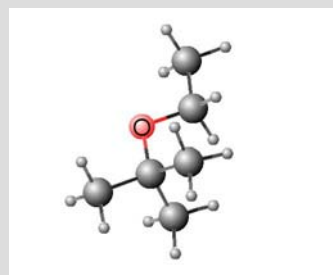




Technical Product Bulletin

ETBE

(Cas number 637-92-3)



June 2006

Disclaimer of Liability

As the conditions or methods of use of ETBE (Ethyl tertiary butyl ether) by you and third parties are beyond our control, we do not assume responsibility and expressly disclaim any liability for any use of ETBE. Information contained herein is believed to be true and accurate but all statements or suggestions are made without warranty, express or implied, regarding accuracy of the information, the hazard connected with the use of ETBE, or the results to be obtained from the use thereof, nor should freedom from any patent owned by others be inferred.

No conclusion may be drawn from the tests with materials specified in this bulletin with respect to any components or material included in the list of tested materials.



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I. INTRODUCTION

Ethyl tertiary butyl ether (ETBE) is a biofuel. It is a clear, colourless to pale yellow liquid organic compound with a distinctive ether-like odour, derived from ethanol (47% v/v) and isobutylene (53% v/v). The ethanol can come from any renewable source, e.g. as a co-product of sugar production from various crops such as wheat, beet; whilst the isobutylene is derived from crude oil or natural gas. The isobutylene sources include cracked stocks from refineries and steam crackers, or from chemical plants via dehydrogenation or dehydration processes.

ETBE is an oxygenated gasoline fuel component and ether. The better known oxygenates used today are methyl tertiary butyl ether (MTBE), ethanol and ETBE. Oxygenates are used as octane boosters to replace toxic and carcinogenic compounds such as lead, they have a positive effect on air quality and thus have a direct positive impact on human health and the environment. Ethers have been used in gasoline for over 30 years at various levels up to 15% and are thus fully compatible with the existing distribution infrastructure and the existing vehicle fleet. ETBE was first used in 1992, in France, and today is widely used and manufactured in most major gasoline markets in the EU.

ETBE's unique properties of high octane, low boiling point and low vapour pressure make it a very versatile gasoline blending component, allowing refiners to address both their octane and bio-component incorporation needs. ETBE also allows petroleum companies to adjust to changing gasoline markets by using it to upgrade naphtha to gasoline or to upgrade lower octane gasoline grades to higher ones while meeting increasingly stringent environmental specifications.

These unique blending properties coupled with ETBE's oxygen content allow petroleum companies to produce cleaner burning renewable gasoline that reduces the vehicle emissions that are the precursors to ozone and particulate matter in the atmosphere. Blending ETBE also helps to achieve the lower aromatic levels specified within the EU Fuel Quality Directive.

The demands on gasoline quality are increasing for many reasons; such as improving vehicle performance and meeting environmental requirements. This is clearly illustrated in the Worldwide Fuel Charter developed by the world's automobile manufacturers. These higher quality demands are leading to increasingly tighter gasoline specifications. ETBE's blending properties help the petroleum industry to produce gasoline that meets these increasingly more stringent specifications at lower manufacturing investment costs and thereby at a lower cost to consumers and society.

EFOA believes that ETBE represents a major opportunity for a practical, efficient development of biofuels and that it will play an increasingly important role in the future as governments and consumers around the world continue to call for cleaner burning gasoline and the use of crude-alternative biofuels.

II. PHYSICAL PROPERTIES

PARAMETER		Conditions	UNITS	ETBE
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ENERGY

COMBUSTIBLE MASS		-	% wt	84.3
COMBUSTION STOICHIOMETRY		-	----	$C_6H_{14}O + 9O_2 = 6CO_2 + 7H_2O$
LATENT HEAT OF VAPORIZATION	$v_{AP}H^\circ$?	<i>kJ/mol</i>	32.97
ENTHALPY OF VAPORIZATION	$v_{AP}H$	72.5°C	<i>kJ/mol</i>	29.76
LOWER HEATING VALUE	LHV	wet	<i>MJ/kg</i>	36.2
HIGHER HEATING VALUE	HHV	dry	<i>MJ/kg</i>	39

CHEMISTRY

NAME		-	----	Ethyl Tertiary Butyl Ether
FORMULA (BRUTE)		-	----	$C_6H_{14}O$
FORMULA		-	----	$(CH_3)_3COCH_2CH_3$
MOLECULAR WEIGHT	MW	-	<i>g/mol</i>	102.18
IR Spectrum	IR	-	<i>cm⁻¹</i>	(see spectrum)
MASS Spectrum	MS	-	<i>amu</i>	(see spectrum)
CARBON CONTENT	C	-	% wt	70.53
HYDROGEN CONTENT	H ₂	-	% wt	13.81
OXYGEN CONTENT	O ₂	EN1601	% wt	15.66
pH	pH	ASTM D6423		~6.4

PHYSICAL

PHYSICAL STATE		normal	----	Liquid
COLOUR		ISO 6271/1	----	Colourless
DENSITY	δ	ISO 3675	<i>kg/l</i>	0.745
SPECIFIC GRAVITY		15°C, 1 Bar	----	0.746
REFRACTIVE INDEX	n_D	20°C	----	1.3756
VISCOSITY		ISO 3104, 25°C	<i>mPa.s</i>	< 1
MELTING TEMPERATURE	FP	1 Bar	°C	-94
VAPOUR PRESSURE	DVPE	EN13016/1	<i>kPa</i>	28
INITIAL DISTILLATION TEMPERATURE	IBP	ISO 3405	°C	71.7
T10	T10	ISO 3405	°C	72.8
T50	T50	ISO 3405	°C	72.8
T90	T90	ISO 3405	°C	73.3
FINAL DISTILLATION TEMPERATURE	FBP	ISO 3405	°C	79.4
RELATIVE VAPOUR DENSITY (Air=1)		15°C	----	~3.5
E 70 °C	E70	ISO 3405	% vol	0-30
SOLUBILITY (Water in Fuel)		21°C	%	0.5
SOLUBILITY (Fuel in Water)	S	21°C	%	1.2
PARAMETER		Conditions	UNITS	ETBE

ENGINE

OCTANE	RON	<i>ISO 5164</i>	<i>RON</i>	119
	MON	<i>ISO 5163</i>	<i>MON</i>	103
	AKI	----	<i>RON+MON/2</i>	111
DRIVEABILITY INDEX	DI	<i>1 Bar</i>	<i>°C</i>	401

