

OCTANE IMPROVEMENT BY ETHERIFICATION OF LIGHT DISTILLATE  
OLEFINS

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OCTANE IMPROVEMENT BY ETHERIFICATION OF  
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by

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ABSTRACT

C<sub>4</sub> to C<sub>6</sub> rich fractions of light olefins obtained from oil refinery catalytically cracked reactor effluent were reacted with methanol to form methyl ethers in a bench-scale pilot reactor. The ethers produced were methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) and tertiary hexyl methyl ether (THME). The yields of ethers were determined for various operating conditions of temperature, pressure, space velocity, and methanol/active olefin molar ratios. The ethers were blended into unleaded gasoline to determine their blending octane numbers and their effect on vapour pressure. Both reactor effluent and purified ethers were used in the quality assessment tests. The average blending octane numbers in regular unleaded gasoline of 94.2 RON and 83.8 MON were: methanol/isopropanol blends at 4% total oxygen, 124 RON and 94 MON; MTBE, 116 RON and 101 MON; TAME, 106 RON and 99 MON; and THME raw reactor effluent, 89.0 RON and 80.6 MON. The influence of these blending agents and the presence of unreacted methanol upon vapour pressure were discussed in terms of incorporating low cost butane into gasoline.

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## INTRODUCTION

The purpose of this study was to evaluate the refinery production of octane boosting ethers as an improvement process for petroleum fuels. The value in specific circumstances of incorporating high octane number ethers has been amply demonstrated with North American capacity in excess of 13 000 m<sup>3</sup>/d (1). However, the majority of the olefins used in this capacity are from petrochemical sources and must be purchased by refiners. The purpose of this work is to evaluate the use of suitable olefins that are available inside a typical Canadian fuels refinery for the production of gasoline blending ethers and ether rich streams. Blending these ethers into automotive gasoline can be considered as a way of using inexpensive methanol to increase the octane number without the established undesirable effects on volatility and material compatibility. Further, since methanol is most commonly made from natural gas, blending these ethers into gasoline provides an opportunity to incorporate inexpensive natural gas into automotive fuel without extensive capital investment.

The methyl ethers studied in this work are methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME), and tertiary hexyl methyl ether (THME). Of these, MTBE has been the most studied and has the largest scale of production. THME has not been produced commercially and its potential is unknown. TAME production is of interest to refiners, mainly because of its analogous nature to MTBE, its octane blending characteristics, and the greater tolerance of unreacted methanol in TAME reactor effluent. Methanol exhibits a high blending research octane number (RON) of 124 in unleaded gasolines but has a lower blending motor octane number (MON) of 99. This is a very high blending sensitivity. In comparison, MTBE has a blending RON of approximately 116 and a blending MON of approximately 101 which is a lower blending sensitivity. It should be noted that only approximate octane values for these oxygenates are reported since this property depends upon the composition of the hydrocarbons with which they are blended.

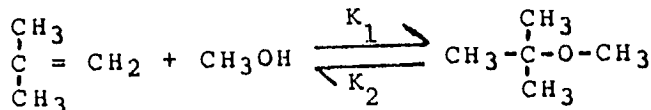
Factors related to the handling of gasoline fuel have caused interest in the use of ethers in the place of methanol. Methanol addition to unleaded gasoline also causes a significant non-linear increase in Reid vapour pressure (RVP) which results in a serious loss of capability to blend surplus refinery butanes of high octane quality. Addition of purified MTBE and TAME actually decreases gasoline vapour pressure so that additional low cost butanes may be blended into gasoline while maintaining vapour pressure specifications (2,3). Methanol will readily separate from gasoline in the presence of small amounts of water while MTBE resists water extraction. This phase separation of methanol from hydrocarbons is significant since the existing fuel distribution networks (storage tanks, cargo ships, pipelines, vehicle gasoline tanks, etc.) are usually in direct contact with water. MTBE is hydrocarbon compatible and does not damage currently used fuel system components to the same extent as methanol.

Most plants currently producing MTBE and TAME in both North America and Europe are associated with petrochemical complexes where naphtha cracking processes produce significant amounts of olefins that are available to refiners. The concentration of C<sub>4</sub> olefins from naphtha crackers (40-50%) is higher than in the corresponding effluent from fluidized catalytic cracker units (FCCU) in conventional refineries (10-20%) (3). However, more than 80% of all isobutene, the only C<sub>4</sub> olefin that reacts with methanol, is produced in FCCU operations at conventional oil refineries (6). This work is a study of the production of C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> methyl ethers from FCCU derived olefins in an add-on single pass fixed bed reactor system. The reactor effluent was assessed with minimal purification

and with the operational goal of providing additional octane barrels to the unleaded gasoline pool.

#### Etherification Reactions

MTBE can be produced from the liquid phase exothermic reaction of isobutene and methanol at mild temperature and pressure conditions over a cationic ion exchange resin catalyst as follows:



Isobutene	+ Methanol	MTBE
m.w. = 56.1	m.w. = 32.0	m.w. = 88.1

The equilibrium reaction is reversible and the rate constants for formation and decomposition are both temperature dependent although the reverse reaction rate increases more rapidly with temperature. As well, at higher reactor temperatures and low methanol/isobutene molar ratios, some di- and triisobutene can be produced (6,7). Higher reaction temperatures also favour the formation of undesirable dimethyl ether from a side reaction of methanol.

