

Ethyl Tertiary Butyl Ether – A Review of the Technical Literature

Graeme Wallace

European Fuel Oxygenates Association

Jacques Blondy

Total

Walter Mirabella

LyondellBasell Industries

Ekkehard Schulte-Körne

Evonik Oxeno

Jorma Viljanen

Neste Oil

Copyright © 2009 SAE International

ABSTRACT

Ethyl tertiary butyl ether (ETBE) has been used as a high octane blending component since the early 1990's. However the strong interest in renewable energy has led to a dramatic increase in its use. This has also resulted in a substantial number of technical studies being carried out around the world to assess its performance with respect to vehicle performance, distribution system compatibility, environmental impact and toxicology. The purpose of this paper is to provide a comprehensive, up to date review of these data. Particular focus will be given to its positive impact on CO₂ emissions.

INTRODUCTION

The drive in the 1980's to improve air quality led to the introduction of catalytic converters to reduce hydrocarbon, carbon monoxide and nitrogen oxide emissions. These required the use of lead free petrol

which created the demand for high octane non-metallic blending components. This demand was met by the introduction of oxygenated materials primarily methyl tertiary butyl ether (MTBE). The ethyl homolog (ETBE) although considered equivalent in performance remained more of technical interest due to its poorer economics.

All this changed in 1992 when France offered incentives to use home grown ethanol in petrol and bio-ETBE entered the petrol pool. A similar system was also introduced in Poland. This remained the extent of its use until the European Union introduced a directive designed to promote the use of biofuels (1). The directive required Member States to set indicative targets, based on energy content, for biofuels use in petrol and diesel with the reference values being 2% in 2005 and 5.75% by 2010. Due to the ease of blending and compatibility with vehicle and distribution systems ETBE quickly became an important route for the delivery of bio-ethanol into petrol. This is reflected in the rapid conversion of the European

ether industry from MTBE to bio-ETBE production. In 2004 bio-ETBE represented less than 10% of the nameplate capacity of the European Fuel Oxygenates Association members whilst in 2007 it was close to 70% (2). Interest in bio-ETBE is by no means restricted to Europe with many other countries, most notably Japan, looking to use it to meet their biofuels goals.

This dramatic increase in the use of bio-ETBE has brought with it a surge in research to understand all aspects of its performance and this paper is intended to summarise these data with respect to vehicle performance, distribution system compatibility, environmental impact and toxicology.

BLENDING PROPERTIES

When blending petrol 3 of the main parameters that have to be controlled to ensure it meets the required specification are; vapour pressure, distillation characteristics and octane number.

The blending Vapour Pressure (DVPE) of pure ETBE is 28kPa, well below that of finished petrol, thus allowing the use of more light hydrocarbons, typically butane during petrol blending. Some polar contaminants of commercial ETBE, such as ethanol, will blend non-ideally in petrol, and thereby generate vapour pressure increases much higher than reflected by their true vapour pressure. Therefore, it is important to keep these contaminants to a reasonably low level in commercial ETBE in order to maximise its vapour pressure benefit.

The following Antoine equation for vapour pressure calculation has been derived for pure ETBE (3):

$\ln p_{ETBE} \text{ (Mpa)} = 8.2493 - 3454.18 / (T(K) - 18.231)$, where T (K) is the temperature in Kelvins.

This is shown graphically in Figure 1 below.

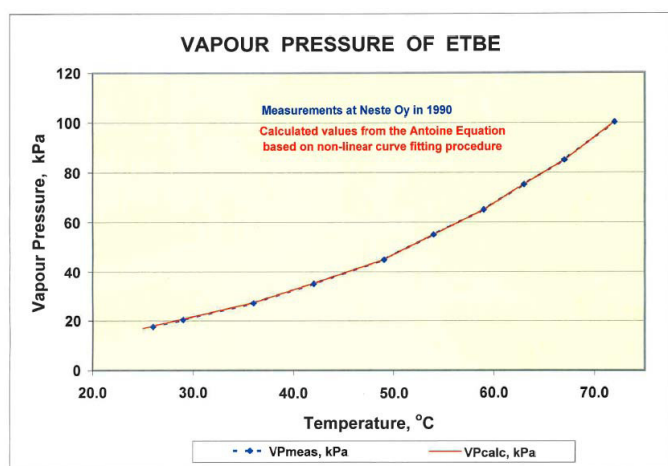


Figure 1: Vapour Pressure of ETBE

ETBE has no azeotropic effects on the distillation curve of petrol. Therefore, ETBE blends into petrol in a smooth, predictable fashion much like any other hydrocarbon that boils in the same temperature range.