ENVIRONMENTAL

AZEOTROPES with BENZENE	----	----	<i>°C</i>	NO
OCTANOL PARTITION COEFFICIENT	log Kow	?	----	1.48-1.56
ORGANIC CARBON PARTITION COEFFICIENT	logKoc	?		1.57
HENRY'S LAW CONSTANT	H	<i>25°C</i>	<i>Pa.m3/mol</i>	166
DIFFUSION COEFFICIENT IN PURE AIR	Dair	?	<i>m²/d</i>	0.6
DIFFUSION COEFFICIENT IN PURE WATER	Dwater	?	<i>m²/d</i>	6.34E-05
ATMOSPHERIC DEGRADATION CONSTANT		?	<i>cm³/mlc*s</i>	4.8-8.8E-12

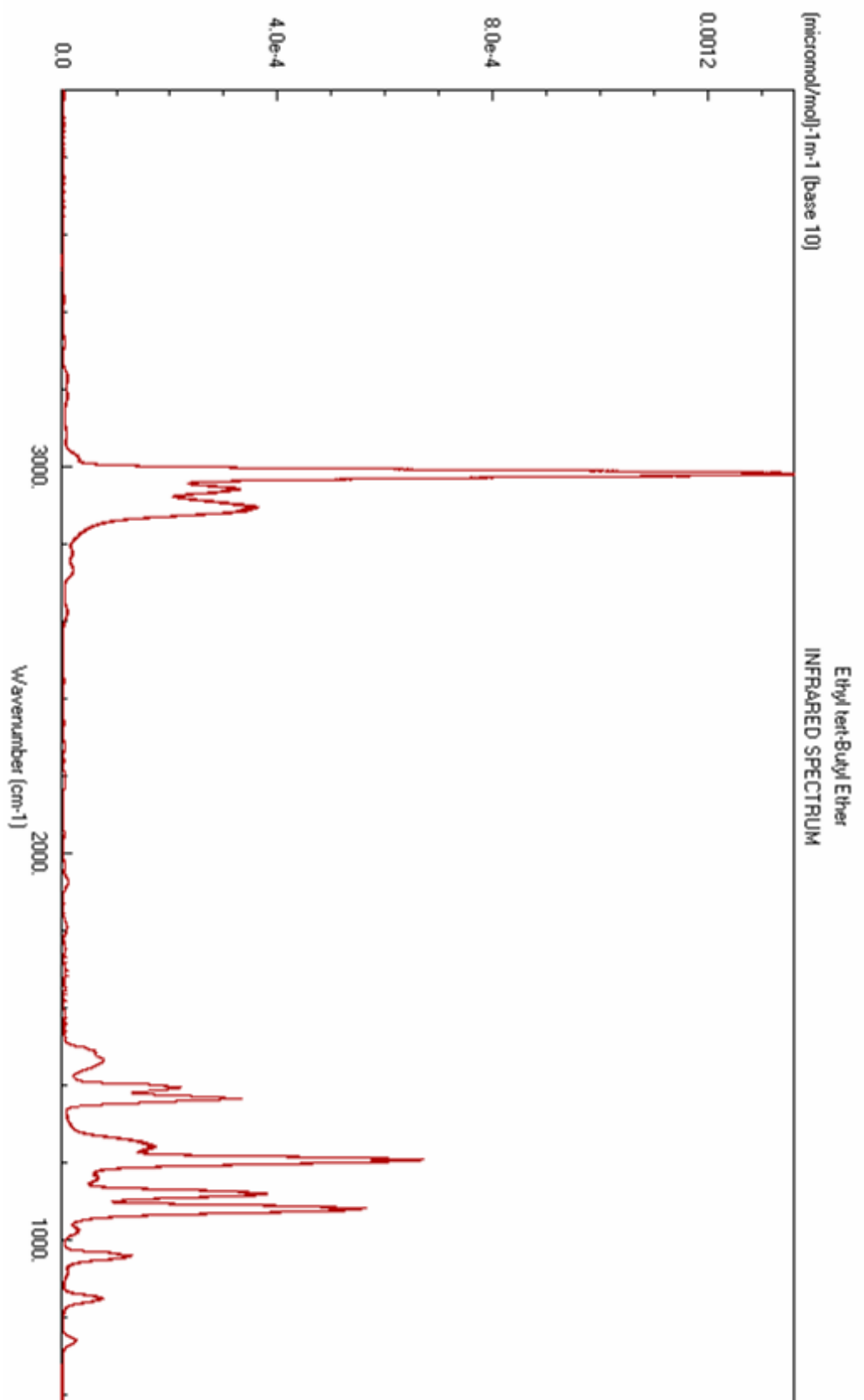
SAFETY/HEALTH

CAS Registry N°	CAS	----	----	637-92-3
EU Inventory	EINECS	----	----	211-309-7
RTECS	RTECS	----	----	KN4730200
OCCUPATIONAL EXPOSURE LIMIT	OEL	<i>8 HRS/TWA</i>	<i>ppm</i>	5
FLASH POINT	FP	<i>ISO 2719</i>	<i>°C</i>	-19
AUTOIGNITION TEMPERATURE	AIT	<i>ASTM E659</i>	<i>°C</i>	310
UPPER FLAMMABILITY LIMIT	UFL	?	<i>%v/v</i>	6
LOWER FLAMMABILITY LIMIT	LFL	?	<i>%v/v</i>	1
FLAMMABILITY CLASSIFICATION	----	<i>OSHA/NFPA</i>	----	1B
R PHRASE	----	----	----	R11
S PHRASES	----	----	----	S16, 23, 29, 33