The MTBE process removes only 9-17% of the olefins from the FCCU-C<sub>4</sub> stream. The reactor effluent contains sufficient olefins for the conventional processes of alkylation and polymer gasoline processes. In most refineries the FCCU-C<sub>4</sub> stream is the only source of C<sub>4</sub> olefins and alkylation and polymerisation processes already exist. These processes use strong acid catalysts (HF or H<sub>2</sub>SO<sub>4</sub> for alkylation, P<sub>2</sub>O<sub>5</sub> for polymer gasoline) that are rapidly degraded by alcohols to form salts and water with a loss of catalytic activity, increased corrosion, and excessive catalyst replacement/regeneration costs. Since most existing refineries have either one or both of these processes, a method for the removal of unreacted methanol and ether product from the remaining olefins must be incorporated into the MTBE process.

Methanol removal is complicated by the azeotropes of methanol with most of the C<sub>4</sub>'s in the MTBE reactor effluent stream, including the olefins necessary for alkylation and polymerisation gasoline processes. Methods that have been considered for the removal of methanol and MTBE from the methoxylation reactor effluent are pressurized azeotropic distillation coupled with water extraction (8,9,10), molecular sieve adsorption (11), and glycol extraction (12). Further, the water limit for the reactor feedstocks is approximately 5 ppm for HF alkylation, 100 ppm (almost saturated) for H<sub>2</sub>SO<sub>4</sub> alkylation, and approximately 80 ppm for the polymer gasoline process. By assuming that these limits are related to the hydroxyl content of water, similar limits on the combined water/ether/methanol content of feedstocks would probably be used.

Another consideration is the competition of the etherification reaction for the 9-17% isobutene in the FCCU stream. Studies of HF alkylation rate the octane performance of C<sub>4</sub> olefins as:

2-butenes>isobutane>l-butene (7,13)

isobutene>2-butenes>l-Butene (14)

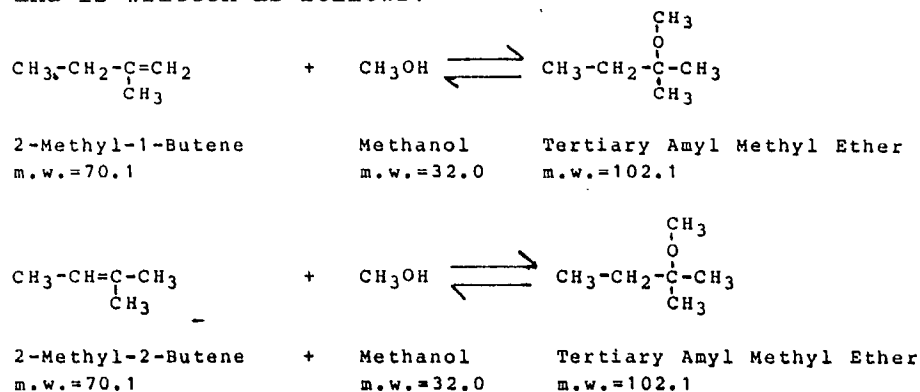
For H<sub>2</sub>SO<sub>4</sub> alkylation, the order of octane importance is reported as:

2-butenes>l-butene>isobutene (15)

Thus both water tolerance and isobutene content suggest a more favorable combination of MTBE with H<sub>2</sub>SO<sub>4</sub> alkylation. In an integrated refining environment, an MTBE etherification unit would be placed downstream from the FCC. It would

then be fed the FCCU-C<sub>4</sub> olefins, and the unreacted olefins would be available for alkylation and polymerization. Removal of methanol and ether from this olefin rich etherification reactor effluent results in a major portion of the etherification process cost.

TAME can be produced from the liquid phase equilibrium reaction of 2-methyl-1-butene and 2-methyl-2-butene with methanol at mild temperature and pressure over the same cationic exchanger resin catalyst used for the MTBE reaction, and is written as follows:



Higher reactor temperatures favour the decomposition of TAME but increase the reaction rate. The equilibrium conversion for the TAME reaction does not favour ether formation as much as in the MTBE reaction from isobutene. However, the selectivity of the C<sub>5</sub> reaction to form TAME is better than isobutene to MTBE because of the lack of diisomyrene formation (7), even with less than stoichiometric amounts of methanol as reported in this work. By using less than stoichiometric amounts of methanol, a TAME reactor effluent of sufficiently low methanol content can be produced without methanol purification, suitable for most gasoline blending purposes. This would represent a cost saving of the TAME process that can be used by refiners, providing the vapour pressure increase of the unreacted methanol is not large.

THME can also be produced with the same catalyst from the reaction of methanol and C<sub>6</sub> olefins. Less information regarding the formation of THME and its use in gasoline octane blending is available. It is included in this work because of its similarities to MTBE and TAME and the abundant supply of inexpensive C<sub>6</sub> olefins.

## EXPERIMENTAL

### Feedstocks and Chemicals

A sample of a light catalytically cracked gasoline blending stream from a Canadian refinery was fractionated into the C<sub>5</sub> fraction boiling between 25-50°C and a C<sub>6</sub> fraction boiling between 50-75°C. An alkylation plant feedstock from the same Canadian refinery was used as the source of the C<sub>4</sub> catalytically cracked hydrocarbons. Large volumes of regular unleaded gasoline were also supplied from the same source. The analysis of the feedstocks is shown in Table 1.

### Reactor Design

A schematic of the pilot plant reactor is shown in Figure 1. The reactor consisted of a 350-700 kPa nitrogen blanketed feed tank on a weighing scale, a preheater, an electrically heated reactor, a product cooler, a back pressure controller and a product reservoir. The mixed feeds (hydrocarbon and methanol) were pumped to the top of the reactor with a metering pump. Premixing of the

methanol and hydrocarbons was used for the production of TAME and THME ethers. The volatility of the C<sub>4</sub> hydrocarbons required a separate handling system for the methanol with independent introduction of the methanol into the reactor. The weight of the feed was recorded at regular intervals to determine the feed rate. The accumulated weight of the product was used to determine the mass balance. Gas chromatographic compositional analyses were used to determine the component balances.

