Evaluation of combustion by-products of MTBE as a component of reformulated gasoline

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Abstract

Methyl tertiary-butyl ether (MTBE) is a gasoline oxygenate that is widely used throughout the US and Europe as an octane-booster and as a means of reducing automotive carbon monoxide (CO) emissions. The combustion by-products of pure MTBE have been evaluated in previous laboratory studies, but little attention has been paid to the combustion by-products of MTBE as a component of gasoline. MTBE is often used in reformulated gasoline (RFG), which has chemical and physical characteristics distinct from conventional gasoline. The formation of MTBE by-products in RFG is not well-understood, especially under ''worst-case'' vehicle emission scenarios such as fuel-rich operations, cold-starts or malfunctioning emission control systems, conditions which have not been studied extensively. Engine-out automotive dynamometer studies have compared RFG with MTBE to non-oxygenated RFG. Their findings suggest that adding MTBE to reformulated gasoline does not impact the high temperature flame chemistry in cylinder combustion processes. Comparison of tailpipe and exhaust emission studies indicate that reactions in the catalytic converter are quite effective in destroying most hydrocarbon MTBE by-product species. Since important reaction by-products are formed in the post-flame region, understanding changes in this region will contribute to the understanding of fuel-related changes in emissions. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Methyl tertiary-butyl ether (MTBE) is an oxygenate that was first synthesized in Italy in 1968 (Schmidheiny, 1992). MTBE has been added to US gasoline since 1979, originally as an octane booster (anti-knock agent) to replace lead. It has become prevalent throughout the US and Europe. In the US, MTBE is now widely used as a component of wintertime oxygenated fuels (''oxyfuels''), primarily to reduce carbon monoxide (CO) emissions. MTBE also comprises a significant fraction (typically 11–15% by volume) of reformulated gasoline (RFG). RFG is required by federal law in the ten most polluted urban areas of the US and by state law for all of California. RFG is intended to reduce automotive emissions of photochemical ozone precursors, especially hydrocarbons, as well as benzene and other toxic emissions (Auto/Oil, 1997).

RFG differs from ''conventional'' gasoline with respect to several key fuel parameters, such as lower vapor pressure and reduced benzene content. RFG must meet

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fuel specifications established by the federal Environmental Protection Agency (EPA) or, in California, more stringent standards set by the California Air Resources Board (ARB) (1994) (see Table 1). RFG usually contains oxygenated compounds such as MTBE, but MTBE is not synonymous with RFG. Current US Clean Air Act legislation requires that oxygen make up 2.0% by weight (wt%) of RFG, but does not mandate any particular oxygenate. In the US, except in those regions where ethanol is plentiful, the oxygenate of choice among refiners has been MTBE. By the late 1990s, about 80% of all oxygenates used in US fuel were MTBE. Where MTBE is used to meet the oxygen requirement, it makes up about 11 vol% of the gasoline.

As a component of reformulated gasoline, MTBE plays a role in reducing vehicle emissions of total hydrocarbons, air toxics and CO (Auto/Oil, 1997). However, the presence of MTBE in RFG is also associated with certain pollutant emission increases. For example, MTBE is emitted to the atmosphere as an unburned hydrocarbon, especially during cold engine starts or from evaporative sources (e.g., breathing losses or refueling). The presence of MTBE in fuel is also associated with increased emissions of its by-products, particularly formaldehyde (Auto/Oil, 1995, 1997).

Apart from its role in reducing air pollution from motor vehicles, MTBE has become an increasing concern because of widespread contamination of groundwater and surface water bodies, including drinking water supplies. MTBE releases to the environment are associated primarily with leaking underground fuel storage tanks, as well as fuel spills and release of unburned fuel directly into the atmosphere and surface waters. Its water solubility, mobility and resistance to biodegradation exacerbate its potential threat to water supplies. While MTBE is not particularly toxic with respect to other gasoline components such as benzene, neither is it entirely innocuous. MTBE has received considerable public scrutiny regarding its acute health effects from inhalation, controversy about its human carcinogenicity and its objectionable taste and odor, exacerbated by low sensory detection thresholds.