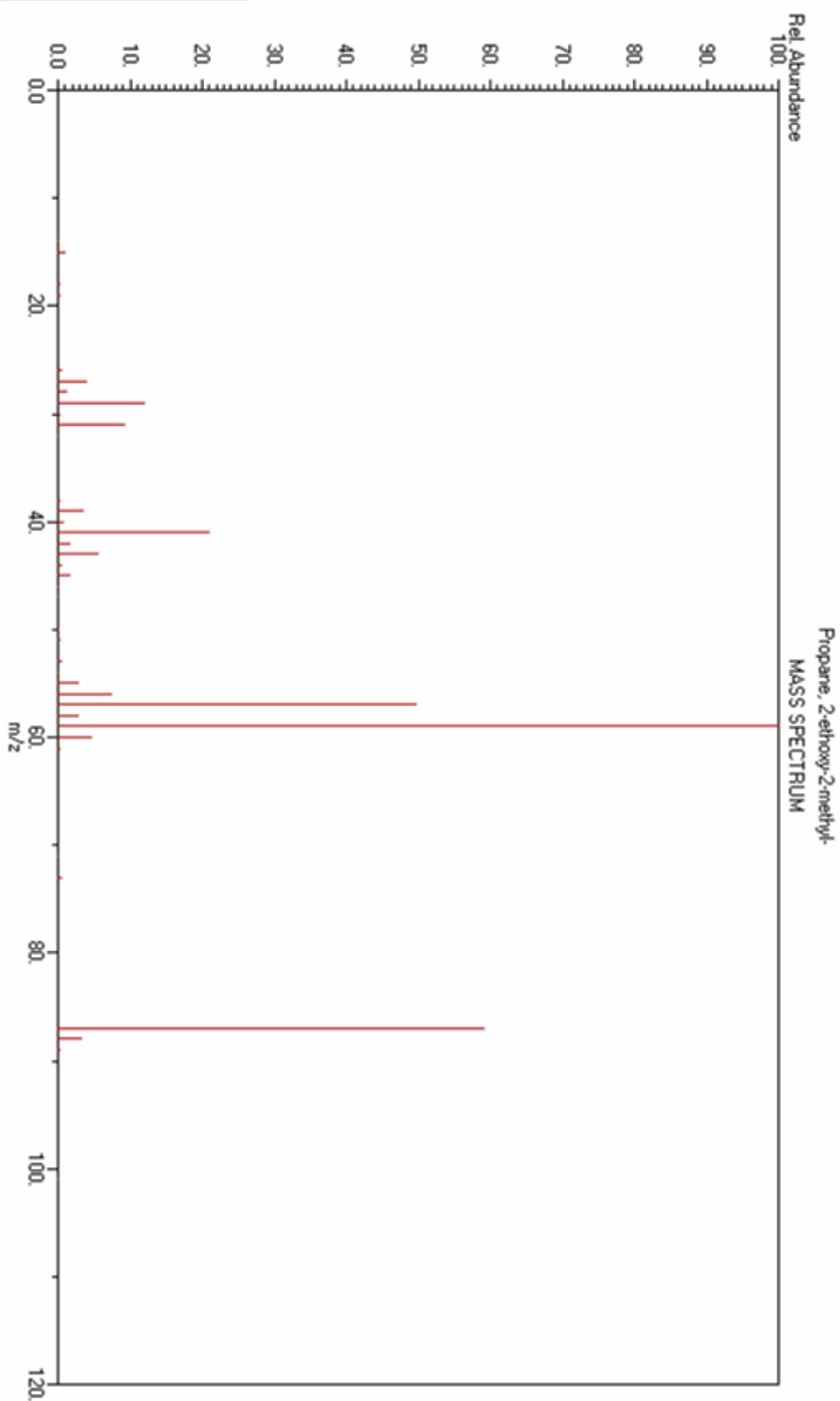
ORGANOLEPTIC

ODOUR THRESHOLD (Detection)	----	?	<i>ppb</i>	13
ODOUR THRESHOLD (Recognition)	----	?	<i>ppb</i>	25
TASTE THRESHOLD (Detection)	----	?	<i>µg/l</i>	47
TASTE THRESHOLD (Recognition)	----	?	<i>µg/l</i>	?

III. GAS PHASE INFRA-RED SPECTRUM



IV. MASS SPECTRUM



V. OCTANE IMPROVEMENT

The octane number improvement with ETBE in general depends on the base gasoline. Clear octane numbers for ETBE are relatively high and therefore ETBE is used widely to improve the octane rating for gasoline.

The blending octane numbers of different ethers and ethanol are illustrated in the table below:

	MTBE	TAME	ETBE	EtOH	Euro Grade Spec (min)
bRON	117	112	117	128	95
bMON	101	98	102	96	85
bAKI	109	105	110	112	---

Source: Neste Oil Oyj

VI. BLENDING VAPOUR PRESSURE

Unlike alcohols, ETBE has no azeotropic (non-ideal) effects on the vapour pressure of gasoline. Therefore, ETBE blends at or near its true vapour pressure. This volatility blending property makes ETBE ideal for improving the front end octane number of gasoline, which is significant in maximising performance in the high RPM engines of today's vehicles.

The blending Vapour Pressure (DVPE) of pure ETBE is 28kPa, well below that of finished gasoline, thus allowing the use of more light hydrocarbons, typically butane during gasoline blending. Some polar contaminants of commercial ETBE, such as ethanol, will blend non-ideally in hydrocarbons such as gasoline, 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 to gasoline.

The vapour pressure of pure ETBE was measured by Petri Lundqvist in 1990 and the results are given in the following table.

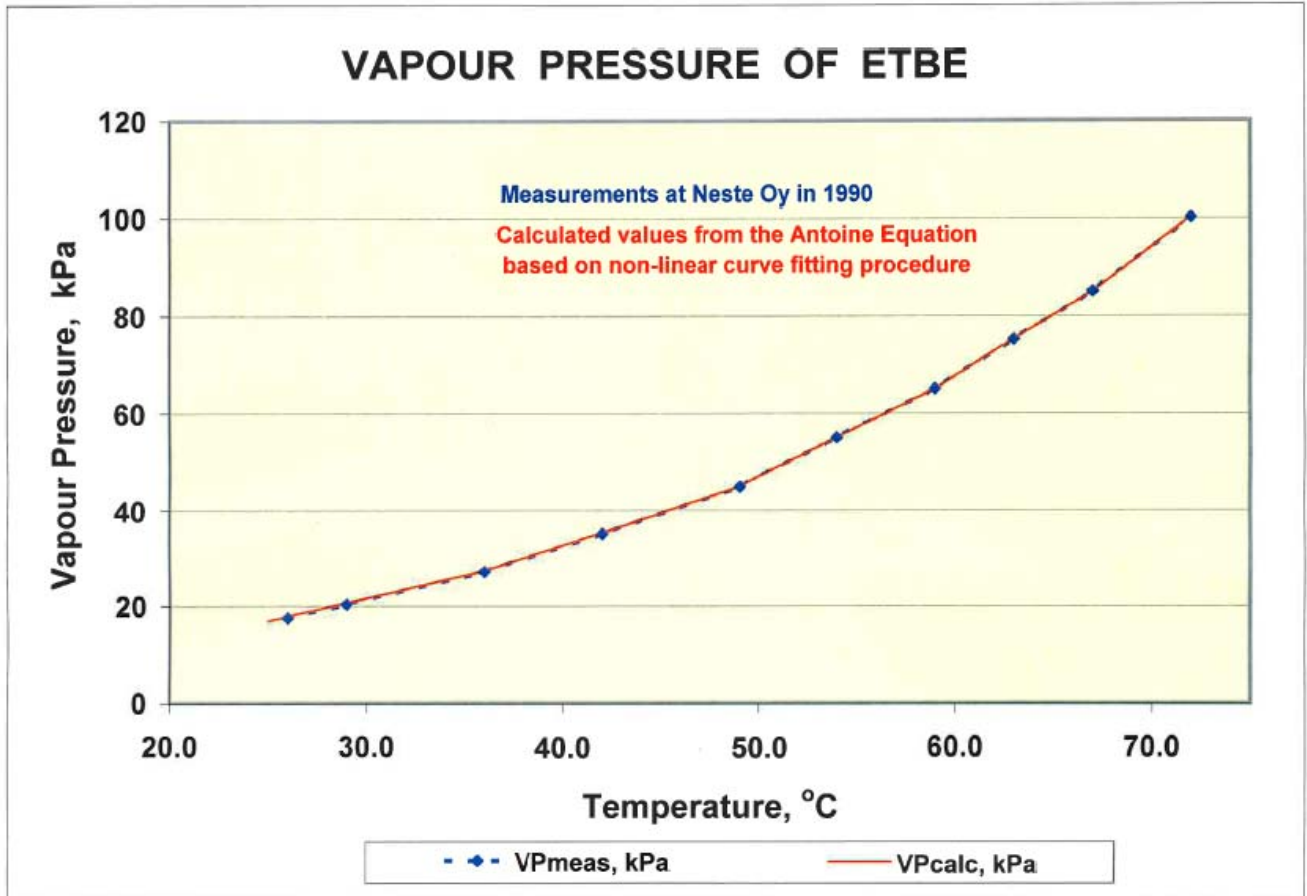
ETBE Boiling Point measurements at different pressures (Neste Oy)	
Ref.: Lindqvist, Petri, Master's Thesis (Diploma Work), 1990	
Temperature °C	Vapour Pressure kPa
26.3	17.4
29.7	20.3
36.5	27.1
42.95	35.0
49.3	44.8
54.8	54.9
59.5	64.9
63.8	75.1
67.4	85.0
72.5	100.2