Reactor temperature was monitored by dividing the reactor into three dimensionally equal sections. Reactor pressure was measured at the outlet of the reactor and maintained by electronically controlling the back pressure control valve. Leaks in the system were ignored if the pressure loss in the system was less than 7 kPa in 1 h during static testing. Reactor products that were to be used in octane number rating tests were stored at -20°C in stainless steel barrels with 10 mg/L of antioxidant (Ethyl Corp Agent 733) to prevent gum and peroxide formation.

#### Catalyst Preparation

The same catalyst, Rexyn 101(H) (Fisher) was used for the C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> ether studies. The catalyst is a cation exchange resin of styrene and divinyl benzene with sulphonic acid ionic groups. The catalyst bed was prepared by sieving the 16-50 mesh Rexyn resin to obtain a particle size of 18-28 mesh (0.6 to 1.0 mm) followed by drying overnight at 70°C. The reactor was charged with 80 mL (63.7 g) of Rexyn 101(H) catalyst and contacted with methanol. The bed expanded to fill the 100 mL reactor. This same bed was used in all of the optimization experiments without a noticeable loss of reactivity. A similar procedure was used to obtain the 1000 mL reactor catalyst bed that was used for the 75 L C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> production runs.

#### Blending Properties

Blending octane numbers and Reid vapour pressures of the ether products and the unleaded gasolines were determined by ASTM test procedures. The RON was determined by ASTM D2699 with a quoted test reproducibility of ±0.35 for 90-100 RON. The MON was determined by ASTM D2700 with a quoted test reproducibility of ±0.55 for 80-95 MON. Oxygen contents of these blends were in the range of 0-6% by weight. As well, the phase separation temperatures were determined. To protect blended fuels from phase separation, sufficient isopropyl alcohol (IPA) was added to equal the analyzed volume of methanol. The IPA content was included in the determination of oxygen content.

#### Ether Formation

MTBE. The optimal reactor conditions for large volume MTBE product runs in the 1000 mL reactor were chosen by surveying the literature (12, 17-19), and are listed below.

Reactor Temperature	100°C
LHSV	1.5 h <sup>-1</sup>
Reactor Pressure	2.7 MPa
Methanol/Active Olefin Molar Ratio	1.2/1

Based upon these process conditions and a C<sub>4</sub> alkylation unit feed containing 10.24% isobutene, an overall active C<sub>4</sub> conversion of 80.0% was obtained as shown in Table 2. This conversion is based upon the following two methods of calculation and the assumption that the isobutane to MTBE reaction was 100% specific.

1. The amount of unreacted isobutene remaining in the product as a percentage of the isobutene feed content (82.0% conversion.)

2. The stoichiometric amount of isobutene necessary to produce the amount of MTBE found in the product as a percentage of the isobutene feed (78.0% conversion.) This conversion is in agreement with values reported in the literature (12, 17-19).

Some difficulties were encountered in performing the mass and component balances for methanol and isobutene because of the design of the reactor system and the volatile nature of the feedstock. The mass of the reactor off-gas was determined by calculating the results from a wet test meter volume and a mass spectrometer hydrocarbon analysis. The selectivity of the isobutene for the formation of ethers was considered to approach 100% under the conditions studied. The formation of dimethyl ether is an indication of the less selective reaction of methanol to form MTBE, and this is aggravated by higher reactor temperatures.

TAME. The TAME reactor conditions were optimized in 12 experiments at a reactor pressure of 1.7 MPa, LHSV of 0.5 or 2.0, reactor temperature at 65, 80 or 95°C, and a ratio of methanol to active olefin molar of 1.09/1 or 0.74/1. The results of these experiments are shown in Table 3. From these results the optimal conditions to produce sufficient TAME product for gasoline engine evaluation with the 1000 mL reactor were chosen as listed below.

Reactor Temperature	65°C
LHSV	0.5 h <sup>-1</sup>
Reactor Pressure	1.7 MPa
Methanol/Active Olefin Molar Ratio	1.09/1

The major reason for the selection of these conditions is to maximize TAME yield since the sensitivity of gasoline engine tests and other gasoline specifications evaluated in this work are not sensitive to low levels of TAME. The 65°C reactor temperature was chosen since the reaction is equilibrium controlled and reversible with decreasing TAME yield as the temperature increases. This confirms the results reported elsewhere (7). The LHSV of 0.5 gave the greatest conversion. However, this would correspond to an unreasonably large and expensive reactor, and a space velocity of 2.0 h<sup>-1</sup> is considered to be a more suitable refinery processing condition. The reactor pressure of 1.7 MPa was chosen since it is sufficient to keep the methoxylation reaction in the liquid phase.

The molar ratio of methanol to active olefins has two effects that are considered important. The conversion of active C<sub>3</sub> olefins to TAME is greater for the higher methanol content but the amount of unreacted methanol in the reactor effluent also increases under these conditions. For example, if a TAME reactor effluent was blended directly into gasoline, small amounts of unreacted methanol could be tolerated. However, if the initial methanol content of the TAME reactor effluent was high, blending restrictions upon this type of stream would be necessary to accommodate butane disposal opportunities and to avoid degrading fuel quality by phase separation, etc. It should be noted that no further processing of unreacted C<sub>3</sub> olefins would be expected in most refineries. From experience with the Canadian markets for gasoline, the lower reactor methanol/olefin molar ratio tested would give a more acceptable blending product. However, the higher molar ratio of methanol/olefin was taken on the assumption that the larger methanol content in the gasoline would be offset by the larger yield of TAME. The results of these experiments are shown in Table 4.