In light of these concerns about MTBE, it is even more critical to ascertain its true role in reducing automotive emissions, particularly as a component of RFG. Despite the passage of ten years since the requirement of oxygenated fuels and reformulated gasoline in the Clean Air Act Amendments, there are still key unanswered questions. For instance, what MTBE by-products are formed from reformulated gasoline under "worst-case" conditions that simulate cold-engine starts and fuel-rich operation when catalytic converters are not operating effectively? What are the implications for automotive emissions and air quality when MTBE is a component of gasoline? What toxic by-products are associated with reformulated gasoline that contains MTBE compared to a non-oxygenated reformulated gasoline? This study reviews what various laboratory, engine dynamometer and on-road measurements have revealed about MTBE and RFG reaction by-products to help answer these questions.

2. Discussion

Laboratory reactor experiments allow differentiation between directly-formed MTBE reaction by-products and secondary by-product formation. Thus, they provide insight into by-product formation observed in the far more complex motor vehicle studies.

Table 1
Comparison of conventional and California Phase 2 reformulated gasoline specifications

Parameter	Industry average, 1991[a]	California Phase 2 reformulated gasoline specifications[b]		
		Flat limit standard	Average standard	Cap for all gasoline[c]
RVP, psi	8.6	7.0	–	7.0
Sulfur, ppmw	349	40	30	80
Aromatic hydrocarbon, vol%	34.4	25	22	30
Benzene, vol%	1.0	1.0	0.8	1.2
Olefins, vol%	9.7	6.0	4.0	10.0
Oxygen, wt%	NR[d]	1.8–2.2	–	1.8[e]–2.7
T_{90}, °F	323	300	290[f]	330
T_{50}, °F	NR	210	200	220

[a] ARCO Products. EC-X Reformulated Gasoline Test Program Emissions Data. Clean Fuels Report 91-06. As cited in Sawyer (1993).
[b] California Air Resources Board (1994).
[c] Cap for all gasoline applies to predictive model.
[d] NR = Not reported.
[e] Wintertime only.
[f] Refinery cap = 310°F.

2.1. Laboratory studies – atmospheric conditions

MTBE may be emitted directly to the atmosphere through the release of unburned fuel from engine exhaust or through evaporation during operation or refueling. Under ambient conditions in the troposphere, MTBE reacts with OH radicals (usually at the methoxy side of the MTBE molecule) to form primarily tert-butyl formate (TBF) and formaldehyde, with lesser amounts of methyl acetate, acetone and tertiary-butyl alcohol (Japar et al., 1990; Smith et al., 1991; Tuazon et al., 1991). Based on smog-chamber studies, there is some evidence that the highly reactive 2-methoxy-2-methyl-propanal (2-MMP) is formed as an intermediate by-product under homogeneous conditions (Japar et al., 1990; Idriss et al., 1997).

2.2. Laboratory studies – elevated temperatures

Laboratory studies of MTBE reaction by-products at elevated temperatures have been conducted in diverse experimental settings ranging from static reactors, flow reactors, jet-stirred reactors and shock tubes. At elevated temperatures, MTBE undergoes a four-center molecular elimination reaction with first-order reaction kinetics, forming isobutylene and methanol. Under partial oxidizing conditions, isobutylene and formaldehyde are the major products formed. Table 2 lists the compounds that have been observed as the by-products of pure MTBE reaction in laboratory settings. Few experimental studies have explicitly addressed the reaction by-products of MTBE in the presence of other gasoline components.

In laboratory studies evaluating the high temperature oxidation of pure MTBE in a flow reactor, isobutylene and methanol are formed in roughly equal amounts at 1025–1110 K (Norton and Dryer, 1990). Brocard and Baronnet (1987) noted that added oxygen had no effect on the formation of methanol, since the four-center molecular elimination reaction accounts for the homogeneous thermal decomposition of MTBE. Others have noted the importance of heterogeneous wall-catalyzed reactions to the overall decomposition rate of methanol (Choo et al., 1974; Dunphy and Simmie, 1989).

In their study of pure MTBE decomposition in a jet-stirred flow reactor at high pressure, Ciajolo et al. (1997) found that the maximum yield of both isobutylene and methanol occurred at 600 K and decreased at higher temperatures.

Dagaut et al. (1997) studied the formation of by-products of pure MTBE and an equimolar mixture of MTBE and n-heptane in a jet-stirred reactor. Their system operated at stoichiometric conditions with a residence time of 0.5 s, temperatures ranging from 800 to 1200 K and a pressure of 10 atm. Isobutylene, formaldehyde and methanol formation increased for pure MTBE relative to an MTBE/n-heptane mixture, while acetaldehyde and 1,3-butadiene emissions relatively increased for the MTBE/n-heptane mixture.

