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Recent advances in bioethanol fuel research

1. Bioethanol, methyl tert-butyl ether, and other oxygenates in petrol blends

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Abstract. In this review recent advances in the research on bioethanol, methyl tert-butyl ether (MTBE), and other oxygenates in petrol blends are presented. MTBE is nowadays the most common additive of petrol in order to enhance its octane value and to reduce the concentration of toxic components in motor exhaust gases. The extensive use of MTBE has caused contamination of surface and groundwater. The carcinogenicity of MTBE has been demonstrated by animal tests. Replacing MTBE with ethanol is currently on the agenda in the USA; the problem should be taken into consideration in Europe as well.

Key words: bioethanol, methyl tert-butyl ether (MTBE), petrol blends, carcinogenicity, water contamination, greenhouse effect.

Abbreviations: BTEX – benzene, toluene, ethylbenzene, xylenes; DIPE – diisopropyl ether; ETBE – ethyl tert-butyl ether; GAC – granular activated carbon; MTBE – methyl tert-butyl ether; TAME – tert-amyl methyl ether; TBA – tert-butyl alcohol; TBF – tert-butyl formate; VOC – volatile organic compound(s).

INTRODUCTION

The basic oxygenate in petrol blends used as octane number increasing additive is nowadays methyl tert-butyl ether (MTBE). Bioethanol containing petrol blends (gasohol in the USA) make up about 10% of the total consumption of petrol in the United States [1]. This paper gives a review of problems in the field of oxygenates and perspectives of using oxygenates in the future.

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MTBE was originally licensed as a motor fuel additive in 1979 by the United States Environmental Protection Agency (US EPA). It was licensed as a lead replacement because of lead's potential to accumulate in the environment and affect adversely human health. Alkyl leads (tetraethyl lead) had been added to gasoline since the 1930s to enhance the octane number and eliminate spark knock. By 1996, leaded petrol was totally banned in the USA [2].

In 1992 and 1995 the US EPA initiated the Oxygenated Fuel (Oxyfuel) and Reformulated Gasoline programs to meet the requirements of the Clean Air Act Amendments. The Oxyfuel Program requires 2.7% (in reformulated gasoline 2.0%) oxygen by weight (15% MTBE by volume) in petrol during autumn and winter months to reduce carbon monoxide emissions [2].

Kirchstetter et al. [3] showed that increasing the oxygen content in petrol from 0.2 to 2.0 wt % (to 11% MTBE) will decrease the emission of carbon monoxide by $31 \pm 5\%$, non-methane volatile organic compounds (VOC) by $43 \pm 8\%$, and nitrogen oxides (NO_x) by $18 \pm 4\%$. Formaldehyde emission is increased by about 10%.

The production of MTBE in the United States was 4.35×10^6 t in 1991 [4, 5], 8.98×10^6 t in 1993 [6, 7], 8.8×10^6 t in 1997 [8, 9], and approximately the same (8.8×10^6 t) in 1998 [10]. In 1970 the total production of MTBE was the 39th highest of all organic chemicals manufactured in the United States [11]. By Mormile et al. [6] and Reisch [7] in 1993 the production of MTBE was the second in rank among all organic chemicals manufactured in the United States and by Johnson et al. [11] in 1998 the MTBE production was the fourth highest after ethene, propene, and dichloroethane. Johnson et al. [11] showed that during the production period (probably 1970–98) 60 million tonnes of MTBE was produced in the USA.

In Europe the model of the United States was followed and in Germany, for instance, the use of MTBE as a fuel additive increased significantly from 1985 and reached the level of approximately 0.45×10^6 t in 1997 [8, 12]. In Europe the use of MTBE in petrol blends began later than in the United States and its scale is smaller than in the USA. The problems of environmental contamination with MTBE have been noticed in Europe as well, especially in Germany [8, 10, 13, 14].

Effenberger et al. [13] state that in the EU there are no standards for oxygen content in petrol but this is not the case. In petrol with research octane number 95 and 98 the maximum oxygen content allowed is 2.7% by mass (98/70/EC, EN 228:1999) and the maximum C_5, $C_6 \ldots$ ether (among this MTBE) content allowed is 15% by volume (98/70/EC, EN 228:1999). It is also interesting to note that since 2001 the maximum lead content allowed in petrol used in the EU is 0.005 g L^{-1} (98/70/EC) [15].

