DOE/PC/90044

HIGH OCTANE ETHERS FROM SYNTHESIS GAS-DERIVED ALCOHOLS

Kamil Klier and Richard G. Herman
with
Roy D. Bastian, Stefaan DeTavernier, Marie Johansson,
Mark Kieke, and Owen C. Feeley

Zettlemoyer Center for Surface Studies
and Department of Chemistry
LEHIGH UNIVERSITY
Bethlehem, PA 18015

For presentation at the
Liquefaction Contractors' Review Meeting
Pittsburgh Energy Technology Center
Pittsburgh, PA

September 3-5, 1991

PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

Contract No. DE-AC22-90PC90044
September 25, 1990-September 24, 1993

OBJECTIVE OF THE RESEARCH

The principal objective of this research project is to synthesize high octane ethers, primarily methyl tertiary butyl ether (MTBE) but also higher tertiary ethers, directly from $H_2/CO/CO_2$ coal-derived synthesis gas via alcohol mixtures that are rich in methanol and 2-methyl-1-propanol (isobutanol). The overall scheme involves gasification of coal, purification and shifting of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers.

The last stage of the synthesis involves direct coupling of synthesis gas-derived methanol and isobutanol that has been demonstrated by us [1] to occur over superacid catalysts to yield methyl isobutyl ether (MIBE) at moderate pressures and a mixture of methanol and isobutene at low pressures. MIBE is an isomer of MTBE and a process is proposed whereby MTBE from the two alcohols is maximized and MIBE is minimized. This will be achieved by the proper choice of reaction conditions, i.e. intermediate pressures, and acid catalysts (organic or inorganic) that are stable at temperatures under which it might be possible to promote the carbonium ion reaction coupling of the two alcohols to MTBE more effectively than the oxonium ion or ester reaction coupling to MIBE.

Both organic and inorganic catalysts will be investigated, and the better catalysts of these classes will be subjected to long term performance studies. The long term performance studies of the combined process will extend to 1000 hr and detailed analytical data for all products will be provided. The project is divided into the following three tasks:

Task 1. Synthesis of High Octane Ethers from Alcohol Mixtures Containing Predominantly Methanol and 2-Methyl-1-Propanol over Superacid Resins,

Task 2. Inorganic Catalysts for the Synthesis of High Octane Ethers from Alcohols, and

Task 3. Long Term Performance and Reaction Engineering for Scale-Up of the Alcohols-to-Ethers Process.

The expected result of the proposed research is a novel process for producing ethers, in particular MTBE, in which all five carbons of the unsymmetric C_1-O-C_4 ethers originate from coal-derived synthesis gas.

SUMMARY OF TECHNICAL PROGRESS

Industrial acid and superacid resin catalysts were obtained and testing of these materials under standard sets of reaction conditions to compare the activities and selectivities for forming the unsymmetric ethers by coupling methanol with isobutanol is being carried out. These catalysts include duPont Nafion H resin and Nafion H microsaddles, Amberlyst-15, Purolite, and Dow Chemical Co. supported (SiC and Al_2O_3) and unsupported fluorocarbon sulfonic acid (FSA) resins. It is found that both Nafion-H microsaddles and Amberlyst-15 resins are active for this synthesis reaction, but the Dow FSA catalyst was less active under the reaction conditions of 123°C and 200 psig

(13.6 atm) with a methanol/isobutanol = 2 reactant mixture. While the Nafion-H catalyst does form the MIBE product fairly selectively under the reaction conditions utilized, the Amberlyst-15 catalyst formed MIBE, MTBE, and dimethylether (DME) under the same reaction conditions. In addition, significantly larger quantities of the C_4 hydrocarbon products were observed over the Amberlyst-15 catalyst at 123°C and 13.6 atm than over the Nafion-H catalyst.

A new Hewlett-Packard (HP) gas chromatographic (GC) analytical system with automated injection valves has been interfaced with a PC-based data station, and new Chrom Perfect software has been installed. The Chrom Perfect software is a complete package that greatly facilitates GC data management and manipulation. It also outputs corrected and scaled chromatograms and product yield tables.

The temperature dependence of ether synthesis was carried out over the Nafion-H microsaddles (MS) catalyst. The principal product formed under the rather severe reaction conditions of 1100 psig pressure and temperatures in the range of 123-157°C was the expected MIBE formed directly by coupling the methanol/isobutanol reactants. In addition, significantly larger quantities of the dimethylether (DME) and hydrocarbon products were observed than were obtained under milder reaction conditions. Deactivation of the catalyst was monitored. After carrying out various tests over a period of 2420 hr, with intermittent periods of standing under nitrogen at ambient conditions, the yields of MIBE and MTBE at 123°C had decreased by 25% and 41%, respectively. This testing demonstrated that the Nafion-H MS catalyst will exhibit very good stability up to temperatures close to 160°C.

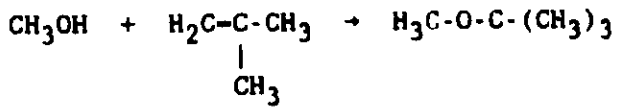
Experimental testing and thermodynamic calculations have been carried out to probe the effect of temperature on the yields of the ethers and hydrocarbons that can be produced from methanol and isobutanol. It is shown that MTBE is a thermodynamically favored product, but kinetic limitations are playing a role in controlling the experimentally obtained products.

In order to gain insight into the role of the surface acidity in promoting the selective coupling of the alcohols to form the unsymmetric ether, the strengths of the acid sites on the catalysts were probed by calorimetric titrations with bases in non-aqueous solutions. It was observed that the acid strength of the sulfonic groups in the Nafion-MS catalyst had a much more homogeneous distribution when titrated with pyridine in the solvents than did the Amberlyst-15 resin.

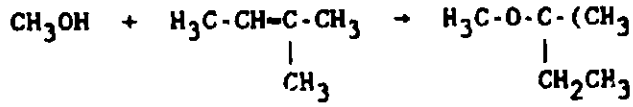
INTRODUCTION

A. Background of C_5-C_6 Ether Synthesis

The synthesis of high octane ethers is one alternative for the replacement of environmentally hazardous fuel additives that maintain the high octane rating of gasoline. At the present time, the commercially produced methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME) are synthesized according to Equations 1 and 2, respectively.



(1)



(2)

These two ethers constitute the fastest growing use of methanol produced from synthesis gas, along with petroleum-derived i-C_4 (isobutene = 2-methylpropene) and i-C_5 (2-methyl-1-butene or 2-methyl-2-butene) hydrocarbons in both the U.S. and Europe [2-6]. They are both high octane additives that compare favorably with trimethylpentane (TMP) and isooctene (IO), as shown in Table 1 [6]. In addition, they both are co-solvents for small amounts of methanol in gasoline [6]. In these syntheses, ethanol can be used in place of methanol to yield the ethyl form of the ethers.

TABLE 1. Comparisons of Octane Numbers RON/MON of Products Formed from Isobutene.

Product	RON/MON
MTBE	118/101
TAME	112/99
TMP	95/92
IO	98/80

The synthesis reactions are typically carried out at ≈70-110°C in the liquid phase over cation exchange resins in their superacidic form at pressures of 7 to 14 atm [6,7]. The currently used resin catalysts tend to decompose above ≈90°C, and thus the temperature is usually maintained in the 70-90°C range, which requires good temperature control since the MTBE synthesis (from methanol and isobutene) reaction is exothermic. The rate of the synthesis is enhanced by pressure, and the pressure also aids in the removal of unreacted methanol in the debutenizer tower, where a methanol/butene azeotrope that contains 6% methanol at 7 atm but 12% at 17 atm is removed [8]. The main impurities in MTBE are t-butanol (TBA) and diisobutene (DIB). In the Gulf Canada TAME process [6,9], methanol is used in a two-fold excess and the unreacted methanol is removed by absorption in glycol rather than by distillation.

The first MTBE plants were built in Europe (in Italy in 1973 and in West Germany in 1976), while the first plant in the U.S. began production in 1979 [6,10-12]. By the end of 1983, there were 14 MTBE plants in operation in the U.S., and all but two of those used relatively concentrated steam cracker feedstock as a source of the C_4 reactant [6]. However, it is possible to synthesize the entire feedstock from coal-derived synthesis gas, and its utilization is the primary objective of the proposed research.

B. Statement of the Problem

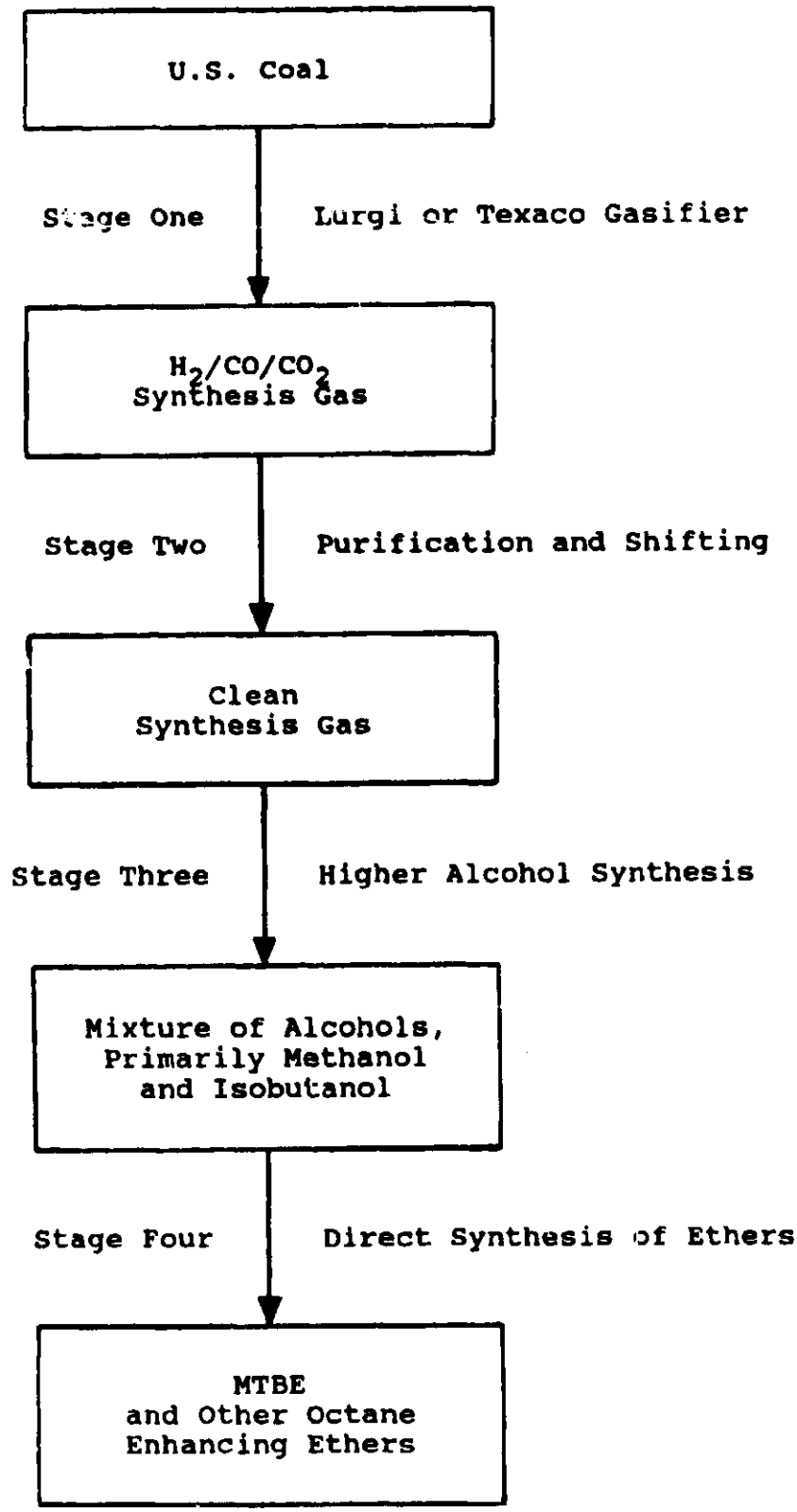
Beginning in the 1970s, environmental concerns led to a phasing out of lead in gasoline. To maintain the octane level of gasoline, approaches such as adding oxygenates, e.g. ethers and alcohols, and light hydrocarbons, e.g. butane, to the gasoline were taken. However, there are now health and environmental concerns and legislative pressures to reduce the volatility of gasoline, and this has forced the reduction of the light hydrocarbons in gasoline, especially in the summer season and in the southern part of the U.S. There is also legislation to reduce the level of carcinogenic aromatics such as benzene to very low levels. Even substituted aromatics such as toluene, which constitute 27-28% of current gasolines, are severe carcinogens. These high octane components must be replaced, and MTBE and mixtures of alcohols have been utilized to fulfill this need.

