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ABSTRACT

The use of MTBE and TAME as octane boosting blending agents was investigated by using a computerized linear programming (LP) study of refinery economics. The use of conventional refining processes with lead and manganese antiknocks was considered, as well as the post lead phase down conditions with an isomerization unit added to the refinery. The LP results for the production of MTBE exclusively from catalytically cracked hydrocarbons inside the refinery were not encouraging. No consideration was given to the use of an exterior source of olefins for the MTBE process nor to the purchase of ethers from offsite. The LP results for the use of TAME gasoline (with unreacted methanol included) suggested that the process was economically viable prior to lead phase down. After lead phase down, the contributions to octane quality of the ethers alone was inadequate, and the use of a standard isomerization unit more than compensated for the octane squeeze.

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INTRODUCTION

The objective of this work is to determine the blending and economic effects of installing C_4 and C_5 etherification processes in a Canadian fuels-only petroleum refinery using linear programming (LP). As much as possible, the specifications for the refinery operations were similar to those used in an earlier study concerned with the purchase of oxygenates from petrochemical plants for the improvement of octane number quality (1). This work is concerned with the intrarefinery fabrication and use of methyl tertiary-butyl ether (MTBE) and tertiary-amyl methyl ether (TAME) for blending into gasoline for the case where lead phaseout requires refiners to use alternative sources of incremental octane.

In our earlier work (2), the blending octane contributions were assessed along with reactor yields and the vapour pressure limitations of purified MTBE (methanol free), purified TAME (methanol free), and TAME reactor effluent (unreacted methanol included). The same properties were also determined for tertiary-hexyl methyl ether (THME) but there was no improvement to the octane number of the reactor effluent and LP evaluation of its economics of production were not considered in this work.

Use of MTBE and TAME is an indirect way to incorporate natural gas into gasoline without the undesirable effects on volatility as measured by Reid Vapour Pressure (RVP) and materials compatibility caused by the direct blending of methanol. In excess of 80% of isobutane available for MTBE formation is produced in fluidized catalytic cracking units (FCCU) in conventional oil refineries (3). The supply of the isoamylenes required to make TAME is entirely within refineries. Blending of MTBE and methanol-free TAME actually decreases the vapour pressure of the gasoline product so that additional low cost, adequate octane value butanes can be added. Other uses for these butanes are difficult to find, and their disposal into gasoline improves the refiner's flexibility. Both MTBE and TAME are resistant to phase separation when contaminated with water, and by themselves they do not require the addition of cosolvent and blending agents.

An alternative strategy for increasing octane capacity is to upgrade light paraffins by isomerization. This alternative was considered as part of the LP study performed in this work. The use of isomerization to increase the octane capability of refiners along with the use of ethers was considered in other economic studies (4,5). In this study, isomerization was used to make a large increase in octane for the case where tetraethyl lead (TEL) and manganese methyl tricarbonyl (MMT) would not be available to the refiner.

PROCESS DATA

LP Refinery Specifications

A simple refinery consisting of a 16 000 m³/SD (stream-day) crude unit (100 000 bb1/SD), a 4800 m³/SD fluidized catalytic cracking unit (FCCU) (30 000 bb1/SD), a 3500 m^3 /SD reformer (22 000 bb1/SD), and a 1000 m^3 /SD alkylation unit (6300 bb1/SD) was used for the LP evaluation of all cases. The annual product demand for the refinery is listed in Table 1 and the gasoline specifications are reported in Table 2. The cost of the crude oil used in the refinery and the other feed streams is reported in Table 3.

MTBE Process and Product Data

The size of the MTBE unit is controlled by the size of the FCCU and the amount of $\rm C_4$ hydrocarbons produced. The FCCU used in this work was assumed to produce 4 800 m /SD with an effluent containing 12.1 vol % C, hydrocarbons of which 11.7 vol % is isobutane. The following MTBE reactor conditions were chosen on the basis of our previous work (2).