Among components improving the octane number of petrol are also aromatic hydrocarbons: benzene, toluene, ethylbenzene, and xylenes (BTEX). The maximum content of benzene as the most toxic and carcinogenic component in BTEX allowed in petrol blends in the EU is 1% by volume (98/70/EC, EN

228:1999). The total maximum content of aromatic hydrocarbons allowed is 42.0% by volume (ISO 3837, ASTM D 1319) [15]. Franklin et al. [16] showed that in conventional reformulated petrol the content of aromatic hydrocarbons is 32% by volume and the content of benzene is 1.5% by volume in the USA (in California 0.8% by volume). The oxygen content required since 1 January 2000 is at least 2.1% by mass. In connection with the extensive use of MTBE as petrol oxygenate in the USA and also in Europe widespread environmental contamination has occurred. The paper tackles this problem thoroughly through the following aspects: properties of all oxygenates used as petrol blending components; toxicity and carcinogenicity of MTBE; environmental contamination with oxygenates, especially with MTBE; analytical methods for detecting MTBE and other oxygenates, especially in water; possibilities of groundwater remediation from MTBE; focusing on alternatives to replace MTBE as a petrol blending component.

As the use of MTBE is growing it is vital to be aware of environmental problems involved. Europe should avoid the mistakes made in the United States. Existence of MTBE in groundwater and surface water must be investigated in the very first phase. In this field only some papers concerning the situation in Germany [8, 10, 13, 14] have been published.

OXYGENATES IN PETROL BLENDS

Properties of oxygenates

The following oxygenates are used in petrol blends: methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), tertiary-butyl alcohol (TBA; 2-methyl-2-propanol), diisopropyl ether (DIPE), ethanol (EtOH), and methanol (MeOH). In the USA MTBE makes up 85% and ethanol about 10% of all oxygenates used in petrol blends. The properties of oxygenates are presented in Tables 1 and 2.

Table 1. Properties of oxygenates

Oxygenate	Constant				
	Molecular mass	Boiling point, °C	Density, kg m^{-3}	Flash point, °C	RON* [4, 6]
MTBE	88.15	55	744	–10	118
ETBE	102.18	73	742	–19	118
TAME	102.18	86	770	–11	111
DIPE	102.18	68–69	725	–12	110
TBA	74.12	83	775	11	103
EtOH	46.07	78.3	789	13	129
MeOH	32.04	64.7	791	11	133

* Research octane number

Table 2. Solubility of BTEX and oxygenates in water [11, 17]

Compound	Solubility in water, mg L^{-1}		
	From conventional petrol		Pure compound
Benzene	18		820 [17]
Toluene	25		570 [17]
Ethylbenzene	3		140 [17]
Xylenes	20		$<$150 [17]
	From RFP[a]	From oxyfuel[b]	
MTBE	4700	6300	43 000–54 300 [18, 19] 23 200–54 300 [2]
ETBE	1300	1750	
TAME	1400	1850	
DIPE	1200	1600	
TBA	Miscible		
EtOH	Miscible		

[a] Reformulated petrol containing 2.0% by weight oxygen, which would correspond to 11.1% MTBE, 12.9% ETBE, 12.4% TAME, or 12.9% DIPE (all by volume).

[b] Oxygenated petrol containing 2.7% by weight oxygen, which would correspond to 15.0% MTBE, 17.5% ETBE, 16.8% TAME, or 17.4% DIPE (all by volume).

Toxicity and carcinogenicity of MTBE

MTBE’s unpleasant, turpentine-like taste and odour are detectable by humans at very low levels in water. By Reisinger & Reid [2] the level is 22 ppb. In controlled studies of the US EPA individuals have detected odour and taste at as low concentration of MTBE as 2.5 ppb for odour and 2 ppb for taste [20]. Individual taste and odour sensitivities vary considerably: taste thresholds range from 2.5 to 680 ppb and odour thresholds from 2 to 190 ppb. Low detection thresholds make MTBE an extremely potent water contaminant [16]. Since MTBE can be detected by both taste and odour at concentrations as low as 35 μg L^{-1}, the EPA has recommended keeping concentrations in drinking water below a nuisance limit of 40 μg L^{-1} [21], which is too high.