However, the supply of MTBE is limited by the availability of isobutene, which is produced as a by-product of several processes, especially from petroleum refinery catalytic crackers. There are about 181 refineries in the U.S. and the number of fluid catalytic cracking (FCC) units has remained constant at 52 since 1981 [13]. These FCC units have a capacity of ≈800,000 m^3/day, and the average product selectivities include 50 wt% gasoline and 8 wt% C_4s [13]. Thus, the availability of isobutene for the manufacture of MTBE has been limited using this principal source and other smaller (but more costly [8]) sources such as dehydration of t-butanol and dehydrogenation of isobutane have been developed [12,14].

It would be very advantageous to develop another route to the synthesis of MTBE and other ethers that would not be supply limited and that did not depend upon imported petroleum. Our research program will investigate and develop a process for producing high octane ethers from alcohols via a catalytic route beginning with coal, as indicated in Scheme 1 on the next page. Stage One and Stage Two have been demonstrated on a commerical scale and Stage Three has recently been developed under DOE-sponsored research [15-22] for alkali-promoted catalysts that produce a mixture of alcohols consisting predominantly of the C_1 and branched C_4 components. Specifically, the alcohols are formed from low ratio H_2/CO synthesis gas, typical of that produced by coal gasifiers, at moderate temperatures (≤325°C) and pressures (≤100 atm).

Considering Stage Four, we have recently demonstrated that the C_1 and branched C_4 alcohols formed (methanol + 2-methyl-1-propanol) can be directly coupled to form a high octane ether or produce an isobutene and alcohol mixture suitable for manufacturing MTBE [1]. Specifically, a mixture of methanol and 2-methyl-1-propanol has been shown [1] to form the methylisobutylether (MIBE, also designated as 1-methoxy-2-methylpropane)

SCHEME 1


U.S. Coal
Stage One
Lurgi or Texaco Gasifier
$H_2/CO/CO_2$
Synthesis Gas
Stage Two
Purification and Shifting
Clean
Synthesis Gas
Stage Three
Higher Alcohol Synthesis
Mixture of Alcohols,
Primarily Methanol
and Isobutanol
Stage Four
Direct Synthesis of Ethers
MTBE
and Other Octane
Enhancing Ethers

over highly stable superacid Nafion H resins, as indicated by Equation 3 and in Figure 1. In this example of the effect of the partial pressure of the

$$CH_3OH + H_3C\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2OH \rightarrow H_3C\text{-}O\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3 \qquad (3)$$

mixed alcohols in N_2 (total N_2 + alcohol feed = 250 mol/kg cat/hr) on the yields of products, the total reactor pressure was 13.2 atm and the experiment was carried out with 2.0 g (particle size = 0.4-1.4 mm) of the non-porous Nafion H resin. At the higher partial pressures, MIBE was the principal product, while an appreciable quantity of dimethylether (DME) was also formed. The minor products observed were butenes and diisobutylether (DIBE).

An example of the product yields observed at 116°C and a total pressure of 7.5 atm with the porous Nafion H microsaddles (1 g) is shown in Figure 2. Once again, the unsymmetric ether MIBE was the preferred ether synthesized, while about one-third of the product mixture was observed to be dimethylether. Increasing the pressure led to a substantial suppression of the alkene formation. In both Figures 1 and 2, if the ether forming reaction were to proceed with equal reactivities of 2-methyl-1-propanol and methanol, the statistics would dictate the product composition to be MIBE/DME/DIBE = 4/4/1 for the methanol/2-methyl-1-propanol ratio employed. Remarkably, the product composition was found to be MIBE/DME/DIBE = 19/9/1 at alcohol pressures greater than 1.5 atm, significantly in favor of the mixed MIBE ether. Also notably, at low pressures it is the butenes (mainly isobutene) that dominate, and thus the selectivity can be switched from ethers to their hydrocarbon precursors by operating pressure only.

A third example shown in Figure 3 describes the effect of temperature in the range of 116-157°C on the activity of the Nafion microsaddles resin (1 g) when tested at 75 atm with the alcohol partial pressure of 6 atm. In this temperature range, the current commercially used organic resins are not stable but the superacid Nafion H type resins are. We see that at ≈135°C the Nafion resin selectively produced the methylisobutylether/dimethylether pair relative to the alkenes and DIBE. At higher temperatures, the C_4 and C_8 alkenes are produced at increasing rates.

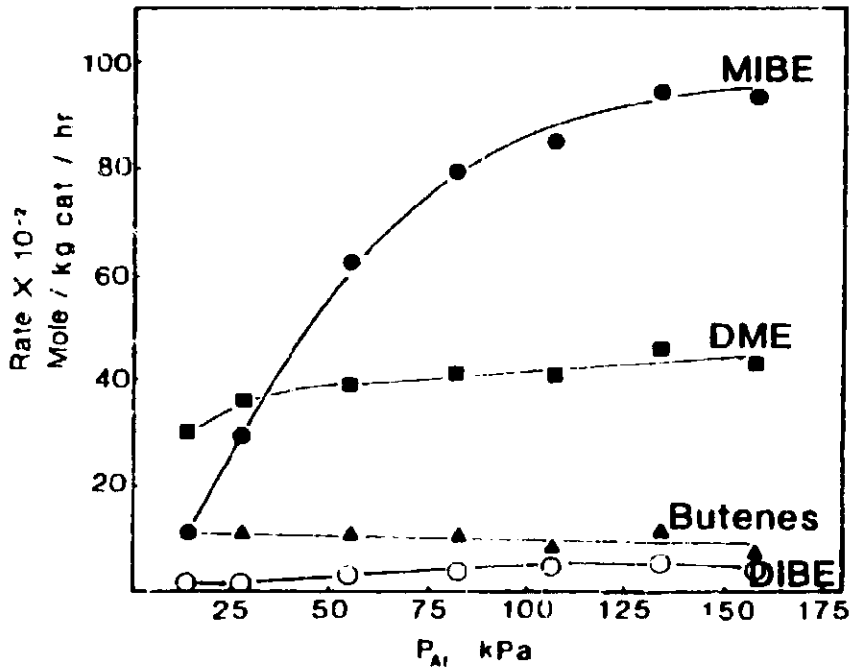


FIGURE 1. Effect of the partial pressure (P_{Al} given in kPa, where 101.3 kPa = 1.0 atm) of the alcohol mixture (methanol/2-methyl-1-propanol = 2/1 mol ratio) on the relative rates of formation of methylisobutylether (MIBE), dimethylether (DME), diisobucylether (DIBE), and butenes over the Nafion H resin at 123°C. A N_2 carrier gas was used and the total reactor pressure was 13.2 atm (1.34 mPa).

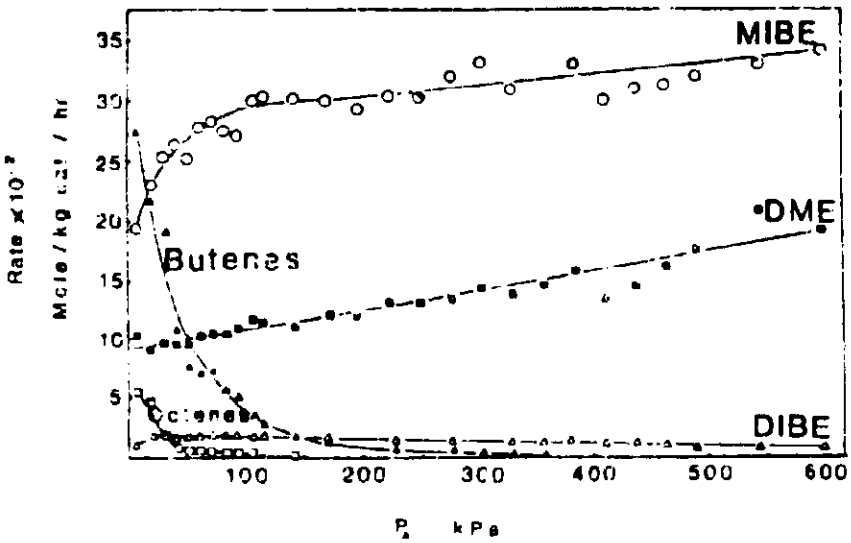


FIGURE 2. Variation of the product yield with the alcohol reactant partial pressure (methanol/2-methyl-1-propanol = 2/1) over the micro-saddles form of the Nafion H resin at 116°C and a total reactor pressure of 7.5 atm. An alcohol feed rate of 15.6 mol/kg cat/hr was used

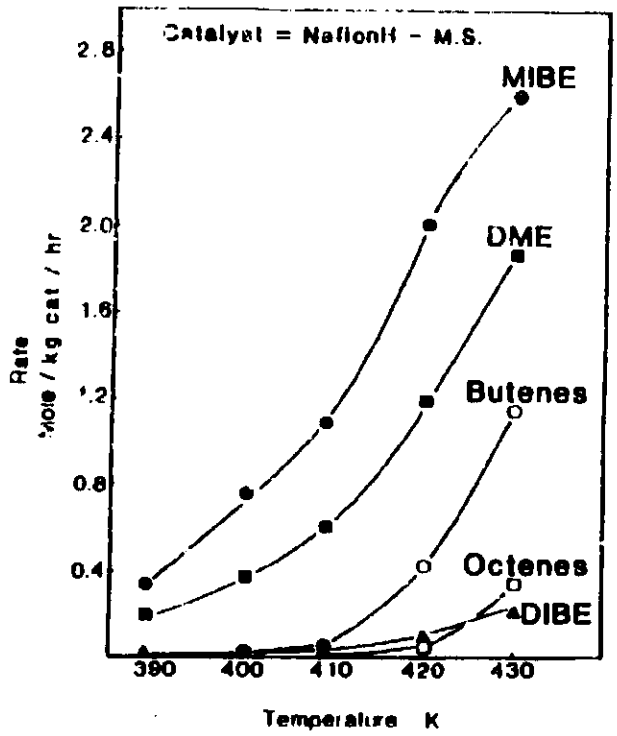


FIGURE 3. Effect of temperature on the formation rate of the ethers and olefins formed over the microsaddle-form of the Nafion H resin at 75 atm, where the alcohol partial pressure was 6 atm. The alcohol feed (methanol/2-methyl-1-propanol = 2/1) rate was 15.6 mol/kg cat/hr.