The results reported in Tables 3 and 4 also indicate that the two reactive C<sub>5</sub> olefins have remained specific with respect to TAME formation throughout the reactor temperature range studied, even when less than stoichiometric amounts

of methanol were used. The MTBE reaction requires an excess of methanol to avoid the formation of undesirable di- and triisobutylenes (7). These results also show that 2-methyl-1-butene has an increased tendency to form TAME or to isomerize to 2-methyl-2-butene. A lower TAME yield can therefore be expected from 2-methyl-2-butene than from 2-methyl-1-butene.

THME. The THME reactor conditions were optimized in 12 experiments with the same range of conditions as described above, and the results are presented in Table 5. The optimum conditions were as follows:

Reactor Temperature	80°C
LHSV	0.5 h <sup>-1</sup>
Reactor Pressure	0.7 MPa
Methanol/Active Olefin Molar Ratio	1.0/1

These reactor conditions were chosen on the basis that they give the highest conversion to THME. This was necessary because of the low conversions of methanol to THME and the large amount of THME product that would be required for octane number blending tests. The results of the 1000 mL reactor experiments are shown in Table 6.

## RESULTS AND DISCUSSION

### Blended Gasoline Performance

An important consideration in gasoline blending with oxygenates is the effect of removing n-butane to maintain specifications for RVP. The effect on RVP of blending n-butane into gasoline was established for a debutanized basestock with calculated butane additions. Figure 2 shows this calculated theoretical relationship which was used to estimate the n-butane back out resulting from blending the various oxygenates while maintaining the basestock's original RVP.

Methanol. Blends of regular unleaded gasoline with three methanol/isopropanol mixtures were prepared at a constant 4% total oxygen content. The data are presented in Table 7 and indicate the following relations:

1. Methanol exhibits a high blending RON of approximately 124.
2. Methanol exhibits a much lower blending MON of approximately 94.
3. There is a serious negative effect on RVP leading to a loss up to 5 vol % butane to maintain the RVP.

4. The front end distillation characteristics as measured by the 10% evaporated temperature are significantly depressed. These results are comparable to published data (2) and demonstrate the serious economic penalty on refinery butane disposal opportunities and the need to use expensive cosolvents to avoid phase separation at low temperatures.

MTBE. Because of the separation required to remove methanol and unreacted MTBE from the reactor effluent for subsequent processing, it was assumed that only purified MTBE would be available to refiners for gasoline blending. From the data shown in Table 8, MTBE has an average blending octane number of 116 RON and 101 MON for regular unleaded gasolines. These results agree with literature values (3,7). Blending MTBE in unleaded gasoline up to 26 vol %, well above the 11 vol % allowed by the United States Environmental Protection Agency, did not markedly disturb the volatility of the blends as measured by RVP and ASTM D86 distillation. The data show that the use of 5-10 vol % MTBE as an octane improver in unleaded gasoline would allow approximately 1 vol % additional n-butane to be added to maintain the original RVP. This butane "disposal" offers an economic advantage for both gasoline processing costs and octane enhancement. This aspect



of MTBE use has been shown to be an alternative to toluene production through high severity reforming (3).

TAME. Three types of TAME were assumed to be available for gasoline blending: purified TAME; 50 vol % TAME; and unpurified reactor effluent. A major objective of TAME production is to upgrade the quality of the C<sub>5</sub> fraction from FCCU gasoline with minimum processing and purification. A second objective is to study the impact of unreacted methanol in the C<sub>5</sub> TAME reactor effluent on gasoline product quality. The results of the blending experiments are shown in Tables 9 to 11, where blends in the range of 0-3 wt % oxygen were prepared. The average blending RON for TAME was 106 and the average MON was 99. These are less than the values for MTBE and are comparable with published values (7).

The effect of blending purified TAME into either premium or regular gasoline on volatility is similar to that found for MTBE. At least 25 vol % TAME can be incorporated into either normal winter or summer gasolines without failing specifications. At a level of 10 vol % TAME in unleaded gasoline, an additional 1 vol % n-butane can be incorporated to maintain the original basestock's RVP. For the C<sub>5</sub> reactor effluent, the blending octane values for the 43.5 vol % active C<sub>5</sub> olefins to TAME conversion were determined for the original C<sub>5</sub> feedstock and for the reactor effluent. These were 95.3 RON and 84.0 MON for the feedstock and 96.3 RON and 85.8 MON for the reactor effluent. This corresponds to an octane improvement of 1.0 RON and 1.8 MON by etherification of the feedstock. However, to maintain the original RVP of the gasoline basestock an approximate 1.5 % removal of n-butane was assigned to the reactor effluent which is attributable to the unreacted methanol.

THME. Both purified THME and C<sub>6</sub> reactor effluent were evaluated for their blending characteristics, as shown in Tables 12 and 13. Under these conditions, THME did not improve the octane quality of the gasoline. This also agrees with reported values in the literature (7,19). The RVP consideration permits the blending of an additional 1.5 vol% n-butane for the purified THME case.

Blending purified MTBE, TAME and THME caused a reduction in the RVP of the gasoline. This would provide the refiner with the ability to blend in low cost butanes that would otherwise have too high vapour pressure. However, this advantage is lost when the ethers are not purified of unreacted methanol. The refiner must balance the extra cost of removing the unreacted methanol with the benefits of using low cost butanes which is further complicated by the differences of each refinery. Direct methanol blending causes a large increase in RVP with the necessary removal of significant amounts of butanes from the gasoline to maintain the volatility specification. This increases the cost of using methanol as an octane booster since the cost of the unused butanes and their final disposition must be considered. The effect of purification on RVP is not a consideration for the MTBE case since the methanol must be removed for alkylation and polymer gasoline processing.