The lethal toxic concentration for 50% of test animals LC_{50} for MTBE in water solution is 880–1240 mg L^{-1} [13].

In fresh water aquatic invertebrates are generally more sensitive than fish to MTBE in both acute and chronic exposures. To fish (*Lepomis macrochirus* etc.) the acute toxicity endpoints range from 472 to 1742 mg MTBE L^{-1}, while chronic endpoints are 57 to 308 mg MTBE L^{-1}. Acute chronic ratios for fathead minnow (*Pimephales promelas*) and the cladoceran *Daphnia magna* are 3.4 and 11.3 mg MTBE L^{-1}, respectively. The measured acute and chronic toxicity are with a 10-fold factor of toxicity allowed and its character is such as of nonpolar narcosis typical of ether compounds [22]. In inhalation experiments with animals it was shown that MTBE metabolizes in organisms to TBA [23–26]; for instance, by exposure to 5 mg m^{-3} MTBE for 1 h its concentration in blood rose rapidly in both male and female subjects and it was metabolized to tert-butyl alcohol (TBA), which gradually increased in the blood and maintained an elevated level for the duration of the sampling [23]. Blood levels of MTBE and TBA were highly correlated with breathing-zone samples, and MTBE blood levels were highly correlated with blood TBA [24]. Ten healthy male volunteers were exposed to MTBE vapour (5, 25, and 50 ppm) and MTBE and TBA were monitored in exhaled air, blood, and urine. The average post-exposure half-lives of TBA in blood and urine were 10 and 8.2 h, respectively [25]. It must be mentioned that TBA is also a toxic compound and animal tests can correlate to humans.

Many authors have shown the carcinogenicity of MTBE to experimental animals [26–30]. The carcinogenicity of MTBE to animals may relate to induction of cell proliferation and inhibition of cell apoptosis [26]. Belpoggi et al. [27] showed that 1000 mg kg^{-1} of MTBE, given as an olive oil gavage to Spraque-Dawley rats, increases the incidences of Leydig cell tumours in males and lymphoma and leukemia (combined) in females. Chronic inhalation administration of toxic concentrations (3000–8000 ppm) of MTBE produces increased incidences of renal tubular cell adenomas and carcinomas (combined) in male rats, and hepatocellular adenomas in female mice [28]. These results show that MTBE is carcinogenic for rats and mice by inhalation or oral routes. MTBE causes increased incidence of Leydig cell testicular tumours in male rats and an increase in leukemia, dysplastic proliferations of lymphoreticular tissues, and uterine sarcomas in female rats [29]. For mice the chronic toxicity range MTBE concentration is 400 ppm, for rats the carcinogenic level is 400 ppm [30]. However, Borak et al. [31] have doubts about the carcinogenicity of MTBE. In their review they conclude that studies judge most adequately on individual criteria and those with highest overall adequacy found no significant association between MTBE exposure and the previously described symptoms.

The US EPA classified MTBE as a "possible" human carcinogen under its 1986 cancer risk assessment guidelines on the basis of results on inhalation tests and suggested that it may be regarded as posing a potential carcinogenic hazard and risk to humans [20]. This classification is based on studies on animals [18]. It must be noted that the carcinogenicity of compounds to humans has been determined only by animal tests, and MTBE is recognized as an animal carcinogen by the International Agency for Research on Cancer (IARC), and the US National Institute of Environmental Health Science (NIEHS) has found inconclusive evidence to classify MTBE as a human carcinogen [16]. Brown [32] identified several ways how people can be exposed to MTBE via air and water and showed the distribution of doses that can result from those exposures. Table 3 presents MTBE atmospheric concentration distributions for exposed populations in the United States (where MTBE is used).

It appears from Table 3 that workers in many industries, especially in transportation, are exposed to high concentrations of MTBE in the air.