These experiments demonstrated that reaction (3) occurred fairly selectively at high pressures, while at low pressures isobutene was formed from isobutanol over the same catalyst, Equation 4. As pointed out above, it is well-established [6-8,10] that isobutene can be further coupled with methanol to produce methyltertiarybutylether (MTBE), Equation 5. At the

$$(CH_3)_2\text{-}CH\text{-}CH_2OH \rightarrow (CH_3)_2\text{-}C{=}CH_2 + H_2O \qquad (4)$$

$$CH_3OH + H_2C{=}C\text{-}(CH_3)_2 \rightarrow H_3C\text{-}O\text{-}C\text{-}(CH_3)_3 \qquad (5)$$

higher pressures, dimethylether was also formed as a side product, but the Nafion resin selectively produced the methylisobutyl-ether/dimethylether pair relative to the alkenes and diisobutylether (DIBE), as shown in Figure 1. However, at higher temperatures the C_4 and C_8 alkenes are produced at increasing rates.

It should be pointed out that dimethylether is not necessarily an undesirable product because it can be easily separated from the higher molecular weight ethers and is a very useful chemical intermediate for the conversion to other useful products. It can also be used as the reactant in the Mobil methanol-to-gasoline (MTG) synthesis process utilizing ZSM-5 zeolite.

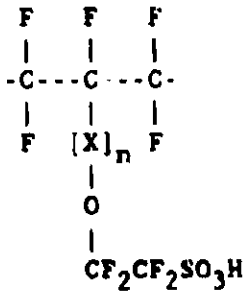
TECHNICAL PROGRESS

A. Selection of the Catalysts

Task 1 of this research is centered on acid organic resins, principally those containing $-SO_3H$ acid functional groups. The two general groups of these resins are

(i) polystyrene ion exchange resins, and
(ii) fluorocarbon sulfonic acid (FSA) polymers.

The first class of FSA polymers were developed by duPont and similar materials were subsequently developed by Dow Chemical Co. Both are copolymers of tetrafluoroethylene and fluorinated vinyl ethers that contain fluorosulfonyl groups as shown below.



Dow Chem. Co.; n = 0
duPont; n = 1,2,3 with X = $-O-CF_2-CF(CF_3)-$

B. Experimental Testing of the Catalysts

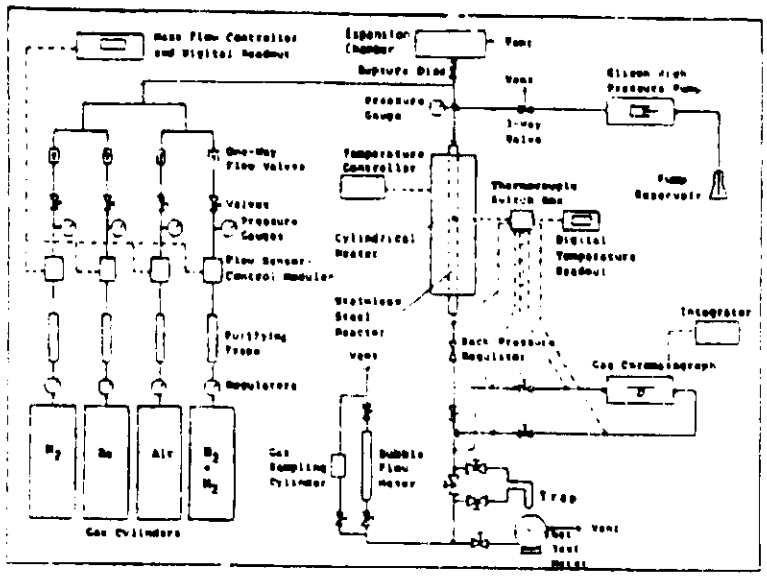
During the course of this research project, the catalysts will be tested for ether synthesis from binary methanol/2-methyl-1-propanol and methanol/ethanol/propanol/2-methyl-1-propanol mixtures in the vapor phase in a continuous flow stainless steel bench-scale reactor system that is automated so that testing can be carried out under continuous operation at designed experimental conditions. A schematic of the reaction system is shown in Figure 4, where typically only the N_2 gas is utilized at the inlet gas and the alcohol mixture is added at the top of the reactor *via* the Gilson high pressure pump. The furnace consists of three independent heating elements and maintains a very constant steady state temperature.

A typical catalytic test is the use of methanol/2-methyl-1-propanol = 2/1 in the temperature range of 90-123°C and a pressure of 6-25 atm (0.6-2.5 MPa) using N_2 carrier gas. The conversion and product composition can be monitored by continual sampling, e.g. semi-hourly, of the exit stream by gas chromatographic analysis using in-line, heated, automated sampling valves and by collection of the liquid product for subsequent analyses by GC, NMR, and GC/MS

The dedicated Hewlett-Packard Model 5890 Series II gas chromatograph (HP GC) has automated heated Valco sampling valves, both thermal conductivity (TCD) and flame ionization (FID) detectors, and both packed column and capillary column capabilities, and is interfaced and controlled by a PC data station (complete Gateway 2000 personal computer system) using

FIGURE 4

THE HIGH PRESSURE ETHER SYNTHESIS REACTOR SYSTEM



a complete package of menu-driven chromatographic software (Chrom Perfect) from Justice Innovations, Inc. At the same time, the GC is interfaced with a Hewlett-Packard Model 3396 Series II recorder/integrator, which can also produce a hardcopy of each chromatogram and listing of the associated integrated peak areas. The initial testing of the catalysts was carried out while the new GC and PC/software portions of the reaction system were being installed.

The more recent catalyst testing was carried out with the new analytical GC/data station, and a 25 m x 0.32 mm ID wall coated open tube (WCOT) capillary column with a chemically bound 5.0 μ thick methyl silicon coating was purchased from Chrompack Inc. The inlet system incorporated the standardsplit/splitless capillary injector with an automated gas sampling valve installed between the regulated gas supply and the injector common supply. This arrangement delivers the gas sample into the GC injector exactly as if it were injected manually by syringe. However, this configuration does make the split and splitless injection modes identical for automated sampling. Since these injections deliver a homogeneous gas phase sample, the splitless mode of operation is unnecessary.

A synthetic mixture composed of water, DME, methanol, tertiary butanol, MTBE, MIBE, and isobutanol was injected, and a chromatogram was collected for use as a qualitative standard for retention time assignments. Figure 5 shows the GC trace and the peak assignments that resulted.

Testing of Nafion-H Microsaddles

Methanol and isobutanol were utilized as reactants by injecting them as liquids by means of a Gilson high performance liquid chromatography pump into a nitrogen gas stream at a designated pressure, 13.6 atm (200 psig) in the initial experiments to be described. The inlet and outlet lines were heated to prevent condensation of the reactant alcohols and the products.

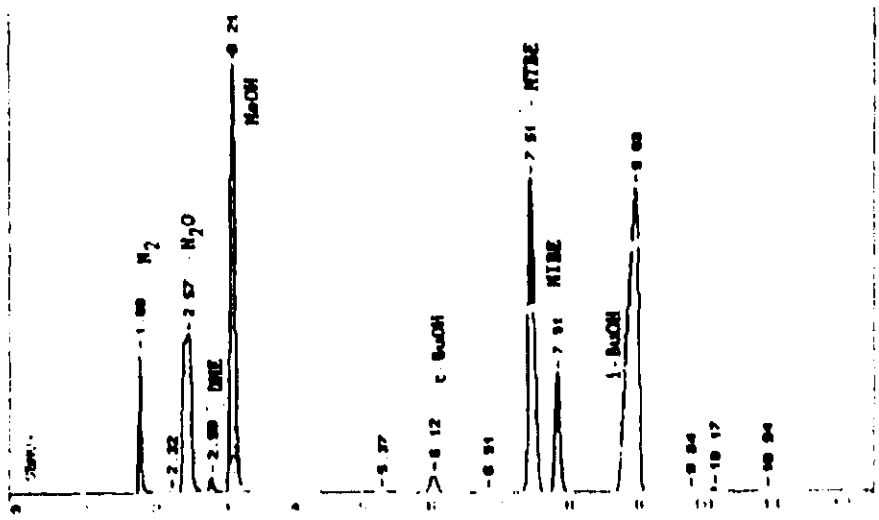


FIGURE 5. Chromatogram of a synthetic mixture of reactants and products.

Prior to this test, the Nafion-H microsaddles (1100 EW obtained from C. G. Processing, Inc. of Rockland, DE) was pretreated with acid to insure that all exchangeable sites were in the acid form and that any organic impurities were removed. The pretreatment consisted of three consecutive washings with 3 N HNO_3 at 80°C for 3 hr each. After the final equilibration, the resin was filtered, washed with distilled water, and dried.

After weighing 2.00 g of the dried Nafion-H MS sample, it was mixed with about 8 ml Pyrex beads and centered in the reactor using additional Pyrex beads. After increasing the pressure of the N_2 flow through the reactor to 13.6 atm (200 psig), the reactor was heated to the reaction temperature of 123°C. A mixture of methanol and isobutanol was then injected in the N_2 stream at a constant rate to yield the following inlet conditions:

Component	Molar Flow (mol/hr)	Partial Pressure (kPa)
Nitrogen	0.444	≈1,190
Methanol	0.0373	≈100
Isobutanol	0.0187	≈50

The flow rate of the N_2 carrier gas corresponded to 10.7 ℓ/hr.