Siegl et al. (1992) studied the formation of by-products from reaction of pure MTBE in a pulse flame combustor operating at a fuel-rich equivalence ratio near 1 atm, at 1073 K. They observed that isobutylene and methanol were the major species formed, but their analytical methods precluded the measurement of

Table 2
Pure MTBE combustion byproducts[a]

Compound	Ambient conditions (laboratory studies)[b]	Elevated temperatures (laboratory studies)[c]	Post-catalyst (laboratory study)[d]
Acetone	Minor product	Minor product	[e]
Acetylene		Minor product	Not detected
Acrolein		Minor product	
Benzene		Minor product	
Ethane			Minor product
Ethylene			Minor product
Formaldehyde	Major product	Major product	
Isobutylene	Minor product	Major product	Minor product
Methacrolein		Minor product	Not detected
Methane		Minor product	Major product
Methanol	Minor product	Major product	
Propene		Minor product	Minor product
Tert-butyl formate	Major product		

[a] Results cited in this table are compiled from multiple studies, as summarized in Franklin et al. (1998).
[b] Cox and Goldstone (1982), Japar et al. (1990), Carter et al. (1991), Tuazon et al. (1991), Arif et al. (1997), Idriss et al (1997).
[c] Daly and Wentrup (1968), Choo et al. (1974), Brocard et al. (1983), Norton and Dryer (1990), Siegl et al. (1992), Arif et al. (1997), Ciajolo et al. (1997), Dagaut et al. (1997), Taylor et al. (1998).
[d] McCabe et al. (1992), Fields et al. (1998).
[e] Blank indicates not reported in literature.

formaldehyde. Other by-product species observed included ethylene, methane, propene and acetylene.

Taylor et al. (1998) conducted a study of stoichiometric oxidation of MTBE at 973 and 1273 K in a flow reactor. Using GC-MS analysis, they observed the formation of benzene and other aromatic compounds at 1273 K. They postulated that these aromatic compounds are in all likelihood formed from the decomposition of isobutylene through propargyl radical intermediates.

Koshland et al. (1998) compared flow-reactor by-product formation of pure (chemical-grade) MTBE, refinery-grade MTBE, California RFG with MTBE and non-oxygenated California RFG. Flow reactor conditions (600–1150 K, atmospheric pressure) were comparable to characteristic conditions of the post-engine exhaust manifold, where unburned fuel that has escaped the combustion chamber may react in the exhaust system to form combustion by-products. Reaction of pure MTBE yielded primarily isobutylene, methanol and formaldehyde. Reaction of RFG with MTBE yielded isobutylene and formaldehyde, with the formation of methanol only in a limited temperature range. Both pure MTBE and RFG with MTBE produced detectable amounts of minor species including tert-butyl alcohol, methacrolein, acrolein, formic acid, acetylene, benzene and ethylene. Relative to non-oxygenated RFG, RFG with MTBE showed increase in the formation of formaldehyde, isobutylene, methacrolein and methanol. The reaction of non-oxygenated RFG did not produce measurable methanol.

Recently, Glaude et al. (2000) conducted an experimental study of the oxidation of MTBE and ETBE, as well as n-heptane mixtures of these ethers, in a jet stirred reactor at 750–1150 K and a pressure of 10 atm. They measured the formation of major products including CO, methane, ethylene, acetaldehyde, isobutylene, formaldehyde and methanol. Using a kinetic mechanism (EXGAS) to model their results, they found good agreement above 800 K. They reported that their simulations mimicked the observed decrease in oxidation-reactivity of mixtures of MTBE or ETBE with n-heptane.

Zervas et al. (1999) evaluated the influence of gasoline formulation on the emissions of specific species using a mono-cylinder spark-ignition test engine using a range of equivalence ratios from 0.8 to 1.2. They evaluated two synthetic fuel test matrices, one with varying amounts of pure hydrocarbons in an alkylate base and one consisting of different oxygenates (methanol, ethanol, isopropanol and MTBE) in a base fuel mixture. Isobutylene is the principal emitted compound that they observed to be specifically correlated with MTBE in the gasoline mixture. They did not observe a strong correlation of methacrolein production associated with MTBE-fuel content. Interestingly, they measured methanol in exhaust gases from all the different fuel formulations.