Table 3. MTBE atmospheric concentration distributions [32]

Population	Arithmetic mean concentration, µg m^{-3}
Manufacturing workers	1 500
Blending workers	5 000
Transportation workers	14 000
Gasoline station workers	5 200
Gasoline station and storage neighbours	66
General public	2.6

MTBE in water

Because of its widespread use as a petrol additive MTBE is released to the surface and ground waters in a number of ways; for example, through leaking of petrol storage and distribution tanks (especially underground tanks and pipelines), from spills, emissions of marine engines into lakes, from air deposition etc. [20]. Infiltration and molecular diffusion (dispersion) can also transport VOC, among these light compounds of unburned petrol with MTBE from urban air, into shallow groundwater [33]. In the United States alone tens of millions of gallons of petrol may be released from storage tanks to the ground each year [4]. The problem was well known as early as in 1983. Today at least 85% of petrol in the USA contains 11–15% MTBE.

MTBE is highly soluble in water, resists biodegradation, moves rapidly with groundwater, and does not adsorb easily to soil particles. The United States Geological Survey has detected MTBE in 21% of ambient groundwater tested in areas where MTBE is used [20]. In the United States the water of 16.9% of the total of 406 wells examined in urban areas contained MTBE from 0.2 to 50 000 µg L^{-1} and 3.4% of the total of 2542 wells examined in rural areas contained MTBE from 0.2 to 200 µg L^{-1} [34].

MTBE is the second most frequently detected VOC in shallow groundwater from storage tank leakages, spills etc. in California. The California Department of Health Services proposed a limit value of 5 mg L^{-1} for MTBE. A range of measures is suggested, among others restriction of the use of MTBE and its replacement, e.g. by ethanol [35].

Gregg et al. [36] conducted a survey to evaluate the concentrations of petrol constituents in groundwater in seven states in the USA. BTEX, MTBE, and TBA were usually detected. Benzene was observed in greater concentrations and was more frequently detected than MTBE and TBA. The absence of ethanol indicated that it had probably degraded. MTBE concentrations ranged from 1 µg L^{-1} to 61 µg L^{-1} in the water of private wells near petrol stations [37]. Statistically, approximately 86% of the change in MTBE concentration in lakes was explained by the use of petrol fuelled motorized watercraft. MTBE concentration ranged from <0.1 µg L^{-1} to as high as 12 µg L^{-1} [38]. In the United States federal regulations limit the concentration of MTBE in drinking water acceptable to consumers to 20–40 µg L^{-1}. Prince [39] notes that the US EPA lifetime health advisory of 20 to 40 ppb of MTBE in drinking water serves still as a wake-up call to the industry and to regulators. In Santa Monica (California) 80% of the public wells were found to be contaminated with MTBE in 1996, thus requiring expensive importation of untainted water from outside the city [40]. However, individual state standards range from 10 to 170 μg L^{-1}. In California the limit value is 50 μg L^{-1}. These limits are too high, as the sensibility of many people to MTBE is 2–2.5 μg L^{-1}.

The EU standards for drinking water give a maximum admissible concentration for dissolved or emulsified hydrocarbons, including MTBE, of 10 μg L^{-1} [41]. The problem of MTBE is not yet perceived in the EU and, therefore, there is no special standard for MTBE in water. In the United States the object of the Clean Air Act was to improve air quality by obligatory addition of MTBE to petrol of up to 15%. Today this is seen as a threat to water quality.

Analytical methods of MTBE detection

As shown above, MTBE can be detected today both in the aquatic and atmospheric environment due to the large amounts that are currently being produced. Therefore, it is essential to know the analytical methods for testing MTBE. Some new methods for testing MTBE also in sub-ppb concentrations are presented. It is necessary to analyse the situation in Europe, including Estonia, as the problems of contamination with MTBE have not been realized yet. EU standards allow already up to 15% content of MTBE in petrol today.