The effects of ETBE and other oxygenates on the petrol distillation curve are illustrated in the following chart which shows the distillation impact for three oxygenates blended at 3.7 wt.% oxygen (23 vol.% ETBE, 20 vol.% MTBE and 10 vol.% ethanol or E 10) as well as a 5.4 vol.% ethanol blend or E 5.4 (2 wt.% oxygen). (4) Of all the distillation specifications for petrol, the volume percent evaporative at 70°C (Evap @ 70°C) is probably the most significant since it has such a large impact on a number of factors such as vehicle's operating performance (hot vapor locking), and evaporative emission performance (5) as well as the refiner's petrol blending flexibility to utilize other non-petroleum components such as light naphthas from natural gas condensates which also contain large amounts of hydrocarbons that boil below 70°C.

As illustrated in the chart, the various oxygenates differ significantly in their impact on the volume percent evaporated at 70°C. Because of the proximity of its boiling point temperature (72°C) to 70°C, blending large amounts of ETBE has little or no impact on the Evap @ 70°C. Most of ETBE's temperature decrease for petrol occurs near the mid-range portion of the distillation curve which should improve vehicle warm-up during cold engine operation without any unfavorable impact on hot driveability performance of the gasoline.

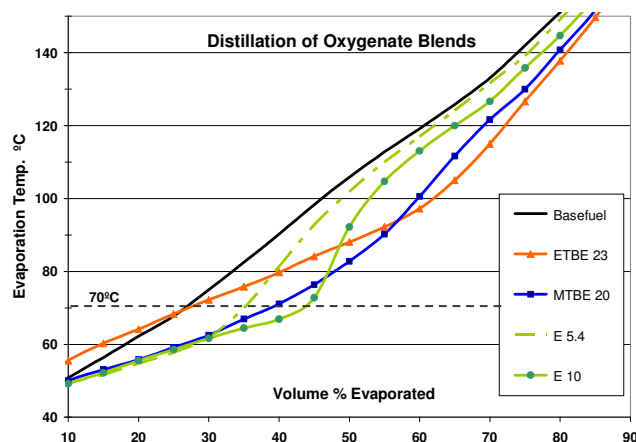


Figure 2: Distillation of Oxygenated Blends

As regards octane number ETBE, like its fellow ethers, is a high octane blending component (RON 119, MON 113). The actual octane increase it will deliver depends on the base petrol into which it is blended and this is reflected in the blending octane numbers. These are illustrated in the table (6) below:

	MTBE	ETBE	Euro Grade Specification (min)
bRON	117	117	95
bMON	101	102	85
bAKI	109	110	-

Table 1: Blending Octane Number

Octane sensitivity is the difference between RON (research octane) and MON (motor octane). The octane of the petrol mixture can increase or decrease as one component replaces another component, and will thereby determine if the petrol will be limited by the MON minimum specification or the RON minimum specification. Figure 3 below illustrates the relative octane sensitivities of components used to supply octane to the petrol. Since oxygenates are used to commonly replace aromatic octane in petrol, the impact on the petrol's octane sensitivity will be dependent on the type of oxygenate used for octane replacement. The octane sensitivity of ETBE is similar to that of aromatics such as toluene thus replacing aromatics with ETBE in the petrol mix will have little impact on the refiner's octane sensitivity balance. Alcohol on the other hand has a wider octane sensitivity and thus supplies less MON. Depending the national octane limit (RON or MON), the octane sensitivity of the oxygenate used will have economic implications for the individual refiner. Historically Europe has been MON limited which is generally a higher cost octane to produce in the refinery.