From these data Lunqvist derived the following Antoine equation for vapour pressure calculation:

$$\ln p_{ETBE} \text{ (Mpa)} = 8.2493 - 3454.18 / (T(K) - 18.231),$$

where T (K) is the temperature in Kelvins.

This is shown graphically in the figure below.



VII. DISTILLATION PROFILE

Unlike alcohols, ETBE and other ethers have no azeotropic effects on the distillation curve of gasoline. Therefore, ETBE blends into petrol in a smooth, predictable fashion much like any other hydrocarbon that boils in the same temperature range. Because of its favorable boiling point (72°C), ETBE will normally reduce the mid-range temperatures of the gasoline's distillation curve. This provides added flexibility in producing high octane and/or low DVPE premium gasoline.

A comparison of typical distillation effects is contained in the following table from Shiblom, C.M., Schoonveld, G.A., Riley, R.K., Pahl, R.H.; "Use of Ethyl-t-Butyl Ether (ETBE) as a Gasoline Blending Component", SAE Technical Paper 902132, October 1990, and is illustrated in the figure below. The figure shows that adding ETBE will significantly improve key distillation performance properties such as the T50 (temperature at 50% volume distilled) and E100 (percent distilled or evaporated at 100°C). These have been identified by automobile manufacturers as key properties to improve volatility of the fuel in the engine. These properties maximise drivability performance of the fuel and minimise the exhaust emissions from the vehicle. ETBE and other ethers are the only available high octane blending components that will lower the distillation temperature of gasoline and also maintain its vapour pressure.

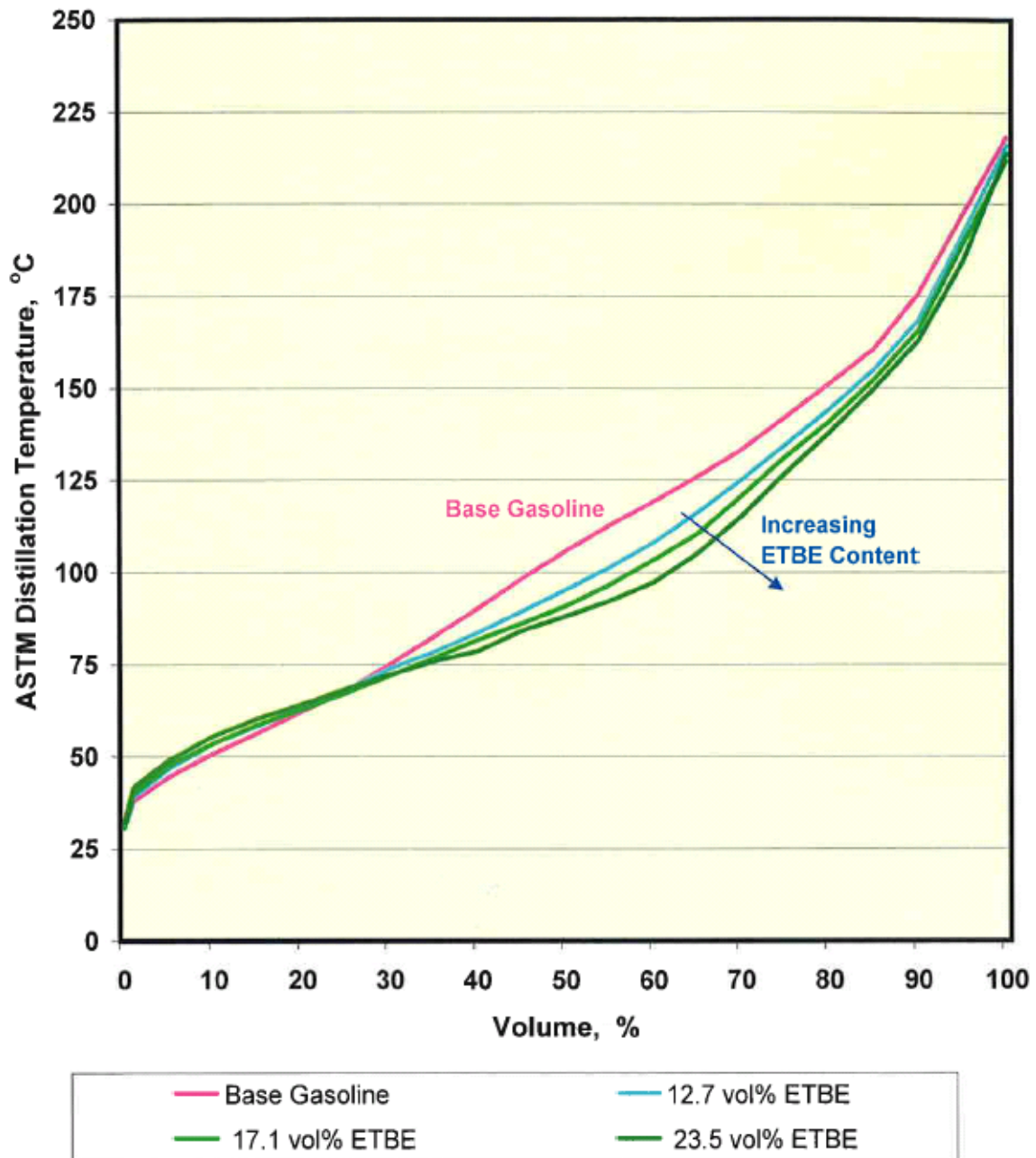
As the boiling point of ETBE is 72 °C, the percentage evaporated at 70 °C, known as E70 is expected to be low. However, in view of the closeness of its boiling point to 70 °C the other components of the blend and impurities like ethanol have a large effect. Low E70 may cause cold start problems, high E70 may cause vapour lock problems.