The yields of products formed over the Nafion-H MS are shown in Figure 6. As expected from our earlier work [1], more MIBE was formed than was DME and DIBE, although the reactant mixture was rich in methanol (methanol/isobutanol = 2). Consideration of the selectivity demonstrates that 60 mol% of the product consisted of the unsymmetric MIBE product.

Testing of Amberlyst-15

The Amberlyst-15 resin was tested for ether synthesis from alcohols, and in this case 1 g of catalyst was used and the feed rate of the reactants

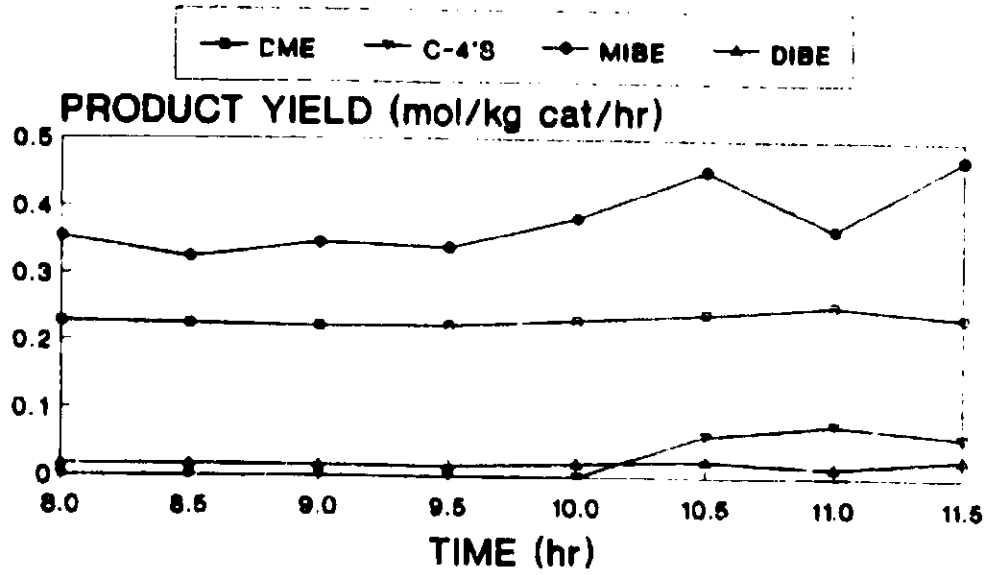


FIGURE 6. Product Yields Over the Pretreated Nafion-H MS Catalyst.

was adjusted accordingly (molar flow rate = 0.25 mol/hr; pressure = 200 psig with 22.4 psig of the alcohol mixture). The yield of products is shown in Figure 7, where it is evident that DME was the major product. It is shown that as the temperature was increased from 113°C to 123°C, the yields of all products increased It is evident from Figure 7 that the biggest influence of temperature on the product yields was to increase the selectivity toward the C_4 hydrocarbon products, butane and butenes. These hydrocarbons constitute ≈25 mol% of the products formed at 123°C, along with ≈45 mol% of DME and ≈30 mol% MIBE + MTBE. During this testing, a packed analytical column (Poropak Q) was used for the GC analysis, and MIBE and MTBE were not separated under the analytical conditions used. However, subsequent GC/MS analysis of the product demonstrated that both MIBE and MTBE were present in the product in comparable quantities.

These experiments show that the Amberlyst-15 resin is a more active catalyst than is the Nafion-H MS. However, the selectivity is shifted toward the symmetric DME and unsymmetric MTBE rather than the higher molecular weight unsymmetric MIBE product that is desired.

Dow Chemical Co. Fluorocarbon Resin/SiC Catalyst

The Dow catalyst consisting of the fluorocarbon sulfonic acid (FSA) polymer on SiC was tested under steady state conditions that were utilized with the previously described catalysts. The preparation of this catalyst for testing involved crushing of the 1 mm x 3 mm hollow cylindrical pellets as received and sieving to 9-20 Mesh.

Because each individual pellet was not homogeneous and resembled a lightly frosted cake, there was some concern about generating a representative batch of crushed catalyst for testing. Specifically, the underlying SiC support seemed to shatter into a fine powder leaving behind large, resilient flakes of the FSA polymer sticking to some remaining SiC

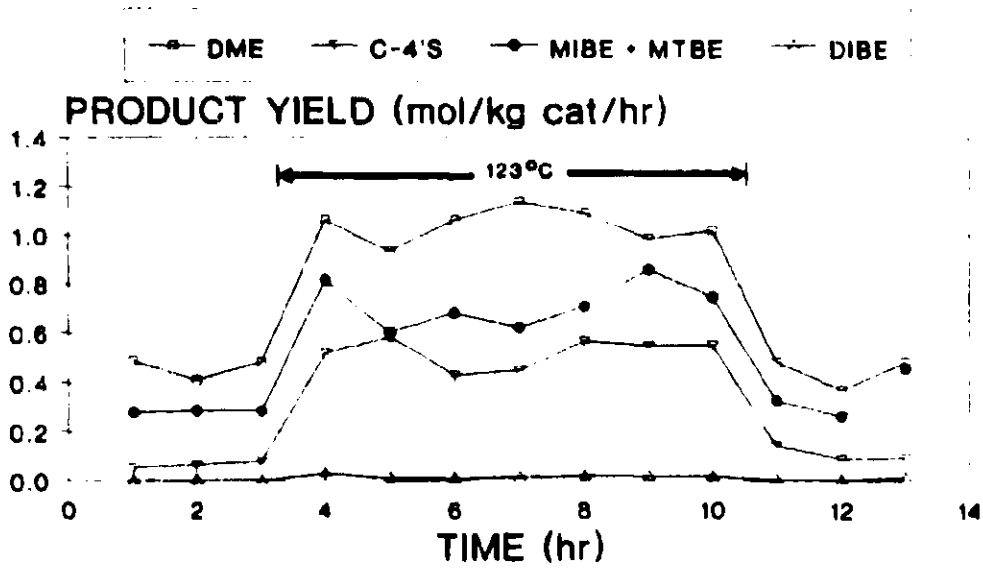


FIGURE 7. Product Yields Over the Amberlyst-15 Catalyst.

support. It is possible that the differing fracture characteristics between the polymer catalyst and its SiC support resulted in some segregation into two different Mesh ranges. A 1.0020 g portion of crushed catalyst was weighed and loaded into the reactor with 10 ml of 3 mm Pyrex beads as diluent. The reactor was then flushed with N_2 for several hr and then heated to 175°C as per manufacturer instructions to achieve dehydration.

The DOW FSA/SiC catalyst was tested under conditions similar to those used previously for other organic acid catalysts. Those conditions are the following: temperature = 123, 150, 175, and 123°C, pressure = 200 psig, GHSV = 250 mol/kg cat/hr, molar flow of N_2 = 0.22254 mol/hr, and molar flow of methanol = 0.01864 mol/hr. Each temperature was studied long enough to provide sufficient steady state data. Therefore, the catalyst was maintained at each temperature for at least 24 hr, but often as long as 72 hr for the higher temperatures where the catalyst was more active. Average product yields were calculated only from those injections for which the GHSV was well-equilibrated. Averaged product yields are plotted in Figure 8.

From Figure 8, it can be seen that increasing the reaction temperature increased catalyst productivity. Upon increasing the temperature from 123°C to 150°C, DME, MIBE, and the C_4 all increased in yield at a comparable rate. However, the largest increases in product yield upon increasing the temperature further to 175°C, expressed as mol product/kg cat/hr, were observed for DME and the C_4 products. This figure also shows that the temperature effect is reversible i indicates that the catalyst did not degrade at high temperature.

C. Preparation of a MIBE Standard

Since MIBE could not be found as a commercial analytical standard with which to calibrate the GC retention time of this compound and the GC/MS fracture pattern, as compared with MTBE, it was necessary to synthesize MIBE

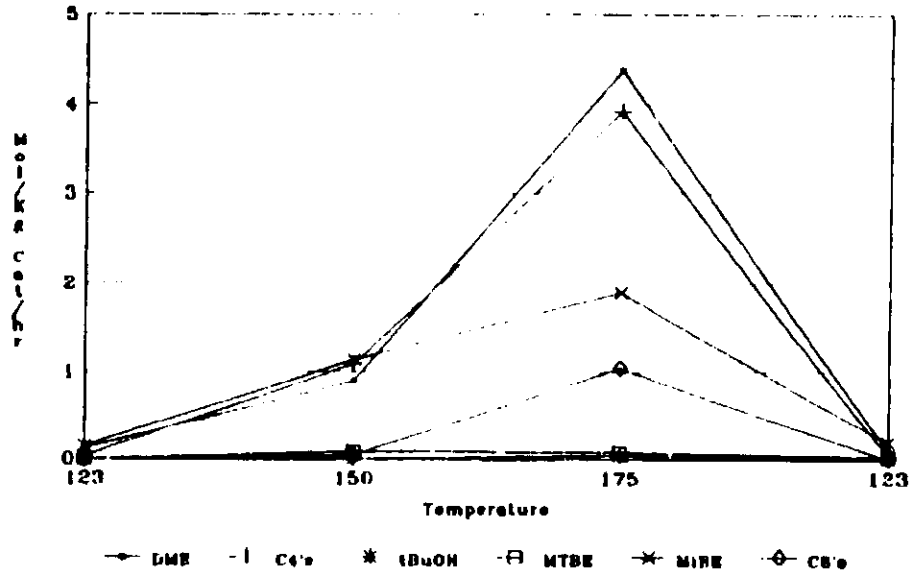


FIGURE 8. Product Yields Over the Dow Chem. FSA/SiC Catalyst.

as a pure reagent. A number of synthesis methods were utilized, and it was found that the following procedure gave the best purity of the MIBE product.

In this sodium alkoxide preparation method, MIBE was produced by the classic Williamson synthesis that combines an alkyl halide with an alkoxide salt to form an ether and a halide salt. Using this approach, methyl iodide and sodium 2-methyl-1-propoxide were combined to form MIBE. However, since no commercial source of sodium 2-methyl-1-propoxide was located, it was necessary to prepare the compound *in situ* by reacting 2-methy-1-butanol with metallic sodium, as shown in Equation 6. Once sodium 2-methyl-1-propoxide was formed, the methyl iodide was introduced to form MIBE and sodium iodide, Equation 7. The quanitities and physical properties of the reactants are given in Table 2, where B.P. = boiling point.

$$Na + HOCH_2CH(CH_3)_2 \rightarrow NaOCH_2CH(CH_3)_2 + 1/2\ H_2\uparrow \quad (6)$$

$$CH_3I + NaOCH_2CH(CH_3)_2 \rightarrow CH_3OCH_2CH(CH_3)_2 + NaI\downarrow \quad (7)$$

TABLE 2. Quantities and Physical Properties of the Reactants and Products of the MIBE Synthesis Reaction Using Metallic Sodium.