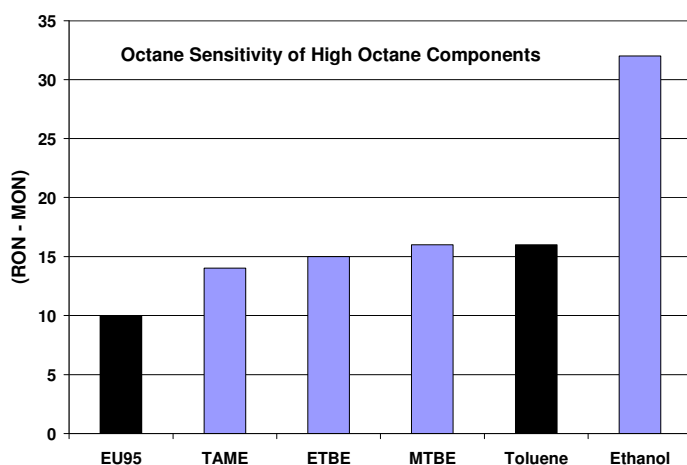


Figure 3: Octane Sensitivity of High Octane Blending Components

COMPATIBILITY

Sealants are a vital part of a vehicle fuel system and OEM's (Original Equipment Manufacturers) take great care to select the most appropriate elastomer. Factors such as temperature, pressure and required service life are taken into consideration along with the nature of the fuel they will be in contact with and the degree of that contact. Compatibility is often assessed by volume swell

in long term immersion tests as the swell is related to the mechanical strength of the elastomer. In general, the greater the increase in volume swell for an elastomer, then the greater will be the loss of the elastomer properties for service in liquid sealing and permeation (7, 8). Whilst OEM's may have different criteria for different elastomers a good rule of thumb appears to be that swells of less than 20% in the fuel solution will provide acceptable service and life (8).

In 1990, ARCO Chemical Company conducted elastomer swell tests for 13% MTBE and 13% ETBE (~ 2 wt% oxygen) fuel blends, and neat ETBE, and found the elastomer swell in neat ETBE to be less than in petrol (premium gasoline) for all elastomers except for the Viton A fluoroelastomer which only experienced a small increase (9).

**Table 2
Elastomer Volume Swell (%) after 30 days @ 24 °C**

<u>Elastomers</u>	<u>Fuels</u>			
	Premium Gasoline	+13% MTBE	+13% ETBE	100% ETBE
NEOPRENE polychloroprene	54	58	50	27
CHEM RAZ perfluoroelastomer	26	29	26	22
BUNA N (nitrile rubber)	25	28	26	13
Polyurethane	21	22	21	19
HYDRIN 200 epichlorohydrin	13	12	12	6
VITON A elastomer	3	11	7	8
Poly vinyl chloride (PVC)	1.6	0.9	1	0.7
DELDRIIN polyacetal	0.7	1	0.9	0.5
Fiberglass (FRP)	0.4	0.4	0.3	-0.1
NYLON 6/6	0.1	0.5	-0.4	-0.4

The most recent swell data for oxygenated fuel blends are reported on DuPont's elastomer website for fluoroelastomers, and an example is plotted in the chart below that includes MTBE, TAME, ethanol and ETBE. In general ETBE blends produced the lowest seal swell. Based on these results, DuPont recommends the use of all fluorinated elastomers for all ETBE concentrations up to 100%.

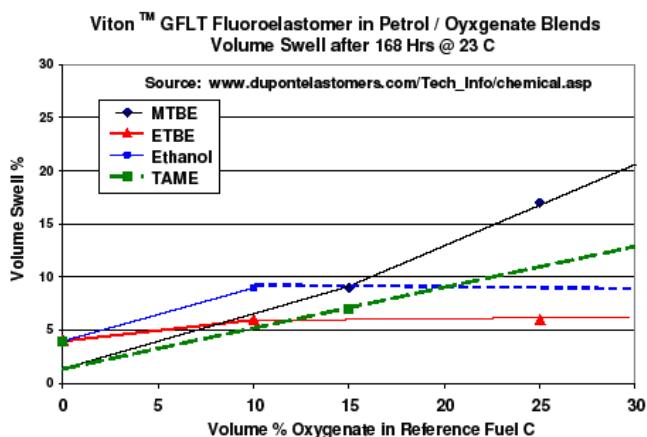


Figure 4: Volume Swell of Viton GFLT Fluoroelastomer

Likewise a comprehensive study by the Japan Auto and Oil industries on ETBE blends up to 17%, in fuel, found no significant difference in elastomer swell as well as no loss in elastomer performance properties (10). A list of all the materials tested in the study follows.