Several studies examine the effect of catalysts on the destruction of MTBE and the formation of intermediate by-products. McCabe et al. (1992), in a follow-up study to that of Siegl et al. (1992), observed the reaction products of MTBE after a pulse flame combustor (PFC) and a three-way automotive Pt/Rh catalyst. Their reactant conditions replicated those of Siegl et al. (1992), with the addition of secondary air so that the catalyst operated at an equivalence ratio of 1.00 and a catalyst temperature of 773 K. The overall catalyst conversion rate of hydrocarbons from MTBE combustion was 66.5%, reflecting a conversion efficiency of nearly 90% for unsaturated hydrocarbons and an efficiency of only about 11–20% for methane. Thus, in the post-catalyst exhaust, the relative concentration of methane increased dramatically. Within detection limits, no new hydrocarbon species were identified in the post-catalyst exhaust. Unburned MTBE and methacrolein were converted by the catalyst with such high efficiency that they were not detected in the post-catalyst exhaust. In this study, the GC/FID measurement technique used precluded measurement of formaldehyde. Species concentrations in the post-catalyst exhaust are summarized in Table 2.

Fields et al. (1998) studied the reaction of MTBE in a flow reactor in the presence of a Pt/Rh monolithic automotive catalyst. Their study conditions were atmospheric pressure, temperatures from 350 to 780 K and equivalence ratios varying from fuel rich to fuel lean. When no oxygen was present (0.42 mol% MTBE in nitrogen), isobutylene and methanol were the primary products of catalytic decomposition. At temperatures below 530 K, the ratio of isobutylene to methanol formation was close to 1, suggesting that unimolecular decomposition was the only significant reaction occurring. A catalyst light-off temperature of 580 K was required to achieve 50% conversion; at 767 K, 96.8% conversion of MTBE was achieved. At higher inlet temperatures (around 620 K), dimethyl ether appeared as a reaction product, presumably as a by-product of methanol.

In their fuel-rich MTBE/air experiments in the presence of catalysts, Fields et al. (1998) found a 94.5% conversion rate at 700 K. This high conversion rate under oxygen-limited conditions suggested that, in addition to oxidation of MTBE, there were also decomposition and/or partial oxidation reactions occurring. Methanol and isobutylene remained the predominant reaction products up to about 480 K, suggesting that under all conditions, MTBE decomposition was relatively rapid compared to oxidation pathways. Methanol and isobutylene were subsequently oxidized, but at slower rates compared to MTBE decomposition; methanol oxidized at a faster rate than isobutylene. Under oxidizing conditions over a range of inlet temperatures, the primary products of MTBE reaction over the

catalyst were methanol, isobutylene and CO_2. Methanol and isobutylene concentrations declined with increasing temperatures, with isobutylene formation always greater than methanol formation.

In their studies of catalytic reaction of MTBE with 2,2,4-trimethyl pentane (TMP, or isooctane), Fields et al. (1998) found MTBE conversions at inlet temperatures above 600 K to be nearly 100%, suggesting that MTBE decomposed in the high temperature catalyst exhaust. Small quantities of formaldehyde (about 40 parts per million, ppm) and methacrolein (a few ppm) were also detected. These compounds may form from partial oxidation of methanol and isobutylene, respectively.

The study of Fields et al. (1998) concluded that the catalyzed decomposition of MTBE to methanol and isobutylene was followed by the parallel oxidation of these compounds at slower rates; this conclusion was supported by the appearance of MTBE and isobutylene in the catalyst effluent. The authors point out that these results per se are insufficient to exclude the possibility of direct oxidation of MTBE.

Thus, a number of laboratory studies of MTBE reaction by-products at elevated temperatures have been conducted at temperatures, residence times and equivalence ratios that approximate conditions in the automotive internal combustion engine. In general, these studies are consistent in their findings that the major MTBE by-products formed at elevated temperatures are methanol and isobutylene. The studies differ in their findings of the relative amount of formaldehyde produced, in all likelihood an artifact of difficulties in measuring this compound accurately. Other species formed in trace amounts include methane, propene, acetylene, acetone, acetaldehyde, propionaldehyde, acrolein, methacrolein ethane and propadiene. Studies of MTBE reaction at elevated temperatures in the presence of automotive catalysts find nearly complete conversion of MTBE and its by-products; no new compounds appear to form over the catalyst.