**PROPERTIES OF
ETBE/GASOLINE BLENDS**

ANALYSIS	UNIT	Base Gasoline	Base Gasoline + 12.7 vol% ETBE	Base Gasoline + 17.1 vol% ETBE	Base Gasoline + 23.5 vol% ETBE
Oxygen Content	wt-%	0.03	2.08	2.76	3.74
API Gravity		57.7	57.8	57.7	57.3
Sp.Gr. (@ 60°F/60°F)		0.748	0.747	0.748	0.749
Distillation, ASTM D86					
IBP	°C	30.6	30.6	30.6	31.9
5 vol%	°C	44.4	46.7	47.5	48.9
10 vol%	°C	50.8	53.6	53.6	55.6
15 vol%	°C	56.4	58.3	58.6	60.3
20 vol%	°C	62.2	63.3	62.8	64.2
25 vol%	°C	67.8	68.1	67.2	68.3
30 vol%	°C	75.0	73.9	71.9	72.2
35 vol%	°C	82.5	78.3	76.7	75.8
40 vol%	°C	90.3	83.6	81.7	78.6
45 vol%	°C	98.3	89.4	86.1	84.2
50 vol%	°C	105.8	95.3	90.8	88.1
55 vol%	°C	112.8	101.4	96.7	92.2
60 vol%	°C	119.2	108.1	103.3	97.2
65 vol%	°C	125.8	116.1	110.3	105.0
70 vol%	°C	133.1	125.0	120.6	115.0
75 vol%	°C	141.9	134.4	131.1	126.7
80 vol%	°C	151.1	144.2	140.8	137.8
85 vol%	°C	160.6	155.0	152.2	149.7
90 vol%	°C	175.6	168.3	165.6	162.8
95 vol%	°C	197.2	191.7	188.9	184.2
FBP	°C	218.3	216.1	211.9	213.9
E70	vol-%	26.5	26.7	27.9	27.1
E100	vol-%	46.1	53.9	57.5	61.8
Reid Vapor Pressure	psi	8.1	7.5		6.8
Research Octane Number		92.0	95.5	96.7	98.1
Motor Octane Number		83.1	85.8	86.5	87.6

¹ Note the E70 and E100 data is interpolated from the published data and was not reported in the original paper.

DISTILLATION OF ETBE/GASOLINE BLENDS



Shiblom, C.M., Schoonveld, G.A., Riley, R.K. and Pahl, R.H.,
"Use of Ethyl-t-Butyl Ether (ETBE) as a Gasoline Blending Component"
SAE Technical Paper 902132, October 1990

VIII. MATERIAL COMPATIBILITY

Ethers have been used in gasoline for some 30 years. In a 1999 literature review commissioned by the State Water Resources Control Board's Advisory Panel of California it was concluded that there are no documented material compatibility issues for retail stations dispensing reformulated fuels containing ethers up to 15% v/v MTBE. It was also postulated that ETBE would provide directionally improved compatibility and permeability to MTBE. This is consistent with the 1993 Dupont product bulletin "Leak Prevention of Reformulated Fuels and Oxygenates" which concludes based on swell testing that "ETBE is the least aggressive ether oxygenate towards elastomeric materials".

Actual test results were presented in SAE paper 902132 by *Shiblom et al.* The results and methodology are given below.

a. Swell Tests

These were carried out by immersing small pieces of the material in each of the 6 fuels for a period of 168 days. They were removed periodically and weighed in air and in water to determine volume changes. All test samples were duplicated in separate containers of fuel. Little differences are seen between ETBE and the base fuels. The most difference being with the high aromatic ASTM "C" blend on the N-butyl "O" ring. Replacement of 5 percent ETBE with ethanol was a little harder on the elastomers in the carburetor pump diaphragm, the N-butyl "O" ring and urethane.

b. Permeability Tests

Duplicate one foot lengths of fuel dispenser hose, hydraulic hose and neoprene fuel line were filled with the same fuels used in the swell tests. These were stored over a period of 168 days at room temperature, and periodically weighed to determine fuel loss. At least for a period of 60 days, all ETBE blends fall between the premium fuel and ASTM "C". The 100 percent ETBE in the fuel line do not show as smooth a curve beyond 60 days as expected and could be due to weighing error. This implies no more problems would encountered than with a normal gasoline.

ELASTOMER COMPATIBILITY

% SWELL AFTER 30 DAYS			
ELASTOMER	FUEL		
	Premium Gasoline	13% ETBE	Neat ETBE
NEOPRENE	53.5	49.8	27.2
CHEM RAZ	26.3	25.5	21.9
BUNA N	25.1	25.7	13.1
URETHANE	20.9	20.8	19.1
HYDRIN 100	13.2	13.5	10.3
HYDRIN 200	13.1	11.5	6.4
VITON	3.2	7.1	7.6
PVC	1.6	1	0.7
DELDRIIN	0.7	0.9	0.5
FIBERGLASS	0.4	0.3	-0.1
NYLON 6	0.1	-0.4	-0.4

IX. WATER SOLUBILITY

Of the oxygenates used in gasoline, ETBE and ethers in general are much different in water solubility than alcohols. Low molecular weight alcohols such as methanol and ethanol have infinite solubility with water which generally imposes significant restrictions on handling the alcohol blended gasoline and prevents them from being shipped in many wet common carrier systems such as barges and pipelines. As illustrated in the physical properties table at the start of the product bulletin, ETBE has relatively low water solubility which allows the refiner to mix and handle ETBE gasoline blends in much the same way as hydrocarbon-only gasolines.

Even though ETBE has low water solubility, it is still important to keep the ETBE product dry. When produced, ETBE will generally have a water content of less than 500 ppm much like many other hydrocarbons. However, neat ETBE can dissolve up to 5,000 ppm or 0.5 % of water. Therefore, it is important to keep the neat ETBE dry. This normally requires storing neat ETBE in a fixed roof tank with an internal floating roof. Also, a common practice of clearing a pipeline of the hydrocarbon line-pack by pushing water through it cannot be used following a neat ETBE movement in the pipeline. A hydrocarbon movement will have to be made before and after an ETBE movement in the pipeline to prevent water from contaminating ETBE.