For the identification of MTBE many testing methods are used: gas chromatography (GC), GC-mass spectrometry, high-performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and total oxygen measurement. Achten & Püttmann [10] developed an effective solid-phase micro-extraction method for the determination of MTBE in surface water at sub-ppb concentrations. For instance, the MTBE concentration in the water of the Rhein River was 136–160 mg L^{-1} on 21.03.1999 and in the Main River at Frankfurt 70 mg L^{-1} on 15.12.1998. An analytical method for the detection of petrol oxygenates (MTBE, ETBE, TAME) and their most characteristic degradation products (TBA, tert-butyl formate (TBF), and tert-amyl alcohol) in water at sub-ppb concentrations is described by Church et al. [42]. It involves GC with direct aqueous injection (DAI) onto a column via a splitless injector coupled with detection by mass spectrometry (DAI/GC/MS). This method simplifies the analysis procedure, as no complementary treating of samples is necessary. In water samples from a variety of aquifers, Church et al. [42] did not yet find TBA besides MTBE and the formation of TBA from *in situ* degradation of MTBE. The degradation of MTBE is not so simple as some authors have suggested.

Schirmer et al. [14] carried out water quality analysis for MTBE with a headspace-autosampler coupled gas chromatograph. The headspace technique was improved by the use of the purge and tape technique, which increased the detection limit. This method allowed concentration of volatile components on an adsorber where the concentrated components can subsequently be thermally desorbed and detected [14].

Remediation methods for water containing MTBE

Degradation processes of MTBE and its decomposition products were investigated by Taylor et al. [43] and Church et al. [44]. It was shown that the half-life period for MTBE is over 2 years and that complete degradation of MTBE may take over ten years [45]. It must be mentioned that the degradation products of MTBE, TBA and TBF, are toxic compounds, although TBF is hydrolysed very quickly. Church et al. [44] showed that the expected half-life for the hydrolysis of TBF is 6 h at pH = 2, 4 °C; 5 days at pH = 7, 22 °C; and 8 min at pH = 11, 22 °C.

In 1981 McKinnon & Dyksen [45] were the first to show the possibility of removing MTBE from groundwater. There are several groundwater remediation methods for removing MTBE, such as extraction, air stripping, adsorption with active charcoal or synthetic sorbents, oxidation, membrane processes, biological degradation, etc.

The treatment of groundwater to remove MTBE increases the treatment costs by 30–80%. Effenberger et al. [13] showed that the best method is air stripping with adsorption on active charcoal. Creek & Davidson [46] evaluated and compared the following groundwater treatment technologies: extraction, soil vapour extraction, air sparing and biosparing, adsorption on charcoal with air stripping, and advanced oxidation. They found that air stripping can effectively remove MTBE, it worked well for a wide range of influent concentrations from 96 to 56 000 $\mu g\ L^{-1}$. In contrast, granular activated carbon (GAC) was far less effective. Only one site successfully using GAC for the treatment of water containing MTBE is known. From [46] it appears that as 10 of the remedial projects are still operating, cost data are varying, and accurate final cost data are not available no comparisons can be made yet. Later Creek & Davidson [47] found that also GAC can be used for cost-effective removal of MTBE from surface water and groundwater.

MTBE's high water solubility, low Henry's constant, and low organic carbon partition coefficient indicate its hydrophilic nature. Thus, treatment technologies that depend on the hydrophobic properties of contaminants are generally ineffective for the removal of MTBE from drinking water. For example, the use of air stripping requires a substantially higher air flow than for other petrol constituents, and the adsorption efficiency for MTBE on activated carbon has been reported to be $<10\%$ of that of other petrol contaminants [48].