## CONCLUSIONS

Optimized reactor conditions for the production of TAME and THME were determined. These were used along with literature values of the optimal conditions for MTBE production to produce samples large enough for the assessment of product quality. These tests indicate that purified MTBE and TAME have valuable octane number improvements with the advantage that they reduce the gasoline's RVP to the point where inexpensive butanes can be added in significant volumes. Unpurified TAME causes a slight increase in vapour pressure and the requirement that butanes be backed out of the gasoline. This effect was even more

pronounced for the case of pure methanol blending. THME did not improve the octane number but it did cause a small reduction in RVP.

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FIGURE 2

# R.V.P. FOR BUTANE/GASOLINE SYSTEMS

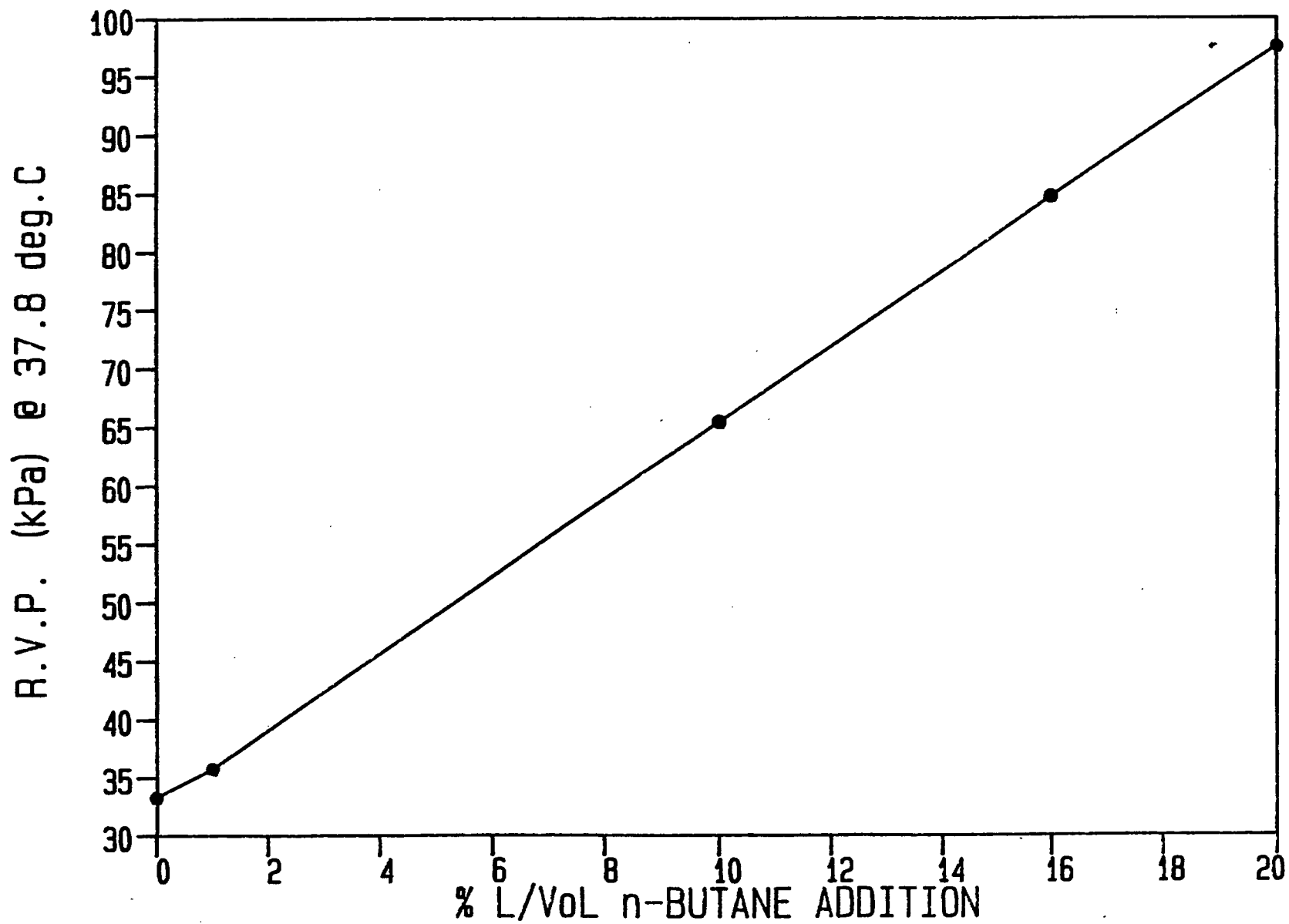


Table 1 Compositional analysis of etherification reactor feedstock

	<u>C<sub>4</sub> Alkylation Feed, vol %</u>	<u>C<sub>5</sub> Cat Cracked Gasoline 25-50°C, vol %</u>	<u>C<sub>6</sub> Cat Cracked Gasoline 50-75°C, vol %</u>
C <sub>3</sub> 's	0.6	-	-
C <sub>4</sub> 's			
saturates	49.3	-	-
olefins	33.7	0.2	-
diolefins	0.3	-	-
isobutane	10.24	-	-
C <sub>5</sub> 's			
saturates	4.5	51.74	1.2
olefins	0.9	14.48	1.0
diolefins	-	0.7	0.9
2-methyl butene-1	0.38	4.72	0.07
2-methyl butene-2	0.07	10.60	0.90
C <sub>6</sub> 's			
saturates	-	11.5	64.0
olefins	-	0.4	8.54
reactive olefins	-	1.33	11.79
Benzene	-	0.31	4.06
C <sub>7</sub> and higher	-	2.30	6.74
Total	<u>99.9</u>	<u>98.7</u>	<u>99.2</u>