Certain physicochemical characteristics determine the behaviour of any fuel component in soil, soil pores and ground water. This information is important in ensuring the correct response in the event of a spill or leak. Among the most important of these is the Henry's Law Constant. This describes the dissolving of a slightly soluble gas into a liquid, most often water. At low concentrations (in the application range of Henry's Law), the "dimensional" Henry's law constant can be calculated from the partition coefficient:

$$KH = R * T * Kaw, \text{ where } R \text{ is the ideal gas constant.}$$

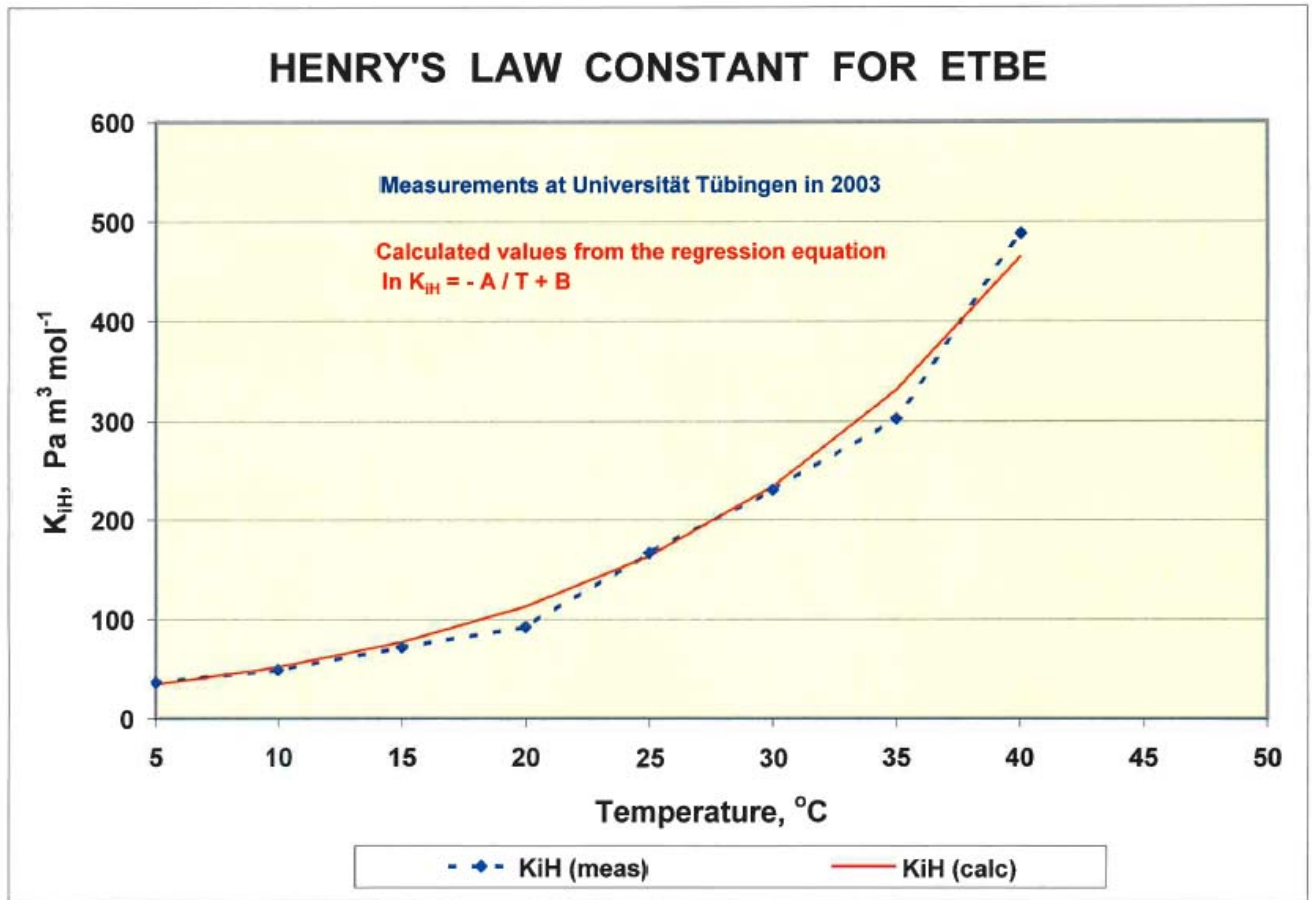
Then follows at $T = 298.15 \text{ K (} 25 \text{ }^\circ\text{C)}$:

$$KH (\text{ Pa } * \text{m}^3/\text{mol}) = 2478.7 * Kaw.$$

The graph below shows the relationship of Henry's law constant and temperature using the data from the Master's thesis by Hans Peter Arp; "The Role of Temperature on the Environmental Fate of MTBE and Alternatives", Eberhard-Karls Universität Tübingen, 24 November 2003. Arp measured ETBE's air-water partition coefficients in the temperature range from 5 to 40°C. The temperature dependence of both partition coefficient and dimensional Henry's law constant was calculated by regression analysis. For the latter the following formula was presented:

$$\ln KH (\text{ atm } * \text{m}^3/\text{mol}) = - 6510 / T (\text{ K}) + 15.4$$

These data were also used to derive the Henry's Law constant quoted in the physical properties section of the product bulletin.



X. STORAGE AND HANDLING REQUIREMENTS

Generally, storage and handling requirements for ETBE are similar as those for MTBE, which are well described in the MTBE Resource Guide (www.efoa.org) and are repeated below. Although the solubility of ETBE in water is somewhat lower than that of MTBE, the same precautions to avoid spills and remediation actions after the occurrence of a spill are applicable. The effect of ETBE on typical elastomer polymers used as seals and gaskets in the gasoline distribution systems is reported to be less aggressive, but materials' compatibility should still be checked especially when handling neat ETBE products.

However, ETBE's reactivity differs from MTBE in one respect: it can form peroxides in the presence of oxygen gas or oxidative agents. Peroxidation reaction is slow in typical storage conditions, but it is enhanced by the UV light. Peroxides in ETBE reduce its octane performance very rapidly even at low concentrations. Higher peroxide concentrations can catalyse gum formation and even lead to breakdown into corrosive acids. Therefore, peroxide formation during storing of neat ETBE should be prevented by the addition of an adequate quantity of a typical gasoline antioxidant agent such as phenylene diamine. When used in gasoline blends, no additional stabilization is needed due to ETBE. The water solubility of neat ETBE, its effect on some elastomeric polymers, and fire fighting foam requirements are different from those for gasoline. Except for these differences, design and operation standards applicable to gasoline storage and handling facilities also apply to ETBE.