Table 3
Summary of Compatibility Testing Methods for Rubber and Resins
Base Fuel with 8% and 17% ETBE Blends

1) Immersion Test for Rubber Materials

Target Rubber Materials:

Hydrin rubber (CHC)
Fluoro rubber (FKM)
Fluorosilicon rubber (FVMQ)
Nitrile butyl rubber (NBR)
Hydrogenated nitrile butyl rubber (H-NBR)
Nitrile butyl rubber/polyvinyl chloride resin (NBR/PVC)

Immersion Condition:

Full immersion in test fuel at 70°C for 144/480/720 hr

Measurement Parameter:

Hardness Test
Tensile Test
Volume & Mass Change Rate

2) Immersion Test for Resin Materials

Target Resin Materials:

Ethylene vinyl alcohol (EVOH)
Polyamide (PA11)
Polyacetal (POM)
Polyphenylene sulfide (PPS)
Phenol resin

Immersion Condition:

Full immersion in test fuel at 70°C for 144/480/720 hr

Measurement Parameter:

Hardness Test
Impact Test
Volume & Mass Change Rate

Source: SAE 2006-01-3381

The study also conducted a 40,000 km durability study with 8% and 17% ETBE fuel blends, and found that the evaporative emissions from the vehicles during the study were not significantly impacted from using ETBE in the fuel.

The ability of a fuel to permeate through elastomers is a strong function of its ability to swell the elastomer. Since prior data sets show that ETBE blends at all ETBE concentrations generate low or little additional elastomer

swell as compared to oxygenate-free petrol base fuel, then ETBE blends would not be expected to increase fuel permeation emissions as compared to the petrol base fuel.

VEHICLE PERFORMANCE

As a part of an extensive test programme with oxygenated fuels in the early 1990's, Neste Oil performed driveability tests on a chassis dynamometer with a series of petrols containing ETBE or ethanol (6). Oxygenate contents exceeding the then allowed European maximum limits were also used.

Both with ETBE and ethanol three summer and three winter grade petrol blends with varying oxygenate contents were prepared from refinery components for hot and cold weather driveability tests, respectively. The test fuels were smart-blended to meet then-current specifications for finished petrol; other than oxygen content. For comparison, tests were also performed on RON 95 Eurograde petrol samples that were taken from the refinery customer distribution outlet. Both the summer and winter grades of this commercial petrol contained approximately 10 wt % of MTBE.

The volatility properties of the fuels are shown in Appendices 1 and 2, where also distillation curves are displayed. The ETBE content varied from 13 wt % to 20 wt % resulting in the oxygen content range of 2 – 3 wt %. While the ethanol blends contained from 7.2 wt % to 12.3 wt % (oxygen 2.5 – 4.3 wt-%). Octane ratings are not reported in the tables, but all fuels met the minimum requirements RON 95 and MON 85.

Two vehicles with relatively low mileage were used in the driveability tests. The main characteristics of the cars are given in Table 4 below.

Table 4
Driveability Test Vehicle Specification Data

	<u>Car A</u>	<u>Car B</u>
Type	Japanese	German
Model year	1990	1993
Mileage, km	23,000	12,000
Engine displacement, L	1.3	1.3
Fuel system	Carburettor	MPI
	Non-catalyst	Catalyst
Transmission	Manual, 5 speed	Manual, 5 speed

The cold weather driveability tests were run according to the test procedure CEC M-08-T-83 and I-CVD-SG(1990) rules at the temperatures of -5°C, -15°C, and -25°C. Starting times were also measured. All fuels had good starting properties and there were no fuel-related problems or differences. In all other tests, time to start was less than 2 seconds but at -25°C Car A required somewhat longer times.