Table 2 MTBE large volume reactor results

	<u>Average</u> <u>Feed</u>	<u>Product</u> <u>No. 1</u>	<u>Product</u> <u>No. 2</u>	<u>Composite</u> <u>Product</u>
Reactor Conditions				
Temperature	-	100	100	100
LHSV, h <sup>-1</sup>	-	1.5	1.5	1.5
Pressure, MPa	-	2.7	2.7	2.7
Methanol/Active Olefin Molar Ratio	-	1.16/1	1.20/1	1.18/1
Relative Concentrations, wt%				
Isobutene	57.2	11.7	10.6	12.1
2-Methyl butene-1	2.4	0.3	0.4	0.3
2-Methyl butene-2	0.4	0.3	0.4	0.3
Dimethylether	-	1.9	1.7	1.3
MTBE	-	77.1	78.8	77.5
TAME	-	1.4	1.1	1.1
Mass Balance, %				
Total feed basis	-	92.0	87.8	90.2
Isobutene basis	-	99.9	94.5	97.0
Methanol consumption basis	-	91.5	86.0	84.5
Conversion, %				
Isobutene basis	-	80.8	83.5	82.0
MTBE Product basis	-	80.7	78.1	78.0

Table 3 Optimization Experiments for C<sub>5</sub> Etherification

	Feed	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Reactor Temperature, °C	-	65	80	95	65	80	95	65	80	95	65	80	95
LHSV, h <sup>-1</sup>	-	0.5	0.5	0.5	2.0	2.0	2.0	0.5	0.5	0.5	0.5	0.5	0.5
Reactor Pressure, MPa	-	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Methanol/Active Olefin Molar Ratio	-	1.09/1	1.09/1	1.09/1	1.09/1	1.09/1	1.09/1	0.74/1	0.74/1	0.74/1	0.74/1	0.74	0.74/1
Relative Concentration, wt %													
Isobutene	0.3	0	0	0	0	0	0	0	0	0	0	0	0
2-Methyl Butene-1	19.3	2.6	3.0	4.5	5.8	35.9	3.9	1.7	3.4	5.5	8.2	5.0	5.5
2-Methyl Butene-2	43.9	23.8	26.5	37.0	29.88	27.1	31.2	28.8	30.8	45.1	36.7	34.2	41.3
Active C <sub>5</sub>	3.6	1.6	1.8	2.3	2.0	1.8	2.1	2.2	2.3	2.9	2.5	2.6	2.4
Methanol	33.0	11.8	11.7	11.0	20.1	16.0	16.1	4.9	7.7	6.8	10.4	8.2	8.9
Dimethyl Ether	0	0.3	1.3	4.8	0.2	0.5	1.3	0.3	0.8	4.2	ND	0.4	1.5
MTBE	0	0.7	0.3	0.1	1.1	0.6	0.4	0.7	0.3	0.8	1.4	0.9	0.6
TAME	0	57.3	53.7	38.4	39.9	49.0	43.7	59.3	52.3	34.2	39.6	47.3	38.7
THME	0	2.1	1.8	1.3	1.1	1.4	1.7	1.7	1.7	1.1	1.1	1.3	1.2
Conversion, %													
Active C <sub>5</sub>	-	58.8	55.3	38.5	42.7	50.6	46.4	42.7	48.4	30.1	34.8	43.5	34.9

Table 4 TAME large volume reactor results

	<u>Average</u> <u>Feed</u>	<u>Product</u> <u>No. 1</u>	<u>Product</u> <u>No. 2</u>	<u>Product</u> <u>No. 3</u>	<u>Composite</u> <u>Product</u>
Reactor Conditions					
Temperature, °C	-	65	65	65	65
LHSV, h-1	-	0.5	0.5	0.5	0.5
Pressure, MPa	-	1.7	1.7	1.7	1.7
Methanol/Active olefin Molar Ratio	-	1.08	1.09	1.08	1.08
Relative concentration, wt%					
2-Methyl butene-1	19.0	2.2	2.1	2.1	2.1
2-Methyl butene-2	43.4	21.0	20.3	20.7	20.4
Active C6 olefins	5.6	3.1	3.4	3.5	3.4
Methanol	32.0	10.0	11.8	9.9	11.0
Dimethyl ether	-	0.4	0.4	0.3	0.3
MTBE	-	-	-	-	-
TAME	-	59.6	57.9	59.6	58.5
THME	-	3.8	4.1	3.9	4.0
Mass Balance, %					
Total Feed basis	-	99.5	98.9	99.2	99.2
Active C5 basis	-	106.2	109.2	109.7	109.0
Methanol consumption basis	-	94.7	104.0	97.9	105.2
Conversion, %					
2-Methyl butene-1 basis	-	87.9	87.9	88.0	87.8
2-methyl butene-2 basis	-	50.2	48.7	49.3	49.0
Active C5 basis	-	61.9	60.6	60.8	60.8



Table 5 Optimization Experiments for C<sub>6</sub> Etherification

	Feed	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12
Reactor Temperature, °C	-	65	80	95	65	80	95	65	80	95	65	80	95
LHSV, h <sup>-1</sup>	-	0.5	0.5	0.5	2.0	2.0	2.0	0.5	0.5	0.5	2.0	2.0	2.0
Reactor Pressure, MPa	-	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Methanol/Active Olefin Molar Ratio	-	1.04/1	1.04/1	1.04/1	1.04/1	1.04/1	1.04/1	0.77/1	0.77/1	0.77/1	0.77/1	0.77/1	0.77/1
Relative Concentration, wt %													
Active C <sub>5</sub>	9.1	5.0	4.7	7.6	6.8	5.0	3.8	3.1	5.4	6.4	7.3	5.9	6.1
Active C <sub>6</sub>	61.6	41.2	38.0	48.6	50.7	41.4	42.8	52.0	46.3	59.6	59.5	57.1	59.6
Methanol	28.8	4.0	8.9	11.2	22.4	18.6	18.2	13.3	14.4	8.4	9.8	7.5	6.4
Dimethyl Ether	0	0.6	1.8	5.2	0	0.5	1.4	0.4	1.1	4.3	0	0.3	1.3
TAME	0	16.4	8.4	5.8	3.7	6.7	6.7	7.8	6.1	3.4	2.7	4.3	4.0
THME	0	32.6	37.5	22.4	16.3	27.8	27.2	22.4	27.2	17.9	20.6	24.6	22.3
Conversion, %													
Active C <sub>6</sub> basis	0	40.3	39.4	35.4	19.8	33.6	34.2	23.2	31.7	8.7	12.6	19.2	18.1
THME product basis	0	34.3	33.3	23.6	18.8	32.4	30.4	24.0	29.2	19.8	22.0	25.3	22.2