Oxidizing processes are customary for treating drinking water. Some oxidizing processes for the degradation of MTBE are presented in [49–52]. MTBE can be treated with the ultra violet/hydrogen peroxide (UV/H_2O_2) process [49]. The UV/H_2O_2 process involves the photolysis of hydrogen peroxide to generate hydroxyl radicals ($^{\cdot}OH$), which are very effective in the oxidation and mineralization of most organic pollutants. The treatment efficiency of water containing 10 mg L^{-1} of MTBE by the UV/H_2O_2 process is not affected by the presence of low concentrations of BTEX (<2 mg L^{-1}). However, the degradation efficiency is significantly decreased at BTEX levels greater than 2 mg L^{-1} [50]. The major degradation products of MTBE by conventional ozonation and the advanced oxidation process (ozone/hydrogen peroxide) under drinking water treatment conditions are TBF, TBA, 2-methoxy-2-methyl propionaldehyde, acetone, methyl acetate, hydroxy butyraldehyde, and formaldehyde. When the level of the disinfection component bromide was 50 μg L^{-1} then only 35–50% of MTBE could be eliminated by the O_3/H_2O_2 process without exceeding the current drinking water standard of bromate (10 μg L^{-1}) [50]. Some of the primary degradation products of MTBE are more toxic than MTBE. Thus these conventional processes for drinking water treatment may give a negative effect in the presence of MTBE in raw water [51]. In bromide containing waters, the ozone induced oxidation of micropollutants is always accompanied by the formation of bromate. In many countries the limit for bromate concentrations is 10 μg L^{-1}. Yeh & Novak [52] showed that the addition of H_2O_2 leads to chemical oxidation of MTBE and ETBE in the microcosms containing soils rich in organisms. Reduced iron from the organic-rich soil acts as a catalyst for the release of hydroxyl radicals that oxidize MTBE and ETBE. ETBE is chemically oxidized faster than MTBE. TBA and acetone are the oxidation products. The reactivity by oxidation decreases as follows ETBE > MTBE > TBA. It must be stressed that TBA is water soluble and toxic.

It is possible to remove MTBE from water by the membrane pervaporation technology [53]. MTBE concentrations below 20 μg L^{-1} can be attained using pervaporation. It was found that the best material for membrane is a silicone rubber sheet and absolute pressure should be less than 3 torr. Maximum MTBE removal efficiency will be achieved at the greatest possible operating temperature, which is mostly limited by the working range of the equipment. Thin silicone membranes should be used to increase process efficiency. The cost to remove MTBE from water is expected to range from US$ 1.3 to 6.6 for 1 m^3 of water treated. It appears that pervaporation costs to remove MTBE from water are relatively high compared to alternative treatment technologies for typical drinking water applications [52]. The pervaporation process has not been introduced yet and it is supposed that it will not be done in the future either.

Many investigations [4, 6, 39, 52, 54–64) have been carried out on biological degradation of MTBE for groundwater heavily contaminated with MTBE. In the United States MTBE is the second most frequently detected contaminant in drinking water [53]. Salanitro et al. [55] were the first to report bacterial degradation of MTBE. Historically, MTBE has been considered recalcitrant under anaerobic conditions [4, 6] and the first attempts showed that anaerobic biodegradation under sulphate and nitrate reducing conditions for MTBE, ETBE, and TAME is practically 0%, but for ethanol the biodegradation under these conditions is 100% [6].

In laboratory studies, biodegradation of MTBE by aerobic bacteria was observed by Hanson et al. [56]. The bacterial strain PM-1 is able to utilize MTBE as its sole carbon and energy source. This strain was isolated from a mixed microbal consortium in a compost biofilter [56]. Bradley et al. [57] reported that microorganisms indigenous to stream and lakebed sediments demonstrate decomposition of MTBE to CO_2 from 15% to 66% over 50 days with little difference between sediments. This result suggests that even the microbal communities indigenous to newly contaminated surface water systems will exhibit some ability to attenuate MTBE under aerobic conditions [57]. In their next investigation Bradley et al. [54] found that microorganisms inhabiting the sediments of streams and lakes can degrade MTBE under a range of anaerobic electron-accepting conditions.

Finneran & Lovley [58] showed that MTBE is degraded to CO_2 and CH_4 in aquifer sediments in the presence of Fe(III) and humic substances. However, both CO_2 and CH_4 from this source increase the greenhouse effect just like burning MTBE in petrol blends. MTBE degradation has been studied under various conditions to get an insight into the microorganisms potentially involved in the process. Pruden et al. [59] investigated a group of organisms belonging to the *Cytophaga–Flexibacter–Bacteroides* (C–F–B) group of bacteria and demonstrated that MTBE can be degraded effectively in bioreactors under several substrate conditions. Salanitro et al. [55] isolated an aerobic culture BC-1 for degrading MTBE from a refinery waste bioreactor. Hanson et al. [56] isolated PM-1, a fast growing MTBE degrader, from a compost filter. Yeh & Novak [52] found that the presence of rich organic matter in soil inhibits degradation. Bruns et al. [60] showed that MTBE undergoes rapid mineralization as the sole carbon and energy source of bacterial strain PM-1, isolated from an enrichment culture of compost biofilter material. Hernandez-Perez et al. [61] demonstrated that ETBE is stoichiometrically degraded to TBA with *Gordonia terrae* strain IFP 2001 with ETBE being the sole carbon and energy source; MTBE and TAME were not degraded in these conditions. It must be mentioned again that TBA is a toxic compound. Hyman et al. [62] developed methods for the degradation and bioremediation of MTBE, ETBE, TAME, etc. in groundwater by microorganisms *Graphium* sp. (Fungi) with biofilter systems. A review by Prince [39] provides a useful summary of MTBE biodegradation research and implications for bioremediation. Even if MTBE is removed from fuel supplies in the future, the legacy of MTBE usage will continue to be a significant environmental challenge. In petrol-contaminated aquifer systems the half-life of MTBE is thought to be considerably longer than that of the other soluble petrol compounds such as BTEX.