REACTANTS	Moles	Mol Wt.	Mass(g)	Density(g/ml)	Vol.(ml)	B.P.
i-BuOH	1.739	74	128.0	0.801	159.8	108
Na	0.870	23	20.0	0.97	20.6	892
CH_3I	0.870	142	123.5	2.279	54.2	42
PRODUCTS						
MIBE	0.870	88	76.5	0.731	104.7	58
NaI	0.870	150	130.5	3.667	35.6	1304

Procedure. The apparatus used consisted of a glass reaction flask containing a thermometer, a distillation water-cooled sidearm, a septum, ports for nitrogen flushing, and a stirring bar to provide homogeneity to the reaction mixture. All of the preparation steps were carried out in an inert atmosphere. In a nitrogen-filled glove bag, approximately 20 g of metallic sodium was placed into a pre-weighed 300 ml round bottomed flask. The flask was sealed, removed from the glove bag, weighed, and attached to the rest of the reaction system. After establishing a flow of nitrogen through the apparatus, 20 ml of anhydrous isobutanol was drawn into a syringe and then slowly injected into the flask through the septum. After several min, the isobutanol injection was repeated and continued until the total volume of 159.8 ml of isobutanol was transferred. The nitrogen flow was periodically confirmed. It was sometimes necessary to encourage the reaction between the metallic sodium and isobutanol, which was effected through careful heating of the mixture, while maintaining a constant vigil against runaway reactions, especially at the melting point of sodium metal. After all of the sodium had reacted, the mixture was allowed to cool to room temperature.

For the synthesis of the ether, the reaction flask containing the sodium isobutoxide/isobutanol mixture was centered in a large container, and sufficient ice was added to cover two-thirds of the flask. The addition of methyl iodide was then carried out while the mixture was near thermal equilibrium by carefully drawing 2 ml of methyl iodide (*methyl iodide is very poisonous*) into a glass syringe and inject the reactant through the septum of the reaction flask. Equilibration was then carried out for 30 min as an induction period. The ice level was adjusted to compensate for melting and another 5 ml of the methyl iodide reactant was added. After waiting for an additional 15 min and maintaining the ice level, addition of the remainder of the methyl iodide, for a total of 54.2 ml, was carried out at a rate that did not cause the mixture to boil excessively. The resultant liquid mixture was then filtered through several hundred g of activated alumina and stored without distillation.

This preparation method resulted in a high yield of MIBE, and the final solution, as stored and as used for GC/MS analysis, consisted of ≈50/50 MIBE/isobutanol.

D. GC/MS Identification of MIBE and MTBE

MIBE and MTBE are isomers that can be difficult to separate by gas chromatography if the proper analytical conditions are not used. To verify the GC analytical data, GC/MS analysis (with the Finnegan GC/MS using a SPB-1 WCOT column (0.25 mm ID x 15 m in length with 0.25 μ film thickness) at 35°C) of the reactor outlet stream was carried out for each initial experiment after the GC/MS was calibrated using standard samples of MIBE (prepared as described in the previous section) and MTBE (obtained commercially), as well as methanol and isobutanol. The fragmentation patterns for these two ethers are distinctly different, with MTBE having intense m/e peaks at 73.0 (the C_4H_9O- fragment), 57.1, 40.9, and 29.0 and MIBE having its principal intense m/e peak at 45.0 (the $-CH_2-O-CH_3$ fragment).

E. Temperature Dependence of Ether Synthesis and Catalyst Stability

The objective is to determine the effect of temperature on the yields and selectivities of products when methanol and isobutanol are pumped over Nafion-H microsaddles (MS) at high pressure.

Catalyst Testing. A second sample of the duPont Nafion-H MS catalyst (1.0039 g) was used as received from C.G. Processing, Inc. of Rockland, DE and was mixed with 10 ml of 3 mm Pyrex beads as diluent. The reactor containing the catalyst was connected to the testing unit and flushed with nitrogen for several hours to remove any residual oxygen or water.

After adjusting the helium-nitrogen carrier gas mixture to the desired flow rate, the reactor was pressurized and then the reactor was heated to a designated temperature. Once thermal equilibrium was achieved, one or two blank injections were made to check for a smooth GC baseline. The 2:1 molar methanol/isobutanol solution was then pumped into the H_2/He gas feed at a previously calculated rate using a Gilson Model 302 pump. The Nafion catalyst was tested under the following conditions:

TABLE 3. Catalytic Test Conditions

Reactor Temperature	123, 137, 147, 157, 123°C
Reactor Pressure	1100 psig
Total GHSV	248 mol/kg cat/hr
Catalyst Weight	0.0010039 kg
Nitrogen flow	0.0206 mol/hr
Helium flow	0.21027 mol/hr
Methanol flow	0.01222 mol/hr
	12.172 mol/kg cat/hr
Isobutanol flow	0.00611 mol/hr
	6.086 mol/kg cat/hr

Results. The catalyst was maintained at each temperature for atleast 48 hr so that a steady state could be verified. The effects of temperature on product yields for the reaction conditions shown in Table 3 (note that the pressure is 1100 psig rather than the 200 psig pressure used previously) are shown in Figure 9, where DME is dimethylether, C4 are butenes, tBuOH is tertiary butanol, MTBE is methyl tertiarybutyl ether, and MIBE is methyl isobutyl ether.

The long term deactivation of the Nafion-H MS was tested at 123°C with the same pressure and reactant flows rates as shown in Table 3. The catalyst had been subjected to many different reaction conditions, e.g. even MTBE decomposition studies, after being loaded into the stainless steel reactor. These included periods of standing under N_2 at ambient temperature and pressure. The times given reflect total time in the reactor, not total reaction time at elevated temperatures and pressures. The results of the deactivation study beginning and ending at 123°C at high pressure (1100 psig) when the catalyst was 0-24, 360, and 2420 hr in the reactor are shown in Figure 10. The tests in Figure 1 up to 157°C are represented in the first 450 hr in Figure 10. Other tests were conducted and then the catalyst

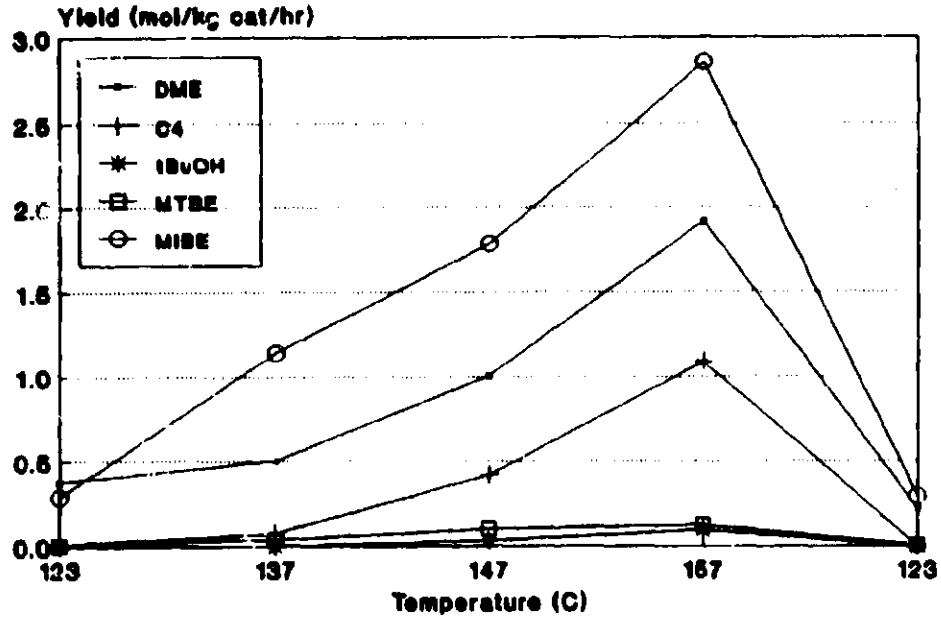


FIGURE 9. Effects of Temperature on the Yield of Products Over Nafion-H.

was retested under the initial conditions of the 123°C experiment. It is important to note that the test at 360 hr is probably not under true steady-state conditions. Fluctuations occurred in the 360 hr test, and the corresponding data points in Figure 9 were obtained by averaging the data at 360 hr. In any case, a comparison of the time at 0 hours and 2420 hours shows deactivations of 50%, 41%, and 25% for DME, MTBE, and MIBE, respectively.

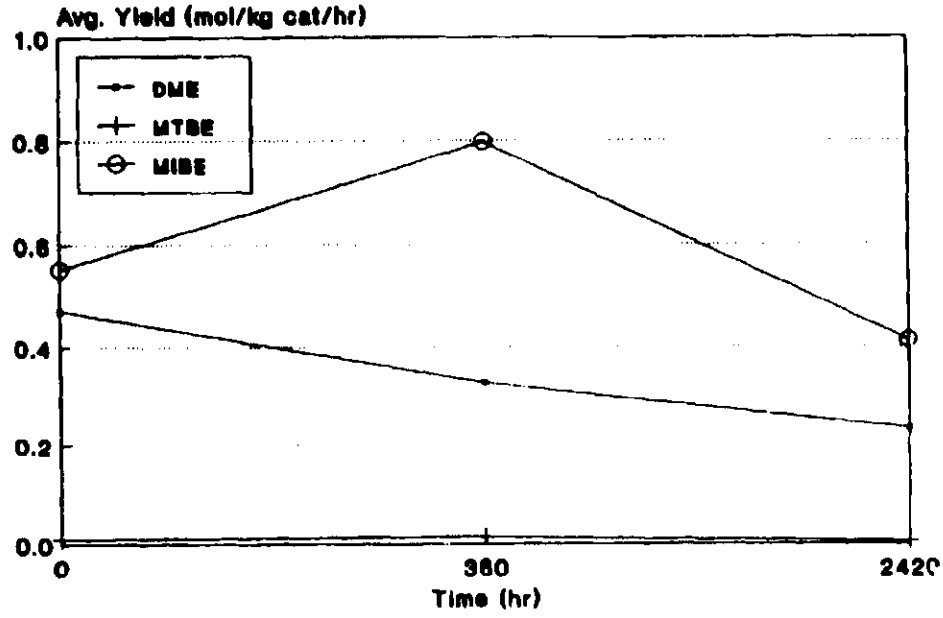


FIGURE 10. Deactivation of the Nafion-H MS Catalyst Under the Reaction Conditions in Table 3.

Activation Energies. The activation energies for the different products were calculated by assuming that the yields are proportional to the reaction rate constants. Tables 4 and 5 list the calculated apparent activation energies for the major products observed to be formed over the Nafion-H MS catalyst under the rather severe reaction conditions given in Table 3. It is evident that DME and MIBE have the lowest apparent activation energies.

TABLE 4. Apparent Activation Energies for the Ethers and t-Butanol Using the Arrhenius Equation.