Reactor Temperature	100°C ₁
LHSV	$1.5 h^{-1}$
Reactor Pressure	2.23 MPa
Methanol/Active Olefin	1.1/1 mol/mol
Feed (isobutene)	11.7 vol %
Conversion	80.0%

Under these conditions, the amount of methanol consumed would be 32.0 m^{-/}SD which includes losses to side geactions of 3.0 m^{-/}SD. The MTBE reactor effluent would be 68.4 m /SD.

The process for synthesizing MTBE includes a reactor, a distillation tower to remove MTBE from the unreactable C, hydrocarbons and methanol, and a glycol extraction column and stripper to remove methanol from the remaining C_{I_1} hydrocarbons to achieve an approximate 10 ppm methanol content. These C, hydrocarbons are then considered suitable for alkylation without the loss of the alkylation catalyst. The installed capital cost of the equipment necessary for the process was estimated to be \$2.5M. The operating demands were estimated to be 101 GJ/h supplied by steam, 17.6 kW/h electricity and 5000 L/h cooling water. The combined ion exchange resin catalyst and make-up glycol extraction solvent costs were estimated to be \$63 k/a.

From blending experiments, it was found that from 5 to 10% MTBE will require an approximate 1.0 vol % of additional n-butane to restore the RVP to the original value of the gasoline blending stock. Up to 15% MTBE can be added to normal gasoline without causing a distillation specification violation. At 18 mg/L MMT a response of 1 Research Octane Number (RON) and 1 Motor Octane Number (MON) was assumed. The octane blending values were assumed to be as follows. MTBE (RON/MON) 116/101 93.8/89.6 (reference 6) Butane (RON/MON) C₄ Alkylate (RON/MON) 93.0/90.0

TAME Process and Product Data

The size of the TAME unit was chosen to correspond with the FCCU,

which was assumed to produce 10.0 vol % C_5 hydrocarbons with 15.3 vol % isoamylenes. The following TAME reactor conditions were chosen based upon our previous work (2). Reactor Temperature 80 C LHSV 2.0 h⁻¹ Reactor Pressure 1.7 MPa Methanol/Active Olefin 0.74/1 mol/mol Feed (isoamylene) 15.3 vol % Conversion 43.5%

Purification of the reactor effluent (TAME gasoline) was not considered. It was assumed that the stream contained sufficiently low unreacted methanol that it would be directly blended into the gasoline pool without the use of cosolvent. With these reactor conditions, the reactor product was estimated to be 495.8 m /SD, with 52.6 m /SD TAME and 5.9₃m /SD methanol. The methanol consumption was estimated to be 20.5 m /SD with an estimated loss to side reactions of 2.5 m /SD. These compositions were taken from pilot experiments at the reactor conditions listed above with similar feed to that assumed in this study (1).

Blending results with 43.5% conversion TAME gasoline were not available, but results from 60.3% conversion TAME gasoline were determined as part of our earlier work (2). These results were used to estimate the octane quality at 43.5% conversion by computing the individual octane contributions of methanol, isopropanol added as a cosolvent for the methanol, unreacted isoamylenes, and TAME. When 10 vol % TAME gasoline is blended into normal gasoline, an approximate 1.5 vol % butanes must be removed to maintain the gasoline's original RVP. Up to 25% TAME gasoline can be added to normal gasoline without causing a distillation specification violation. At 18 mg/L MMT, a response of 1 RON and 1 MON can be expected. The relevant octane blending characteristics are assumed to be as follows.

TAME, purified (RON/MON)	106/99
Butane (RON/MON)	93.8/89.6
C ₅ TAME Reactor Feed	
25-50°C (RON/MON)	95.3-84.0
TAME Gasoline	
43.5% conversion (RON/MON)	96.3/85.8
FCCU C ₆ Stream (RON/MON)	92.5/80.6
	~ .

The installed capital cost of the equipment for the TAME process was estimated to be \$500 k which includes a reactor and two pumps. The operating demands were assumed to be steam requirements of 55.6 GJ/h and electricity requirements of 2.5 kW/h. The catalyst replacement cost was assumed to be \$30 k/a.