The supply of oxygen is a major constraint for MTBE biodegradation under *in situ* conditions. In a groundwater discharge location a significant decrease in MTBE concentrations was found to be associated with the onset of oxic conditions [63]. Note that the oxygen content in groundwater or contact with it is not always sufficient for the degradation of MTBE. Hopefully the use of MTBE as a petrol oxygenate will be finished in the coming years. In the United States it may happen in 2004 or 2005. When it may take place in Europe is not yet known. However, the problem of groundwater contamination with MTBE will remain. In spite of the elaborated methods for the degradation of MTBE in water, natural *in situ* decomposition will take place and the final solution for the problem may be reached after ten years or more has passed since the use of MTBE in petrol blends was ended.

DISCUSSION

It is interesting to note that in the United States, as well as in Europe, MTBE as a petrol additive to improve the octane number and to reduce the concentration of CO and hydrocarbons in the vehicle exhaust gases was promulgated and introduced into practice on a very large scale without a comprehensive evaluation of environmental or health consequences. Franklin et al. [16] find that the history of MTBE in the United States illustrates several typical, but problematic, features of environmental policymaking. Federal policymakers did not evaluate comprehensively MTBE's potential adverse health and environmental effect and its full energy and economic impacts before they allowed wide use of the compound.

The toxicity and carcinogenicity of MTBE are known issues just as the contamination of surface water and groundwater with MTBE. Although the negative properties of MTBE and its analogues are well known and it is time to replace MTBE as a petrol blending compound, numerous papers were published also in 2000 and 2001 about new methods for their synthesis [65–70]. The only current alternative to MTBE is bioethanol. On the other hand, ethanol's tendency to phase-separate from petrol upon contact with water in pipelines and tanks precludes blending it with petrol at the refinery, requiring separate pipelines and storage that add significantly to infrastructure costs. Bioethanol is more expensive to produce than MTBE. Current bioethanol production in the USA and in Europe does not meet the needs, but this problem can be resolved. MTBE is produced from fossil raw materials and the burning products of MTBE increase the greenhouse effect. The carbon dioxide emission from bioethanol is in environmental recirculation. The octane number of ethanol is higher than that of MTBE and ethanol reduces the concentration of CO and hydrocarbons in emissions more than MTBE [1].

Three reports [71–73] that show the possible negative effect in using ethanol as petrol oxygenate are cited here. Davidson & Creek [71] suppose that since ethanol is soluble in water, ethanol from petrol blends may occur locally in groundwater and neat ethanol spills may produce in groundwater ethanol concentrations that are high enough to cause increased levels of aromatic hydrocarbons (BTEX). Therefore, at the present time very few field data are available which show that ethanol as a petrol component may be used with complete safety. Pereira & de Oliveira [72] showed that an E24 (Brazil petrol containing 24% of ethanol) spill would move faster to distances compared to pure petrol. Corseuil et al. [73] indicated that ethanol can persist in the aquifer for periods much longer than initially expected and interfere in the biodegradation of the more toxic BTEX compounds. The first-order biological decay coefficients in the petrol–ethanol blend (E24) are: for toluene 0.41 yr^{-1}, benzene 0.17 yr^{-1}, xylenes 0.07–0.15 yr^{-1}, and ethanol 0.42 yr^{-1} [73]. However, the distresses with using MTBE are much worse compared to ethanol being used as petrol oxygenate.