X - Axis		Y - Axis					
		DME	tBuOH	MTBE	MIBE	DTBE	DIBE
T (K)	1/T	log Yield	log Yield	log Yield	log Yield	log Yield	log Yield
430	0.002326	0.273	- 1.005	- 0.883	0.468	- 1.059	- 0.307
420	0.002381	- 0.031	- 1.449	- 0.956	0.280	- 1.166	- 0.725
410	0.002439	- 0.295	-	- 1.355	0.0796	- 1.521	- 0.872
396	0.002525	- 0.562	-	- 1.926	- 0.167	- 1.882	- 1.128
Slope Log vs 1/T		- 4151	- 8019	- 5467	- 3187	- 4320	- 3888
$E_{activation}$ in Kcal/mol		19.0	36.7	25.0	14.6	19.8	17.8

TABLE 5. Apparent Activation Energies for the C_4 and C_8 Compounds Formed During Ether Synthesis *via* Alcohol Coupling (Calculated by Using the Arrhenius Equation).

X - Axis		Y - Axis				
		isoButene	1-Butene	2-Butene	isoOctene1	isoOctene4
T (K)	1/T	log Yield	log Yield	log Yield	log Yield	log Yield
430	0.002326	- 0.034	- 0.834	- 1.095	-0.3158	- 0.7712
420	0.002381	- 0.385	- 1.680	- 1.897	- 1.849	- 1.813
410	0.002439	- 1.088	-	-	-	
396	0.002525	- 2.356	-	-	-	
Slope Log vs 1/T		- 11863	- 15279	-14582	- 27690	- 18815
$E_{activation}$ in Kcal/mol		54.3	69.9	66.7	126	86.1

F. MTBE Decomposition Study

The temperature dependence study of ether synthesis *via* coupling of methanol and isobutanol over the Nafion-H MS catalyst was interrupted by an MTBE pumping experiment to determine the major products formed when MTBE decomposed on the catalyst. This experiment will allow reaction conditions to be optimized in future studies for the synthesis of MTBE. MTBE was

injected into the inert gas stream pumped over the Nafion-H MS catalyst at 123°C under 1 atm of pressure at three different flow rates. The results are given in Table 6. It is evident that MTBE very readily decomposed over this catalyst, principally to methanol and isobutene, under these reaction conditions. Calibration of the GC thermal response factors is being carried out to increase the accuracy of this data, but the semi-quantitative yields clearly show that MTBE is decomposed at 1 atm and 123°C, and thus lower pressures and lower temperatures will be investigated in planned alcohol coupling experiments in order to probe the prevention of MTBE decomposition if it is directly synthesized from the alcohols.

TABLE 6. Formation of Products *via* MTBE Decomposition.

Yield at different GHSV, 123°C and 1 atm (101.327 kPa)
Catalyst: Nafion-H MS
Catalyst weight: 0.0010039 kg

Compound	GHSV 230 (mol\kg cat\hr)	GHSV 496 (mol\kg cat\hr)	GHSV 1748 (mol\kg cat\hr)
MTBE in	6.11	12.22	46.55
MTBE out	0.73	0.20	1.93
Water	0.98	0.39	0.30
DME	0.84	0.22	0.26
MeOH	5.39	10.21	44.17
Isobutene	7.55	7.90	43.08
1-butene	0	0	0
2-butene	0	0	0
n-butane	0.03	0	0
MIBE	0	0	0
Isooctene1	3.38	0.41	0.33
Isooctene2	1.18	0.14	0.12
Isooctene3	0.47	0.06	0.01
Isooctene4	0.80	0.08	0
Isooctene5	2.13	0.25	0.11
C-12	3.07	0.42	1.03
C-12	0.68	0	0.01

G. Thermodynamic Considerations for Ether Synthesis from Alcohols: MIBE vs MTBE

As discussed here and elsewhere [1], MIBE can be obtained as a major product over a Nafion-H resin at high pressures and moderate temperatures (123°C) from a 2:1 molar mixture of methanol and isobutanol. This invention pointed out that a "new" acid catalyzed chemistry is occurring at the acidic sulfonic groups at the surface of the Nafion resin. Kinetic studies

obtained for the same catalyst system [23] showed that the chemistry is mainly characterized by the following features: (a) a bimolecular process at the catalyst surface is occurring, i.e. the ether is formed after interaction of two separate surface-held intermediate complexes, (b) the interaction between the sulfonic acid groups and the adsorbing alcohols is competitive and a preference for isobutanol exists, and (c) the nature of the adsorbed transition state complex is of primary importance in determining which ether will be formed. If the complex were carbonium-like, MTBE would be expected to be formed *via* an initial dehydration of isobutanol to isobutene and subsequent reaction of the isobutene with methanol. If instead the transition state complexes would be oxonium or ester complexes, then MIBE would be formed from isobutanol and methanol. The exact nature of the transition state complexes in the formation of MIBE is yet to be proven. More recent catalytic tests (discussed here) with the Nafion-H resin showed that MTBE could also be found in small concentrations in the product stream. Testing results obtained with the Amberlyst-15 resin under similar conditions showed that MIBE and MTBE were both present as products but in a more equal amount.

Both reaction mechanisms probably occur at the surface of the Nafion-H and Amberlyst-15 resins. Since the experimental testing conditions were equal for both catalysts, one can conclude that the nature of the local environment around the sulfonic acid groups plays a role in determining which process will be favored.

Since one of the major commercial uses of non-petroleum derived C_5 ethers, as being investigated in this research, would be as additives to gasoline to maintain or improve the high octane rating of this gasoline, it is essential that their octane enhancement behavior be known. An extensive study describing the effect of the addition of oxygenates on the research octane number of a regular gasoline was published in 1986 by Spindelbalker and Schmidt [24]. Different alkylbutylethers, including MIBE and MTBE, were included in this study as represented in Table 7.

TABLE 7. Effect of Small Additions of Alkylbutylethers and Butanols on the Octane Numbers of a Gasoline Basestock with 82.4 RON and 76.6 MON (from Reference 24).

Type of Butylether	% added	ΔRON	ΔMON
1-Methoxy-butane	5	-3.1	-2.1
	10	-5.7	-4.4
2-Methoxy-butane	5	-1.1	-0.1
	10	-2.4	-0.5
2-Ethoxy-butane	5	-1.0	+0.1
	10	-2.0	0.0
2-Ethoxy-2-methyl-propane (= ETBE)	5	+0.5	+0.8
	10	+2.1	+2.2

1-Methoxy-2-methylpropane (= MIBE)	5	-1.0	-2.1
	10	-1.9	-3.0
2-Methoxy-2-methylpropane (= MTBE)	5	+1.3	+1.4
	10	+3.4	+2.8
1-Butanol	5	+1.7	+1.1
	10	+3.1	+2.2
2-Butanol	5	+1.4	+1.0
	10	+2.9	+2.3
Isobutanol	5	+1.5	+1.2
	10	+3.1	+2.1
Tert. Butanol	5	+1.0	+0.8
	10	+1.9	+2.0

The results presented in this table show that while the butanols were octane enhancers, the only type of branched alkylbutylether with a positive effect on the RON were the ones characterized by the presence of a t-butyl group. While MTBE was a powerful octane enhancer, the addition of MIBE led to a small decrease of the RON. This indicates that MTBE is a preferred product over MIBE, and catalysts and reaction conditions should be sought whereby the yield of MTBE is maximized.

Two ways can be proposed to achieve this goal: (a) by the isomerization reaction of MIBE to MTBE after the initial highly active synthesis of MIBE and (b) by enhancement of the selective dehydration of isobutanol to isobutene followed by selective isobutene coupling with methanol to form MTBE. The efficiency and occurrence of the second pathway, the dehydration step procedure, already seems to be strongly controlled by the type of catalyst when one compares the previously described behavior of Nafion-H and Amberlyst-15. Therefore, an intensive study to characterize the acid sites was undertaken as outlined in our technical reports.

It is also important to know whether the right experimental conditions are being used to achieve or optimize the synthesis of MTBE via one or both of the above mentioned pathways. The importance of the right experimental conditions was proven by recent studies in the field of MTBE synthesis from isobutene and methanol over catalysts like Amberlyst-15 [25,26], which indicated that the decomposition of MTBE to isobutene and methanol is an important factor at higher temperatures. Therefore, a detailed thermodynamic study was initiated and this is discussed in this section of the report.

The following specific problems concerning the choice of the right experimental conditions for ether syntheis over acid resin catalysts were formulated and studied.

(1) What is the overall thermodynamic effect of the reactor temperature and pressure on the different reactions occurring during the C_5 ether synthesis from isobutanol and methanol?

(2) Which reactions are exothermic and which are endothermic?

(3) Is it possible to make predictions about the selective conversion of isobutanol and methanol into MTBE by applying basic thermodynamic principles for a specific set of experimental conditions?

Description of the Methodology. The following scheme, shown in Figure 11, can be drawn to describe the main reactions that can occur during the reaction of isobutanol and methanol over acidic catalysts. In this simple scheme, the two assumptions made were: (a) the only dehydration product of isobutanol considered is isobutene, although one could expect that n-butenes could also be formed in the dehydration process [26], and (b) secondary reactions such as the formation of octenes, etc. are not considered in this first reaction scheme.

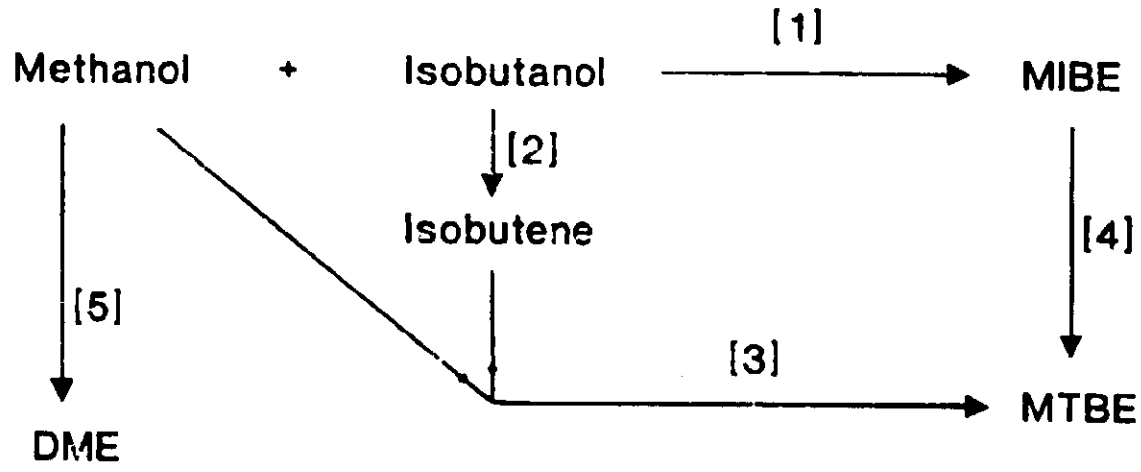


Figure 11. Synthesis Reactions of MTBE, DME, and MIBE from Alcohols.

