on activity of components in solution
K_{eq}	thermodynamic equilibrium constant based on mole fraction of components in solution
n	numbers of moles of ether in the box
$[^{\cdot}OH]$	concentration of hydroxyl radical in the box
psig	pounds per square inch gauge pressure
R	thermodynamic gas law constant
S	thermodynamic entropy function
T	temperature
V_{air}	volume of air in the box
$V_{air,\ in}$	volume air flowing into the box
x	mole fraction of a species in solution

Greek symbols

γ_i	thermodynamic activity coefficient of species *i* in solution
ε	extent of reaction

ACRONYMS

CAAA	Clean Air Act Amendments
CDC	Centers for Disease Control
DB	dimethylbutene runs
DOE	Department of Energy
DME	dimethyl ether
DM1B	2,3-dimethyl-1-butene
DM2B	2,3-dimethyl-2-butene
ECOSAR	Ecological Structure-Activity Relationships
EC_{50}	median effective concentration. Statistically derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions.
EPA	Environmental Protection Agency
EPI	Estimation Programs Interface
EtBE	ethyl tertiary butyl ether
EtHxE	ethyl tertiary hexyl ether
EtOcE	ethyl tertiary octyl ether
EUSES	European Union System for the Evaluation of Substances
FCC	Fluid Catalytic Cracking
FID	Flame Ionization Detector
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
HZSM	the protonated form of a proprietary zeolite catalyst (Zeolite Socony Mobil)
ISO	isomerization runs
LC_{50}	lethal concentration, the concentration of a chemical in water that kills 50% of the test animals in a given time
LUFT	Leaking Underground Fuel Tank

MO	mixed olefin runs
MOS	Margin of Safety
Mpa	megapascals
MtBE	methyl tertiary butyl ether
MtHxE	methyl tertiary hexyl ether
MtOcE	methyl tertiary octyl ether
NAAQS	National Ambient Air Quality Standards
NOAEC	No observed adverse effect concentration
NOAEL	No observed adverse effect level
OD	outside diameter
OECD	Organisation for Economic Co-operation and Development
PEC	Predicted environmental concentration
PM	particulate matter
PMSA	Primary Metropolitan Statistical Area
PNEC	Predicted no effect concentration
RCR	Risk Characterization Ratio
RFG	reformulated gasoline
SS	stainless steel
TAME	tertiary amyl methyl ether
tHxA	tertiary hexyl alcohol
tOcA	tertiary octyl alcohol
TM1P	2,4,4-trimethyl-1-pentene
TM2P	2,4,4-trimethyl-2-pentene
TP	trimethylpentene runs
VOC	volatile organic compound