Isomerization Process and Product Data

The data for the isomerization reactor used in this study were taken from reference 1. It would have a capacity of 1000 m/SD of deisohexanizer (DiH) naphtha with an increase of (RON + MON)/2 of 17 octane numbers, with an octane sensitivity (RON - MON) of 3 numbers, and an increase in RVP of 2.5 psi. The yield was taken to be 98% C₅ and C₆ product with a 2% fuel gas loss. The catalyst was assumed to have a 10 year life, and the hydrogen consumption was taken to be 18 SCF/bbl feed. The operating costs were estimated to be \$1.9 M and the

installed cost was estimated as \$18 M. Both of these were extrapolated from reference 1.

LP Study Cases

The LP program was used to evaluate the economic viability of various refinery configurations using the ether processes and isomerization to obtain the product slate specified in Table 2. The base case was taken to be the refinery as described above, with permissible lead and manganese use of less than 0.29 g/L and 0.018 g/L, respectively. As well, current pricing was used for this case as well as all of the other cases studied. The MTBE process consisted of processing the entire C_4 hydrocarbon effluent from the FCCU, with recovery of unused olefins for processing in the alkylation unit. The TAME process consisted of taking the entire C_5 hydrocarbon effluent from the FCCU and processing it followed by direct blending into the gasoline pool, with unreacted methanol included. The isomerization process used the light straight run naphtha from the crude processing unit. Base case No. 2 did not include lead or manganese to represent the phase down of both of these components. Study cases No. 4 to 6 also do not include the use of lead and manganese. The nature of the study permits the comparison of the base cases. The LP study cases are summarized in Table 4.

RESULTS AND DISCUSSION

The process data described above were used in a computerized LP model of a typical Canadian refinery. The economic predictions of the LP model are shown in Table 5 for the study cases and base case No. 2. Only study case No. 2 and the cases with the isomerization unit installed have an economic advantage over the original refinery of base case No. 1. Negative economic impacts for both the C_4 and C_5 ether processes either together or separately are predicted for the lead free/manganese free isomerization cases. A return on investment factor (ROI) was defined as the number of years required to recover project costs after payment of income tax at 50% of incremental profits. For base case No. 2, the isomerization unit (\$18 M) had a ROI of approximately 11 years, and in study case No. 2, the TAME unit (\$500 M) had a ROI of 4 years.

MTBE Process

The LP study denied the use of C_4 ethers as an economic means of gasoline octane enhancement in all of the cases studied. One reason is the octane competition of the MTBE process with the existing alkylation process. The results of the LP study reported in Tables 6 and 7 show that the MTBE process is the smallest octane-m² contributor and has the smallest processed yolume. The MTBE process had a negative contribution to the octane-m² of the refinery. This negative octane-m² is best demonstrated by the results in Table 7. The existing alkylation unit has been sized directly in relation to the volume of FCCU C3 and C_4 olefins. Octane quality in the alkylation unit is optimized by controlling the ratio of FCCU olefins and the FCCU saturated hydrocarbons, light hydrocarbons from the crude unit and even from outside purchase when necessary. The total alkylation feed is then reduced by approximately 20% when coupled with the MTBE process. The approximate 20% under utilization of the alkylation unit results in a 15-20% reduced field butane purchase at a cheaper cost than processed crude oil.

Further evidence of the negative FCCU based MTBE process economics as related to this study is that after the installation of the 1000 m /SD isomerization unit, the LP predicted no ether octane enhancement was necessary and cut back on MTBE production utilizing more of the FCCU derived isobutene as alkylation feedstock. As well, the isobutene content of the FCCU total effluent is quite small, approximately 1.5%. Exclusive MTBE production from this source will neither constitute a large volume nor make a significant impact upon the total refinery gasoline pool.