Table 6 Large volume reactor results

	<u>Average</u> <u>Feed</u>	<u>Product</u> <u>No. 1</u>	<u>Product</u> <u>No. 2</u>	<u>Product</u> <u>No. 3</u>	<u>Composite</u> <u>Product</u>
Reactor Conditions					
Temperature, °C	-	80	80	80	80
LHSV, h-1	-	0.5	0.5	0.5	0.5
Pressure, MPa	-	1.7	1.7	1.7	1.7
Methanol/Active Olefin Molar Ratio	-	0.97/1	0.97/1	1.07/1	0.99/1
Relative Concentration, wt%					
Active C5	5.3	2.8	2.8	2.7	2.7
Active C6	67.4	41.5	41.6	41.7	42.6
Methanol	27.3	10.8	12.2	12.9	10.8
Dimethyl Ether	-	1.6	1.4	1.4	1.2
TAME	-	5.5	5.1	5.3	5.4
THME	-	37.9	37.0	35.9	37.2
Mass Balance, %					
Total Feed basis	-	99.0	99.9	101.1	99.8
Active C6 basis	-	106.4	103.9	107.1	105.3
Methanol Consumption basis	-	88.7	97.4	96.2	91.2
Conversion, %					
Total Active C6 basis	-	36.0	36.8	34.0	35.6
THME Product basis	-	42.4	40.8	41.1	40.8

Table 7 Gasoline quality results for methanol/isopropanol blends with regular unleaded gasoline

Blend Composition % vol:				
Regular Unleaded	100.0	90.68	91.45	89.71
MeOH/IPA	0	9.32	8.55	10.29
MeOH:IPA Ratio	0	1.00	2.00	0.50
<hr/>				
Oxygen Content, % wt	0	4.0	4.0	4.0
<hr/>				
Blend Research ON	94.2	96.9	96.5	96.9
Blend Motor ON	83.8	84.5	84.7	84.9
Delta Res ON over basefuel	0	2.7	2.3	2.7
Delta Motor ON over basefuel	0	0.7	0.9	1.1
Blending Res ON	-	123.2	121.1	120.4
Blending Motor ON	-	91.3	94.3	94.5
Blending Sensitivity	-	31.8	26.8	25.9
Reid Vapour Pressure, kPa	81.9	91.6	96.0	91.2
D867 Distillation, °C				
IBP	32	29	27	28
10% evap. @	53	40	42	40
50% evap. @	112	93	93	97
90% evap. @	181	176	176	176
FBP	216	214	215	213
Recovery, % vol	98.5	95.1	97.5	96.0
Residue, % vol	0.6	0.4	0.5	1.0
Loss, % vol	0.9	4.5	2.0	3.0
Phase Separation Temperature °C	<-40.0	<-40.0	<-40.0	<-40.0

\*Table 8 Gasoline quality results for MTBE with regular unleaded gasoline

Blend Composition % vol:					
Regular Unleaded	100.0	94.7	89.8	81.2	74.8
MTBE	0	5.3	10.2	18.8	26.2
Oxygen Content, % wt					
	0	1.0	2.0	4.0	6.0
Blend Research ON	94.2	95.0	96.4	98.0	99.4
Blend Motor ON	83.8	84.7	85.1	86.4	87.9
Delta Res ON over basefuel	0	0.8	2.2	3.8	5.2
Delta Motor ON over basefuel	0	0.9	1.3	2.6	4.1
Blending Res ON	0	109.3	115.8	114.4	114.1
Blending Motor ON	0	100.8	96.6	97.6	99.5
Blending Sensitivity	0	8.5	19.2	16.8	14.6
Reid Vapour Pressure, kPa	81.9	77.7	78.3	76.7	68.8
D867 Distillation, °C					
IBP	32	29	29	28	32
10% evap. @	53	45	45	45	47
50% evap. @	112	102	97	87	79
90% evap. @	181	178	176	175	169
FBP	216	213	212	213	208
Recovery, % vol	98.5	96.5	97.4	98.6	98.0
Residue, % vol	0.6	1.0	1.1	0.4	1.0
Loss, % vol	0.9	2.5	1.5	1.0	1.0
Phase Separation Temperature °C	<-40.0	-21.0	-21.8	-28.8	-35.8

Table 9 Gasoline quality results for TAME with regular unleaded gasoline

Blend Composition % vol:				
Regular Unleaded	100.0	94.12	88.8	84.0
TAME	0	5.88	11.2	16.0
Oxygen Content, % wt				
	Nil	1.0	2.0	3.0
Blend Research ON	94.2	95.0	96.0	95.6
Blend Motor ON	83.8	84.5	85.1	85.6
Delta Res ON over basefuel	0	0.8	1.8	1.4
Delta Motor ON over basefuel	0	0.7	1.3	1.8
Blending Res ON	0	107.8	110.3	103.0
Blending Motor ON	0	95.7	95.4	95.0
Blending Sensitivity	0	12.1	14.9	8.0
Reid Vapour Pressure, kPa	81.9	78.8	75.7	70.1
D867 Distillation, °C				
IBP	32	28	30	32
10% evap. @	53	49	52	54
50% evap. @	112	105	103	101
90% evap. @	181	178	177	175
FBP	216	214	216	213
Recovery, % vol	98.5	98.0	98.2	99.0
Residue, % vol	0.6	0.4	0.3	0.4
Loss, % vol	0.9	1.6	1.5	0.6
Phase Separation Temperature °C	<-40.0	-19.0	-26.5	-25.0