As indicated by this scheme, the five different reactions that can occur simultaneously are:

[1] Methanol + Isobutanol → MIBE + H_2O
[2] Isobutanol → Isobutene + H_2O
[3] Isobutene + Methanol → MTBE
[4] MIBE → MTBE
[5] Methanol + Methanol → DME + H_2O.

The reaction labels [i] will be used further in the tables to refer to a specific reaction. Two standard reference works [27,28] were used as references for the thermodynamic calculations.

Effect of Temperature. The enthalpies, free energies, and entropies at room temperature and 1 atm for the different reactions were obtained using the thermodynamic values of the different compounds as given by the TRC Thermodynamic Tables for Non-Hydrocarbon and Hydrocarbon Compounds [29].

The enthalpies of the reactions ($p_i\Delta H_{products} - r_i\Delta H_{reactants}$) of Figure 11 are given in Table 8. All the reactions are exothermic except the dehydration of isobutanol to isobutene and H_2O (Reaction [2]).

TABLE 8. Enthalpy of Reaction in kcal/mol

Reaction	Enthalpy of Reaction (kcal/mol)
[1]	-5.53
[2]	+5.78
[3]	-15.61
[4]	-4.3
[5]	-5.68

Figure 12 represents a more general overview of the enthalpy changes that can occur during the synthesis of MTBE or MIBE from methanol and isobutanol. As shown, MTBE + H_2O are the thermodynamic favored products for the reaction scheme outlined in Figure 11. Considering the enthalpy changes, an increase in temperature will have a disadvantagous effect on the two reaction pathways to MTBE, i.e. the MIBE synthesis and its eventual subsequent isomerization and the MTBE synthesis from isobutene and methanol. More detailed calculations via the relationship of Van't Hoff should still be performed.

Through the thermodynamic relation of $\Delta G_i = \Delta H_i - T\Delta S_i$, it is possible to determine which effect the temperature has on the free energy of a particular reaction and consequently on its thermodynamic equilibrium constant K. Assuming that the enthalpy and entropy do not change significantly with a change in temperature, the values given in Table 9 for the free energies changes (ΔG_i) can be obtained.

TABLE 9. Free Energies Changes for the Ether Synthesis Reactions.

Reaction	ΔH_i (kcal/mol)	ΔS_i (cal/mol-K)	ΔG_i (kcal/mol) Temperature (K)		
			298.15	400	500
[1]	-5.53	-12.9	-1.67	0.37	0.92
[2]	5.78	24.1	-1.41	-3.86	-6.27
[3]	-15.61	-42.1	-3.05	1.23	5.44
[4]	-4.3	-5.1	-2.77	-2.26	-1.75
[5]	-5.68	-6.0	-3.90	-3.28	-2.68

Figure 13 gives a schematic overview of the changes in free energy during the synthesis of MIBE and MTBE at the two temperatures of 298.15 and 400K. At room temperature, all the considered reactions are exo-energetic. However, an increase in the temperature has a variable effect, e.g. the synthesis of MIBE from methanol and isobutanol (Reaction [1]) becomes less exo-energetic at 400K, and Table VIII shows that at 500K, this reaction has become endo-energetic. The same trend exists for the MTBE synthesis from

FIGURE 12

Reaction enthalpies of ether synthesis reaction pathways

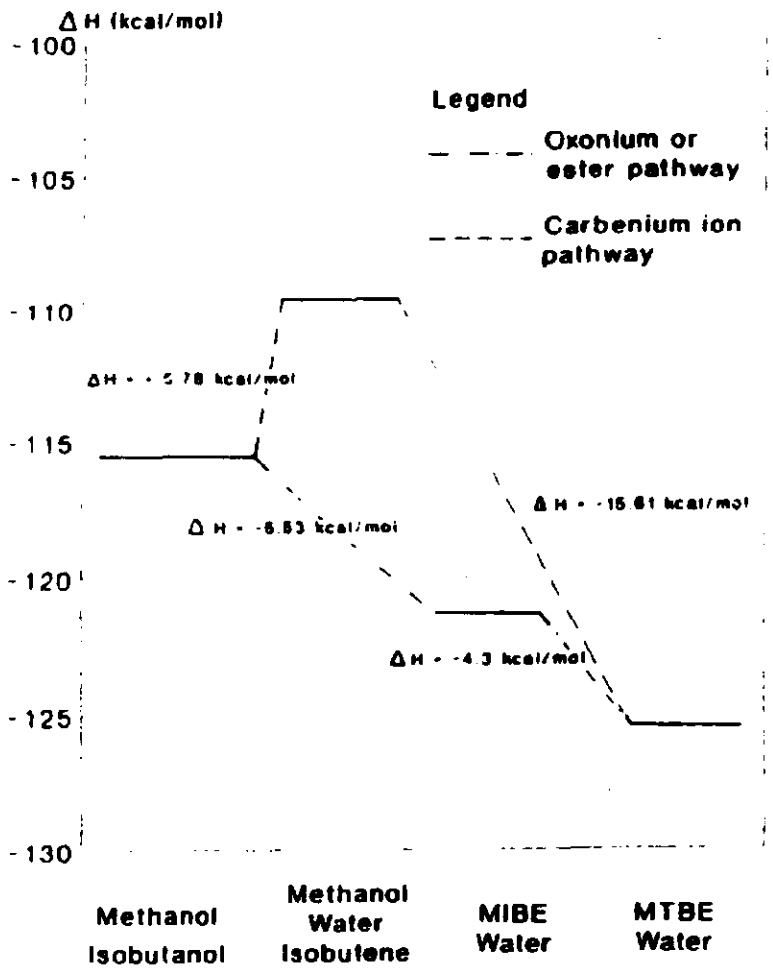
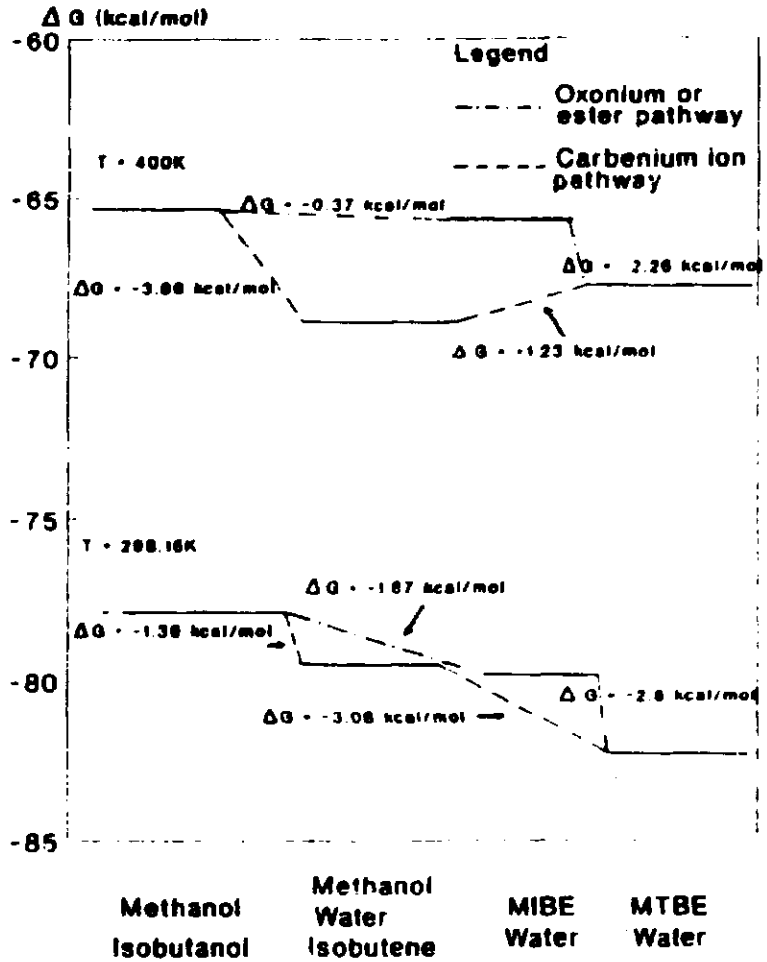


FIGURE 13

Free energy of ether synthesis reaction pathways



isobutene and methanol (Reaction [3]), where the reaction has already become endo-energetic at 400K. On the other hand, the three remaining reactions (isobutanol dehydration, MIBE isomerization, and DME synthesis) are always exo-energetic in the studied temperature-range.

The calculation of the standard free energies for the different reactions at different reaction conditions can also be transformed into specific equilibrium constants. Table 10 gives an overview of these equilibrium constants as a function of temperature.

TABLE 10. Equilibrium Constants for the Ether Synthesis Reactions

Reaction	Temperature (K) 298.15	400	500
[1] MIBE synthesis	16.57	1.59	0.396
[2] Isobutanol dehydration	10.80	128.52	550.26
[3] MTBE synthesis	172.06	0.210	0.004
[4] MIBE isomerization	107.25	17.17	5.82

The calculated thermodynamic data make it possible to make the following conclusions: (1) an increase in the temperature will disfavor the carbonium-ion pathway because of the appearance of a endo-energetic sub-reaction, and (2) under all temperature conditions (and in the case of a thermodynamic control of the occurring reactions) no limitations can be found that would prevent the isomerization of MIBE to MTBE. The reality that this isomerization cannot be observed over the Nafion-catalyst indicates that kinetic factors play an important role in this reaction.

Effect of the Total Pressure on the Reaction Equilibria. Initial studies were carried out to obtain information about the effect of the total pressure on the reaction equilibria, and only the following two reactions of the previously shown reaction scheme (Figure 11) can be influenced when studied independently.

[2] Isobutanol → Isobutene + H_2O
[3] Isobutene + Methanol → MTBE

The extent of these reactions as a function of pressure, obtained by using the earlier calculated equilibrium constants and activity coefficients (see Table 10), was found to decrease with increasing pressure in both cases. It was also found that decreasing temperatures also decreased the extent of reaction at a given pressure. However, the temperature effect on Reaction [2] was not significant at temperatures in the 400-500K range (extent of reaction was >97% at pressures up to 80 atm for this temperature range).

Figures 12 and 13 were calculated for single reaction sytems and show the pronounced effect of pressure and temperature on these two reactions. However, more studies would be certainly required in which all the main

reactions are considered at the same time since they would influence each other. For example, the presence of methanol in the feed would influence the degree of decomposition of MTBE at reaction equilibrium. In addition, the calculations can be improved by considering the effect of non-ideal gas behavior and introducing fugacity coefficients into the calculations.

H. Determination of the Acid Strength of Acid Polymers

The number of acidic sites on a solid catalyst is expressed as the number of milliequilivalents of acid sites per unit weight of catalyst (meq/g), and the two methods being employed in this research are:

(i) ion exchange/acid-base titration, and
(ii) thermometric amine titration to the equivalence point.