Although this study does not show encouraging economics for the MTBE process coupled with a FCCU, MTBE is currently produced for gasoline blending. In North America, there is a large amount of MTBE processing on the U.S. Gulf Coast where the combined processing of isobutene rich petrochemical steam cracker effluent and FCCU olefins not only produce a larger volume of MTBE but also leave an effective olefin/hydrocarbon ratio for alkylation. Further, the effective separation of 1-butene from isobutene by etherification of isobutene to MTBE provides a chemical byproduct incentive for MTBE production. This result demonstrates the refinery site specific economics of MTBE production. MTBE may have an economically productive role as a gasoline blending agent for the formulation of specialty products or as an octane "trimming" blending component. For example, after lead phase down, refineries will have more difficulty in maintaining octane quality. If this octane quality shortage is small, the use of MTBE could have an economic advantage over the installation of other more expensive alternatives such as isomerization.

TAME Process

The LP results predict that TAME gasoline is profitable with the current refinery and with lead and manganese permitted. These savings are caused by the reduced TEL and MMT requirement. However, after the installation of the isomerization unit in base case No. 2, the refinery had surplus octanes processing capability. Unlike the MTBE process, Table 6 shows a small positive octane-m /year contribution ranging from 0.7 to 1.0 for the TAME gasoline when the total FCCU gasoline octane-m data are considered. However, since the isoamylene content of the FCCU reactor effluent is only 1.5% active olefin and conversion is only 43.5%, octane upgrading from such a process will not have a large effect on the gasoline pool, approximately 0.35 calculated octane numbers. For this reason, the TAME process must be considered as an octane trimming operation.

Isomerization Process

The DiH naphtha was improved by 5.1-6.9 x10⁶ octane-m³/year in the four study cases where the isomerization unit was installed. This octane upgrade was sufficient to permit the refinery to dispense with other forms of octane improvement including the etherification processes and the lead and manganese additives. The large capital cost of the isomerization reactor unit, estimated at \$18 M for this study, required an 11 year ROI to recover the cost. Additional LP studies involving refinery flexibility, volume and mix of product sales and associated penalties would probably enhance the economics of the isomerization installation.

Additional Considerations

Given lead phasedown and the possible prohibition of MMT, the refiner would be required to make drastic changes to his operation to account for the octane shortage. For the typical Canadian refinery studied in this work, the LP study suggests the isomerization reactor would be successful in accommodating the octane shortfall. However, the refiner would prefer to exhaust other low capital cost alternatives such as:

- i) The FCCU would be operated at high severity with the appropriate high octane catalysts;
- ii) The reformer units would be optimized for maximum octane and high severity;
- iii) The crude oil and product slates would be modified to allow the reformer capacity to rise to the nominated design; and
- iv) The purchase of higher naphtha content raw materials.

These modifications would increase the octane content of the gasoline pool to where purchase or on-site manufacture of MTBE and

TAME could complement or provide the final octane trimming. Presumably, operation of the FCCU at high severity with high octane catalyst could possibly provide the additional olefins necessary to allow the alkylation units to remain at full capacity if an MTBE plant was brought on-stream. It should be noted that this assumes that prices of the various components shall remain stable after the imposition of lead phase down.

CONCLUSIONS

LP results suggest that MTBE processing from FCCU olefins only is not economically viable in all of the cases studied. Other cases that include the use of C_4 olefins from outside the refinery limits were not included in this work. The LP results indicate that the TAME process can be economically viable for the current refinery configuration with the use of lead and manganese. However, the contribution of TAME gasoline and MTBE were inadequate to provide sufficient octane after lead phase down. The installation of an isomerization unit overcompensated for the octane loss at a high cost, and the use of additional ethers was not necessary.

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Table 1 Annual Refinery Product Demands¹

Product	Demand, <u>m /day</u>
Leaded Regular Gasoline	730
Unleaded Regular Gasoline	5110
Unleaded Premium Gasoline	1460
Jet Fuel B	150
Jet Fuel A	810
Kerosine/Stove Oil	90
Diesel Fuel, Winter	1750
Diesel Fuel, Summer	1170
Light Furnace Oil	1700
Total ²	12970

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2 Refinery product demand is an estimate for the middle 1990's.
Heavy fuel oil, light petroleum gas, and fuel gas are produced to balance
refinery operations.