These three reports were presented at the same conference. We have no cause to doubt the results, but they do not diminish the necessity to replace MTBE as oxygenate in petrol blends.

The use of MTBE in petrol will be phased out in California by the end of 2002 partly due to serious concerns about surface water and groundwater contamination [74]. The US EPA intends to reduce significantly the use of MTBE in petrol on a nationwide level [20]. These decisions will lead to greater dependence on ethanol–petrol blends and/or petrol formulations without oxygenated compounds. MTBE was recently scrutinized for potential environmental damage in groundwater and in the atmosphere [75]. Toxicity [32] and carcinogenicity [28] studies have linked MTBE to actual human illness. There is a real need for more effective and less harmful oxygenates.

According to the EU standards a petrol blend can contain up to 5% of ethanol. In the USA gasohol contains 10% of ethanol. This amount of ethanol in petrol diminishes considerably the content of toxic components in the motor exhaust gases, but has only a little influence for reducing the greenhouse effect. The petrol brands E85 and E95 contain respectively up to 85% and 95% of ethanol. Using these brands may essentially eliminate the greenhouse effect.

Car manufacturing companies prognosticate that in ten years fuel-cells will replace the Otto and diesel engines in cars. Daimler-Chrysler has already designed and built a series of fuel-cell-powered experimental cars, fuelled by methanol [76]. In 2000 approximately 45% of investigations in the field of fuel were about fuel cells, and the *Chemical Abstracts* published over 1800 abstracts about fuel cells [77]. The main fuel for cells is hydrogen. Hydrogen is produced from natural gas (fossil, not renewable raw material), the production of biomethane from biomass forms nowadays less than 0.01% of the natural gas methane production. In producing hydrogen from methane (natural gas) the by-product is carbon dioxide, which will increase the greenhouse effect.

Another way to produce hydrogen is by electrolysis of water. Electricity production is nowadays based mainly on fossil fuels. It is clear that hydrogen from an unrenewable resource such as a cell fuel will increase the greenhouse effect, just as cells fuelled with synthetic methanol will do. Only bioethanol, which is also known as a cell fuel, can reduce the greenhouse effect.

CONCLUSIONS

Ethanol as a petrol additive has many advantages over MTBE. First, the octane values of ethanol are higher than those of MTBE. Secondly, at equal additive amounts ethanol reduces the concentration of toxic compounds (especially carbon monoxide) in exhaust gases more than MTBE. Furthermore, ethanol is less toxic than MTBE. Recent investigations have shown that MTBE is carcionogenic. MTBE's solubility in water is up to 54.3 g L^{-1}. It is a very stable compound and therefore it cumulates in surface and ground waters. Bioethanol as petrol additive and also as Otto motor fuel abates the increase of greenhouse effect. Today bioethanol as a cell fuel is the only cell fuel obtained from renewable resources that does not increase the greenhouse effect. In the USA the use of ethanol instead of MTBE in petrol blends may be realized in 2004 or 2005. The problem of replacing MTBE with ethanol has not yet been solved in Europe. However, this issue must be taken on the agenda as soon as possible.

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Tänapäevased edusammud bioetanoolkütuse uurimisel
1. Bioetanool, metüül-tert-butüüleeter ja teised oksügenaadid bensiinisegudes

Heino Rang ja Jüri Kann

Ülevaates on käsitletud uusimaid andmeid ja uurimistulemusi bioetanooli, metüül-tert-butüüleetri (MTBE) ning teiste oksügenaatide kasutamise kohta bensiinisegudes. MTBE on seni enim kasutatav bensiini lisand, mis suurendab bensiini oktaanarvu väärtust ja vähendab mootori heitgaasides mürgiste komponentide kontsentratsiooni. On tuvastatud, et laialdane MTBE kasutamine reostab nii pinna- kui ka põhjavett. Loomkatsetega on tõestatud MTBE kantserogeensus. MTBE asendamine etanooliga bensiinisegudes on USA-s käesoleval ajal päevakorras. Sellele küsimusele tuleks pöörata tähelepanu ka Euroopas.