The amine that is typically used [30,31] is n-butylamine, and we have also utilized this base.

The strength of acidic sites can be obtained by

(i) the determination of the Hammett acidity function H_o, and
(ii) enthalpimetric titration.

We have employed the latter method with a Sanda Facts 2000 thermotitrator, which give temperature *vs* volume of titrant (for continuous addition) or time of equilibration for each volume of titrant added (for batch addition experiment). The temperature is monitored with a thermistor immersed in the titrand solution, e.g. 25 mol of organic solvent in which 1-2 g of the acid that is to be analyzed, that is contained in an adiabatic titration vessel. A detailed description of the theory and applications of this method is given in References 32 and 33. The thermal titration data can be used to obtain thermodynamic information about the strength of the acid groups being analyzed.

Enthalpimetric Titrations of Amberlyst-15. Thermometric titrations of vacuum-dried (110°C, 5 hr) Amberlyst-15 samples (0.5-1.0 g) were carried out in a variety of solvents including cyclohexane and in acetonitrile, which were predistilled to remove traces of H_2O and acetic anhydride. Pyridine was used as the titrating base, which was added batch-like (in 0.5 to 1 ml amounts), and the heat releases were monitored as a temperature change of the solvent slurry. Each of the temperature increases could exactly be determined using the software package connected with the Sanda Facts 2000 Thermotitrator, and subsequently the ΔT values were converted into enthalpy values for the specific acid-base reaction.

The results of the titrations of Amberlyst-15 in different solvents with pyridine are represented in Figure 14. The results in Figure 14 give the following information: (1) the acid base titration could be performed with an endpoint reached and (2) the acid strength of the sulfonic acid groups in the Amberlyst-15 resin showed a heterogeneous distribution.

Enthalpimetric Titrations of Nafion H-MS Resin. In a typical experiment, about 2 g of the vacuum-dried (150°C, 24 hr) Nafion sample was

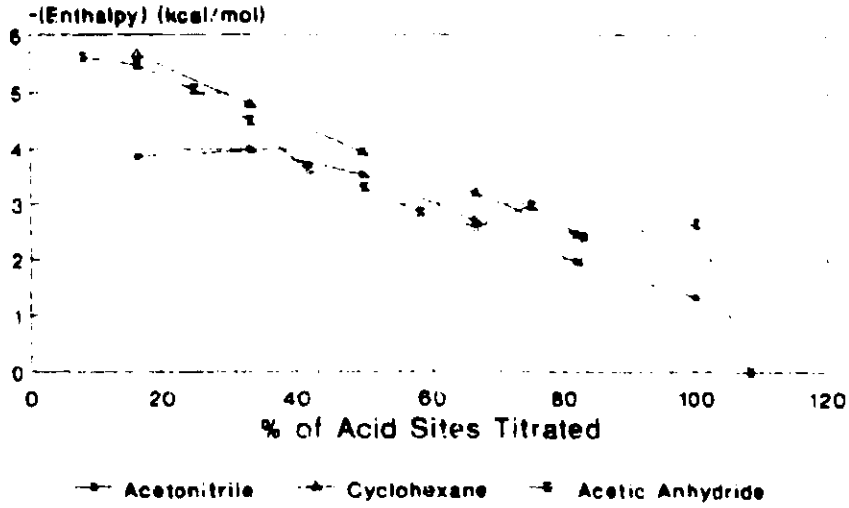


Figure 14. Enthalpimetric Titrations of Amberlyst-15 with Pyridine in Different Organic Solvents.

placed into 20 ml of predistilled acetonitrile or acetic anhydride and allowed to swell. The titrant was added batch-like (in 0.5 to 1 ml amounts) and the heat releases were monitored as a temperature change of the acetonitrile solution. The results were treated in the same way as for the Amberlyst-15 titrations for converting the ΔT values into "enthalpy" values for the specific acid-base reaction. No correction was yet made to include the endothermic dissociation of the acetonitrile-sulfonic acid complex. The results for the Nafion H-MS titrations are represented in Figure 15.

The titration results, partially shown in Figure 15, gave the following information: (1) the acid-base titration could be performed in acetonitrile until equilibrium is reached but could not be completed in acetic anhydride where only about 75% of the acid sites could be titrated, (2) the calculated acid strength of Nafion-H as measured by the enthalpy/mol of the acid-base reaction is larger in acetic anhydride than in acetonitrile (whether this

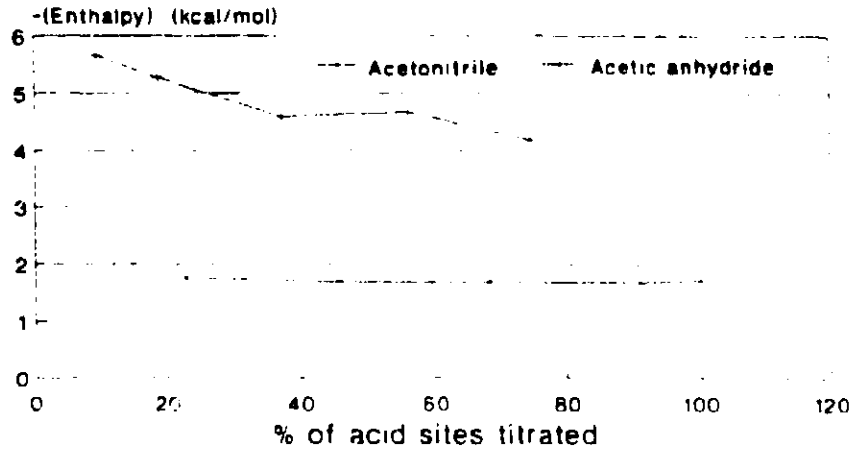


Figure 15. Titration of Nafion-H-MS with 1 N pyridine in various solvents.

difference should only be contributed to the endothermic dissociation of the acetonitrile-sulfonic acid group complex is yet unclear), and (3) the acid strength of the sulfonic groups in the Nafion-MS catalyst seemed to have a very homogeneous distribution when titrated in acetonitrile in contradiction with the results obtained for the Amberlyst-15 resin. In acetic anhydride, some difference can be seen in the acid strength as represented by the enthalpy values but this is not so pronounced as for the Amberlyst-15 resin.

REFERENCES

1. Nunan, J. G., Klier, K., and Herman, R. G., *J. Chem. Soc., Chem. Comm.*, (1985) 676.

2. Davis, J. C. and Kohn, F. M., *Chem. Eng.*, (May 21, 1979) 91.

3. Stinson, S. C., *Chem. Eng. News*, (June 25, 1979) 35.

4. Chase, J. D. and Galvez, B. B., *Hydrocarbon Process.*, 60(3) (1981) 89.

5. *Chem. Eng. News*, (January 24, 1983) 27.

6. Chase, J. C., in "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals," ed. by R. G. Herman, Plenum Press, New York (1984) 307.

7. Ancellotti, F., Mauri, M. M., and Pescarollo, E., *J. Catal.*, 46 (1979) 49.

8. Bitar, L. S., Hazbun, E. A., and Piel, W. J., *Hydrocarbon Process.*, 63(10) (1984) 63.

9. Woods, H. J., Chase, J. C., and Galvez, B. B., *U.S. Patent 4,204,077* (1980); assigned to Gulf Canada Ltd.

10. *Hydrocarbon Process.*, 61(9) (1982) 177.

11. Morandi, F., Trotta, R., Pecci, G., and Sposini, M., *Energy Prog.*, 8(1) (1988) 1.

12. Mills, G. A. and Ecklund, E. E., *CHEMTECH*, 19(10) (1989) 626.

13. Haggin, J., *Chem. & Eng. News*, (June 19, 1989) 31.

14. Ancillotti, F., Pescarollo, E., Szatmári, E. and Lázar, L., *Hydrocarbon Process.*, 66(12) (1987) 50.

15. Klier, K., Herman, R. G., and Young, C. W., *Preprints, Div. Fuel Chem., ACS*, 29(5) (1984) 273.

16. Klier, K., Herman, R. G., Nunan, J. G., Smith, K. J., Bogdan, C. E., Young, C.-W., and Santiesteban, J. G., in "Methane Conversion," ed. by D. M. Bibby, C. D. Chang, R. F. Howe, and S. Yurchak, Elsevier, Amsterdam, (1988) 109.

17. Bogdan, C. E., Nunan, J. G., Santiesteban, J. G., Herman, R. G., and Klier, K., in "Catalysis 1987: Proc. 10th North Am. Catal. Soc. Meeting," ed. by J. W. Ward, Elsevier, Amsterdam, (1988) 745.

18. Klier, K., Herman, R. G., Simmons, G. W., Nunan, J. G., Smith, K. J., Bogdan, C. E., and Himelfarb, P. B., "Direct Synthesis of 2-Methyl-1-Propanol/Methanol Fuels and Feedstocks," Final Technical Report DOE/PC/70021-F, Rev. 1, 285 pp (August 1988).

19. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., and Herman, R. G., *J. Catal.*, 116 (1989) 195.

20. Nunan, J. G., Herman, R. G., and Klier, K., *J. Catal.*, 116 (1989) 222.

21. Smith, K. J., Herman, R. G., Klier, K., *Chem. Eng. Sci.*, 45 (1990) 2639.

22. Smith, K. J., Young, C.-W., Herman, R. G., and Klier, K., *Ind Eng Chem. Res.*, 29 (1991) 61.

23. Nunan, J. G., Klier, K., and Herman, R. G., unpublished results.

24. Spindelbalker, C. and Schmidt, A., *Erdol, Erdgas and Kohle*, 102(10) (1986) 469.

25. Cunill, F., Tejero, J., and Izquierdo, J. F., *Appl. Catal.*, 34 (1987) 341.

26. Tejero, J., Cunill, F., and Izquerdo, J. F., *Ind. Eng. Chem. Res.*, 28, (1989) 1269.

27. Lewis, G. N. and Randall, M., "Thermodynamics," McGraw-Hill Series in Advanced Chemistry, New York (1961).

28. Freifelder, D., "Principles of Physical Chemistry," Jones and Bartlett, Boston (1982).

29. TRC Thermodynamic Tables for Hydrocarbons and Non-Hydrocarbons, Texas Research Institute.

30. Trambouze, Y., de Mourgues, L., and Perrin, M., *J. Chim. Phys.*, 51 (1954) 723.

31. Tanabe, K. and Yamaguchi, T., *J. Res. Inst. Catal., Hokkaido Univ.*, 14 (1966) 93.

32. Tyrrell, H. J. and Beezer, A. E., "Thermometric Titrimetry," Chapman and Hall, London (1968).

33. Eatough, D. J., Christensen, J. J., and Izatt, R. M., "Experiments in Thermometric Titrimetry and Titration Calorimetry," Brigham Young University Press, Provo, Utah (1973).