Gasoline Specifications Table 2

Average Octane,	Leaded ¹	Unleaded ²	Premium ²
<u>(RON+MON)/2, min.</u>	<u>Regular</u>	<u>Regular</u>	<u>Unleaded</u>
Prairie Provinces	88.3	88.3	90.8
Elsewhere	89.8	89.0	91.8
Volatility, ³	Minimum	Maximu	m
	<u>RVP, kP</u>	<u>a RVP,</u>	<u>kPa</u>
Summer	-	76.	3
Average	-	90.	2
Winter	62.4	104.	1

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2 Lead content less than 0.29 g/L, 1987.
3 Manganese methyl tricarbonyl content of less than 0.018 g/L.
6 Canadian Grades and Standard Board (CGSB) specifications CAN2-3.1 and
6 C CAN2-3.5.

Table 3 Raw Material Costs¹

Source	<u>\$/m</u> 3
Syncrude B.C. Light Crude Peace River Crude Field Butane Natural Gas Methanol	119.40 120.90 120.90 102.80 87.40 94.80

¹ Costs from reference 1.

Table 4 LP Study Cases

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	Base				Base			
	Case							
			2	3		4	5_	6
Lead/Manganese Permitted	yes	yes	yes	yes	no	no	no	no
MTBE Processing	no	yes	no	yes	no	yes	no	yes
TAME Processing	no	no	yes	yes	no	no	yes	yes
Isomerization	no	no	no	no	yes	yes	yes	yes

Table 5 Comparison of Gross Income for LP Study Cases

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Unit Process	Octane-Volumes/Year, Octane-m ³ /a x 10 ⁶							
	Case	Case	Case	Case	Case	Case	Case	Case
		1	2	3	2	4	5_	6
MTBE	-	2.7	-	2.7	-	2.6	-	1.2
Alkylate	33.0	26.3	32.8	26.3	32.8	25.7	32.7	29.4
MTBE Contribution	-	-4.0	-	-4.0	-	-4.5	-	-2.2
TAME Gasoline	-	-	16.1	16.1	-	-	16.1	16.1
FCCU Gasoline	93.3	93.0	78.2	77.9	93.3	92.5	77.8	77.9
TAME Contribution	-		+1.0	+0.7	-	-	+0.7	+0.7
Mixed C_{r}/C_{c}	25.3	26.3	25.5	26.3	-	-	-	-
Isomerate	-	_	-	-	30.4	32.2	30.5	31.8
Isomerate Contr.	-	-	-	-	+5.1	+6.9	+5.2	+6.5
Platformate	33.1	35.0	33.5	35.2	32.0	34.1	32.2	33.1
Butane	28.4	28.4	27.4	27.4	27.4	27.3	26.4	26.3
Lead/MMT Addtive	3.7	4.4	3.2	4.1	-	-	-	-
Total	239.3	239.3	239.2	239.3	239.1	238.9	239.0	239.7

Table 6 Refinery Gasoline Octane-Volumes

Unit Process	Processed Volume, $m^3/a \times 10^6$							
	Base	Base Base						
	Case	Case	Case	Case	Case	Case	Case	Case
	1_	1		3	2_	4_	5_	6
MTBE	-	0.025		0.025		0.024	-	0.011
A1ky1ate	0.359	0.287	0.357	0.287	0.357	0.280	0.356	0.320
TAME Gasoline	-	-	0.177	0.177	-	-	0.177	0.177
FCCU Gasoline	1.060	1.054	0.888	0.880	1.059	1.049	0.888	0.884
Mixed C_{c}/C_{c}	0.340	0.354	0.343	0.354	-	•••	-	-
Isomerate	-	-		-	0.334	0.353	0.335	0.344
Platformate	0.351	0.372	0.355	0.375	0.352	0.374	0.353	0.363
Butane	0.299	0.299	0.289	0.289	0.288	0.287	0.278	0.277
Total	2.668	2.670	2.699	2.667	2.669	2.668	2.670	2.668

Table 7 Refinery Gasoline Processing Volumes

LP.DOC April 8, 1988 Ottawa

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