Generally, all technical requirements and operational practices which apply for gasoline, are applicable for neat ether oxygenates and also gasolines containing ether oxygenates. However with the following areas requiring specific attention:

- gasket materials compatibility to be checked
- vapour recovery design, capacity to be checked
- storage tanks should have floating roofs and domes
- tank bottom water phases to be directed to adapted waste water treatment
- special emphasis on leak prevention/detection and soil/groundwater protection
- emergency response: oxygenates-compatible extinction foams, adsorbents
- minimised response time for soil/groundwater remediation in case of a leakage or splash
- medical emergency response (MSDS)

With respect to spills or leaks, owners and operators of installations that handle gasoline should be well aware of local, regional and national regulations and legislation. As a minimum, EFOA recommends to alert local water authorities in any major gasoline spill or leakage whether there is ETBE or other ether oxygenates involved or not. The same applies even for small spills and leakages in sensitive areas.

Neat ETBE is a chemically stable, highly flammable, and highly volatile liquid. Although it is relatively non-toxic to humans, it behaves as an anaesthetic when very high vapour concentrations are inhaled. It does not polymerise, nor will it decompose under normal conditions of temperature and pressure. Like most ethers, ETBE does tend to form peroxides (auto-oxidise) during storage and hence a stabiliser is normally added during manufacture.

ETBE is non-reactive. It does not react with air, water, or common materials of construction. The reactivity of ETBE with oxidising materials is probably low, however, without definitive information it should be assumed that ETBE reacts with strong oxidisers, including peroxides.

ETBE may hydrolyse in the presence of some acids. ETBE is very stable in the presence of reducing agents and reactive monomers.

Bulk quantities of neat ETBE should be received, stored, processed, and disposed of only in facilities designed for those purposes. Storage systems should be inspected for elastomer compatibility before introducing ETBE for the first time. After initial inspection, storage systems should be operated as outlined in the product safety bulletin. Appropriate emergency notification and response systems for fire and spill management should be in place at each facility where ETBE is received, stored, or used. ETBE should be handled only by workers trained in safe handling methods and response to emergencies such as spills or fires.

For more information regarding safe handling and storage always consult the manufacturer's safety data sheet.

XI. HEALTH & ENVIRONMENTAL EFFECTS

Due to the growing potential for wide dispersive use of ETBE (ethyl tertiary butyl ether) as a biofuel and as a substitute for MTBE (methyl tertiary butyl ether) in 2002 the European Commission called for additional toxicity data to be generated under Article 12 (2) of the Existing Substances Regulation (EEC No 793/93; Commission Regulation 1217/2002).issued Regulation 1217/2002.

The draft risk assessment report prepared by the Finnish rapporteur, using the data provided by industry, was reviewed by the EU Technical Committee for New and Existing Substances on November 23, 2005.

This group of national experts on health and environmental risks accepted the draft report and its conclusions i.e. not classifiable as a carcinogen, mutagen or reproductive toxin. In effect, this means that the EU will consider the ETBE risk assessment to be essentially the same as that of MTBE and will thus recommend equivalent associated risk reduction measures.

The risk assessment is expected to be finalised by the end of the 2nd quarter of 2007.

Health Effects

ETBE has very low odour and taste thresholds in air and water. In water the thresholds are in the order of 13 and 47 µg/l, respectively.

In the case of non-repeated swallowing, contact with the skin and inhalation, ETBE is not classified as harmful to health according to EU health effects classification and labeling criteria.

ETBE is neither a skin nor an eye irritant, however degreasing of the skin is possible. The substance is not classified as a skin-sensitiser.

Studies on animals with repeated administration of ETBE at high doses resulted in liver and kidney effects, which are not thought to be relevant to man and produced transient narcotic effects.

ETBE produced negative results in both 'in-vitro' and 'in-vivo' genotoxicity assays, it is not a genotoxin.

The available data on ETBE and analogous ethers suggests that ETBE is unlikely to present a carcinogenic risk to man. No indications of reproductive toxicity were found in animal experiments. In summary, ETBE is not classified for mutagenicity, carcinogenicity or reproductive toxicity.

Environment Effects

The substance may be harmful to marine invertebrates.

The substance does not accumulate in the organism.

Good biodegradability in water is possible with adapted bacteria only.

Binding to soils and water sediments is not expected.

Based on the good solubility of ETBE in water, it can be expected to enter the groundwater when it reaches the soil. In groundwater under anaerobic conditions biodegradation is very poor.

Because of the high volatility of the substance, it can be expected to preferentially enter the atmosphere if released unintentionally. It will be rapidly degraded there when exposed to light or be washed out with the rain, which will then enter the surface and groundwater.

Stability

The majority of research studies show that ETBE is intrinsically biodegradable.

➤ In air

ETBE has an estimated half-life in the atmosphere of about 2 days, based on a rate constant for reaction with hydroxyl radicals of 8.5×10^{-12} atm-m³/mol-sec and an assumed hydroxyl concentration of $5 \cdot 10^5$ OH/cm³.

➤ In water

ETBE can hydrolyse in the presence of certain acids; it is likely to be stable in water at neutral pH.

➤ In soil

Biodegradation aerobic

Whether or not biodegradation occurs depends on the specific bacteria present in the contaminated soil. The soil must be rich in organic substance and hydrogen peroxides like oxygen source for microsomes. ETBE is degraded into tertiary-butanol (TBA).

Biodegradation anaerobic

ETBE is poorly degraded under anaerobic conditions.

Bioaccumulation

ETBE is not bioaccumulative. Log Pow = 1,58

Toxicological data

Overview

Absorption

Inhaled ETBE is absorbed via the respiratory tract in humans. The absorbed dose, retention is estimated to be of the order of 30%.

Distribution

ETBE and a metabolite, TBA, were detected in the blood of human subjects and the metabolites were excreted in the urine.

Metabolism

In rats, ETBE is oxidized and dealkylated by hepatic microsomes. (5)
Others metabolites are TBA, acetone, 2-methyl-1,2-propanediol and 2-hydroxybutyrate. This metabolism is under the dependence of cytochrome 2B1, cytochrome 2E1 plays a secondary role in the oxidative dealkylation of ETBE. In humans, it is CYP (P450 2A6) which plays key role but with a lot of inter-individual variations. (5)

Elimination

For MTBE and its metabolites, elimination is around 60% by urinary tract. The rest is exhaled.

Acute toxicity

The conclusions of the main experimentation in rats are:

- LD₅₀ of 2 000 mg/kg without symptom. (6)
- LC50 of 5.88 mg/l without symptom. (7)

Subchronic toxicity

Main studies are:

- Fischer 344 rat (males and females aged of 5 weeks) were exposed at 0, 500, 1 750 and 5 000 ppm, 6hr/day, 5days/week during 90 days. The main symptoms for 500 ppm are for the females an increase in heart weights and for males nephropathy associated with $\alpha_2\mu$ -globulin production. At 1,750 ppm additional effects included increased kidney and liver weights, bone marrow congestion and degeneration of the testes. Transient ataxia, increased growth rate (females only) and minor changes in haematological and clinical chemistry parameters were seen at 5 000 ppm.