Table 10 Gasoline quality results for C<sub>5</sub> etherification reactor effluent with regular unleaded gasoline

Blend Composition % vol:				
Regular Unleaded	100.0	75.9	50.6	31.1
C <sub>5</sub> Reactor Effluent	0	24.1	49.4	68.9
Oxygen Content, % wt				
	Nil	1.0	2.0	3.0
Blend Research ON	94.2	95.2	95.6	96.2
Blend Motor ON	83.8	84.5	85.3	85.8
Delta Res ON over basefuel	0	1.0	1.4	2.0
Delta Motor ON over basefuel	0	0.7	1.5	2.0
Blending Res ON	0	98.4	97.0	97.1
Blending Motor ON	0	86.7	86.8	86.7
Blending Sensitivity	0	11.7	10.2	10.4
Reid Vapour Pressure, kPa	81.9	93.6	91.2	95.7
D867 Distillation, °C				
IBP	32	30	27	28
10% evap. @	53	41	37	35
50% evap. @	112	85	65	52
90% evap. @	181	172	158	131
FBP	216	213	202	194
Recovery, % vol	98.5	97.9	97.1	98.0
Residue, % vol	0.6	0.4	0.8	0.3
Loss, % vol	0.9	1.7	2.1	1.7
Phase Separation Temperature °C	<-40.0	-25.0	<-40.0	<-40.0

Table 11 Gasoline quality results for C<sub>6</sub> etherification reactor effluent.  
partial methanol removal, with regular unleaded gasoline

Blend Composition % vol:				
Regular Unleaded Mogas	100.0	88.12	76.3	64.7
50% TAME	0	11.88	23.7	35.3
Oxygen Content, % wt				
	Nil	1.0	2.0	3.0
Blend Research ON	94.2	94.8	95.8	96.7
Blend Motor ON	83.8	83.3	83.1	86.0
Delta Res ON over basefuel	0	0.6	1.6	2.5
Delta Motor ON over basefuel	0	-0.5	-0.7	2.2
Blending Res ON	0	99.3	101.0	101.3
Blending Motor ON	0	79.6	80.9	90.0
Blending Sensitivity	0	19.7	20.1	11.3
Reid Vapour Pressure, kPa	81.9	82.9	81.9	79.5
D867 Distillation, °C				
IBP	32	28	30	30
10% evap. @	53	47	44	44
50% evap. @	112	102	92	87
90% evap. @	181	176	172	166
FBP	216	214	211	207
Recovery, % vol	98.5	97.5	98.1	98.0
Residue, % vol	0.6	0.3	0.4	0.4
Loss, % vol	0.9	2.2	1.5	1.6
Phase Separation Temperature °C	<-40.0	-19.0	-28.5	<-40.0

Table 12 Gasoline quality results for THME with regular unleaded gasoline

Blend Composition % vol:			
Regular Unleaded	100.0	97.25	94.16
Pure C <sub>6</sub> (THME) Ether	0	2.75	5.84
<hr/>			
Oxygen Content, % wt	0	0.50	1.0
<hr/>			
Blend Research ON	94.2	94.0	94.2
Blend Motor ON	83.8	83.3	83.1
Delta Res ON over basefuel	0	-0.2	0.0
Delta Motor ON over basefuel	0	-0.5	-0.7
Blending Res ON	0	86.9	94.2
Blending Motor ON	0	65.6	71.8
Blending Sensitivity	0	21.3	22.4
Reid Vapour Pressure, kPa	81.9	76.0	73.6
D867 Distillation, °C			
IBP	32	31	32
10% evap. @	53	48	50
50% evap. @	112	109	111
90% evap. @	181	178	179
FBP	216	214	217
Recovery, % vol	98.5	97.4	97.5
Residue, % vol	0.6	0.6	0.5
Loss, % vol	0.9	2.0	2.0
Phase Separation Temperature °C	-40.0	-12.5	- 8.5



Table 13 Gasoline quality results for C<sub>6</sub> etherification reactor effluent with regular unleaded gasoline

Blend Composition % vol:			
Regular Unleaded	100.0	53.5	10.0
C <sub>6</sub> Reactor Effluent	0	46.5	90.0
Oxygen Content, % wt			
	0	1.0	2.0
Blend Research ON			
	94.2	91.9	89.3
Blend Motor ON			
	83.8	82.2	81.1
Delta Res ON over basefuel			
	0	-2.3	-4.9
Delta Motor ON over basefuel			
	0	-1.6	-2.7
Blending Res ON			
	0	89.3	88.8
Blending Motor ON			
	0	80.4	80.8
Blending Sensitivity			
	0	8.9	8.0
Reid Vapour Pressure, kPa			
	81.9	68.1	56.3
D867 Distillation, °C			
IBP	32	33	45
10% evap. @	53	51	56
50% evap. @	112	77	67
90% evap. @	181	158	88
FBP	216	206	168
Recovery, % vol	98.5	99.0	99.0
Residue, % vol	0.6	0.4	0.7
Loss, % vol	0.9	0.6	0.3
Phase Separation Temperature °C			
	<-40.0	<-40.0	<-40.0