The NOAEL could be estimated at 500 ppm. (8, 10)

- CD-1 Charles River mice (males and females aged of 5 weeks) were exposed at 0, 500, 1 750 and 5 000 ppm, 6hr/day, 5days/week during 90 days. An increased rate of liver cell turnover, increased liver weights were observed at 1 750 ppm. Mice suffered transient solvent-induced ataxia and liver cell changes (centrilobular hypertrophy) at 5 000 ppm.

The NOAEL could be estimated at 500 ppm. (9, 10)

The molecular weight of ETBE is 102.18 g/mol, so the NOAEL becomes 2 090 mg/m³.

Genotoxicity, carcinogenicity and reproductive toxicity

At the present time, no studies indicate a mutagenic effect (11) or that ETBE is a reproductive substance. (12). Studies on Carcinogenicity are not available. However the analogous ethers are not classified as carcinogenic.

XII. REFERENCES

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XIII. ANNEX 1: DEFINITIONS

a. Heating Values

Definitions

Higher Heating Value (HHV) = Total energy from combustion process.

Lower Heating Value (LHV) = Assumes that the vaporization heat of the water in the combustion product cannot be recovered by condensation.

HHV and LHV are engineering terms used since the 19th century.

The LHV number usually is more realistic.

The HHV of hydrogen is 18.2% above its LHV or, in absolute numbers, 142 MJ/kg vs. 120 MJ/kg for the two cases. For all fuels the difference depends on the hydrogen content of the fuel and equals 22 MJ/kg of hydrogen (at 25°C). For gasoline and diesel the HHV exceeds the LHV by about 110% or 107%.

b. Density and Specific gravity

Definitions

Density and specific gravity have very similar, but not quite identical definitions.

Density is the amount of something per unit volume. Most typically, one expresses the mass per unit volume for a solid or liquid. For example g/cm³. For gases or dusts (very low densities) we might express this as g/m³.

Specific gravity is a ratio of the mass of a material to the mass of an equal volume of water at the same temperature. Because specific gravity is a ratio, it is a unitless quantity. For example, the specific gravity of water at 4°C is 1.0 while its density is 1.0 g/cm³.

Additional Info

At 4°C, the density of water is 1.0 g/cm³. Therefore, density and specific gravity have the same numeric value at this temperature.

As we change temperature the volumes of different materials change in different ways. Most, but not all, materials expand (occupying a greater volume) as temperature is raised, meaning that their densities decrease. As the change in volume of water and other materials are not generally equal, the density and specific gravity may no longer be identical as temperature is changed.

For most materials, the volume change going from 4°C to room temperature (20°C, typically) is not very large. Therefore, we often use the terms density and specific gravity

interchangeably as these values will not differ by more than one or two percent in most cases.

c. Volatility

Definitions

Evaporation Rate (ER) for a liquid is expressed in unitless values relative to butyl acetate, which is assigned an evaporation rate of 1.

Vapor Pressure (VP) is the pressure which exists over every liquid (or solid). In a closed vessel, given sufficient time, equilibrium is attained, in which as many molecules leave the liquid surface to form vapor as return to it from the vapor phase to form liquid. The pressure of vapor above any liquid or solid at any temperature, when equilibrium exists, is the vapor pressure of the liquid or solid at that temperature.

- **Dry Vapour Pressure Equivalent (DVPE)** (EN13016/1)
- **Reid Vapour Pressure (RVP)** (EN13016)

Distillation

- **E70** is the percentage by volume of product that evaporates when it is heated to 70°C
- **T50** is the temperature at which 50% by volume of the product has evaporated

Drivability Index (DI), also called Distillation Index, is another parameter that describes gasoline volatility and is defined by the following equation:

$$DI = 1.5 \cdot T_{10} + 3.0 \cdot T_{50} + T_{90} + 11 \cdot \% \text{ oxygen}$$

Where T_{10} = temperature (°C) at which 10% of the fuel is vaporized; T_{50} = temperature (°C) at which 50% of the fuel is vaporized; T_{90} = temperature (°C) at which 90% of the fuel is vaporized.

Drivability Index quantifies the relationship between drivability and gasoline distillation properties. T_{10} represents the fuel's ability to vaporize quickly and enable cold starting. T_{50} and T_{90} represent the heavier gasoline components' ability to vaporize as the engine warms up and be burnt during combustion. Poor vaporization leans the vapor air-to-fuel ratio in the combustion chamber and leads to loss of engine power and roughness, and increases engine hydrocarbon emissions.

d. Octane

Definitions

Octane number is a value used to indicate the resistance of a motor fuel to premature detonation in the combustion chamber of an internal-combustion engine. Such detonation is wasteful of the energy in the fuel and potentially damaging to the engine.

Octane numbers are based on a scale on which isooctane is 100 (minimal knock) and heptane is 0 (bad knock).

The **Research Octane Number (RON)** simulates fuel performance under low speed, low severity engine operation whilst the **Motor Octane Number (MON)** simulates high speed or high load conditions.

Both numbers are measured with a standardized single cylinder, variable compression ratio engine. For both RON and MON, the engine is operated at a constant speed (RPM's) and the compression ratio is increased until the onset of knocking. For RON the engine speed is set at 600 rpm and MON is at 900 rpm.

e. RTECS

The Registry of Toxic Effects of Chemical Substances (RTECS) is a compendium of data extracted from the open scientific literature. The data are recorded in the format developed by the RTECS staff and arranged in alphabetical order by prime chemical name.

Six types of toxicity data are included in the file:

- (1) primary irritation;
- (2) mutagenic effects;
- (3) reproductive effects;
- (4) tumorigenic effects;
- (5) acute toxicity; and
- (6) other multiple dose toxicity.

Specific numeric toxicity values such as LD50, LC50, TDLo, and TCLo are noted as well as species studied and route of administration used. For each citation, the bibliographic source is listed thereby enabling the user to access the actual studies cited. No attempt has been made to evaluate the studies cited in RTECS. The user has the responsibility of making such assessments.

XIV. ANNEX 2

EFOA

Founded in 1985, EFOA, the European Fuel Oxygenates Association, is a sector group of Cefic, the European Chemical Industry Council. It represents the European producers of the fuel ethers (MTBE, ETBE & TAME), assembling 9 member companies from all around Europe.

- EFOA is dedicated to the responsible usage and the promotion of ethers as components of gasoline.
- EFOA supports and disseminates state-of-the art scientific research on the benefits and impact of ethers on health and the environment.
- EFOA believes in the application of sound scientific principles and actively promotes constructive co-operation with all stakeholders: regulators, legislators, industry, NGOs etc.