2.3. Automotive studies

Because vehicle emission studies involve more complex variables than laboratory reactor studies of pure compound reactions, it is difficult to isolate the effect of change in a single fuel parameter (MTBE content) on exhaust emissions. Only a limited number of studies have evaluated engine-out or exhaust products of incomplete combustion of MTBE in RFG by comparing speciated hydrocarbon emissions for reformulated fuels with and without MTBE (Koehl et al., 1993; Hood and Farina, 1995; Auto/Oil, 1995, 1997; Howard et al., 1997). In general, oxygenate emission effects vary among emission control technologies and even among individual vehicles of the same type (Koehl et al., 1993; Auto/

Oil, 1995, 1997). Several studies compare vehicle emissions from RFG with MTBE to vehicle emissions with conventional gasoline (non-reformulated and, typically, non-oxygenated). However, because the reformulated fuel differs from the conventional fuel with respect to several parameters besides MTBE content (e.g., vapor pressure, sulfur content, aromatic content, benzene content and distillation profile; see Table 1), it is problematic to attribute changes in the vehicle emissions profile simply to changes in fuel MTBE content.

2.4. Dynamometer studies

Standardized vehicle dynamometer studies using the Federal Test Procedure (FTP) are used to measure either engine-out or exhaust vehicle emissions. Composite emissions are averaged over the entire test cycle and incorporate cold-start, stable-running and hot-start emissions. "Bag 1" emissions represent the cold-start emissions from the first five cycles of the FTP test. Dynamometer testing is commonly cited for its failure to accurately reflect either the range of real-world driving conditions or the diversity of the actual on-road vehicle fleet by under-representing emissions from gross polluters and malfunctioning vehicles. However, despite their limitations, vehicle dynamometer studies are important tools in evaluating vehicle emissions.

In his study of exhaust emissions from 19 vehicles (model years 1970–1990), Hoekman (1992) compares a non-reformulated premium gasoline with a reformulated gasoline containing 11 vol% MTBE. One of his key findings is that vehicle control technologies – particularly the catalytic converter – play a key role in vehicle emissions; these differences outweigh the emission effects associated with reformulating fuel.

Oxygenated gasoline compared to conventional gasoline. Compared to conventional fuels, oxygenated fuels typically have lower emissions of total hydrocarbons, CO and toxics. Vehicle technology, especially the presence of catalytic converters and oxygen sensors, has important effects for different pollutants. In general, older, higher-emitting vehicles produce larger emission reductions than newer technology vehicles, because the uncontrolled emissions from the older vehicles are so much greater in absolute magnitude.

For instance, the Auto/Oil study (1997) observed that adding oxygen to conventional fuel at 2.7 wt% (e.g., 15 vol% MTBE) reduces CO emissions by 11–14% in 1983–1985 and 1989 model year (MY) vehicles, but this level of oxygen has no significant effect on 1994 and later MY vehicle CO emissions. Thus, the fuel oxygen level does not greatly affect emissions from vehicles equipped with more sophisticated catalytic converters and oxygen sensors. Even among similar model years, the impact of fuel oxygen content has widely disparate effects. For example, in normal-emitting (older) vehicles, fuel

oxygen reduces CO in the range of 2% per wt% oxygen, but in high-emitting (older) vehicles, fuel oxygen yields up to 12% CO reductions per wt% oxygen (Knepper et al., 1993; Mayotte et al., 1994a,b).

Vehicle dynamometer studies indicate that vehicle hydrocarbon exhaust emissions are reduced by 1–7% per wt% oxygen in oxyfuels (NSTC, 1997). Here too, vehicle technology plays an important role in determining emissions reductions. For instance, the presence of oxygenate at 2.7 wt% oxygen produces a 5–9% reduction in hydrocarbon emissions in 1989 MY and 1983–1985 MY vehicles (Auto/Oil, 1997). Yet, in newer vehicle technologies (e.g., mid-1990 prototypes), MTBE and other oxygenates are found to have no significant effect on exhaust emissions of volatile organic compounds (VOC) or benzene (Auto/Oil, 1997). In general, studies show that vehicle oxides of nitrogen (NO_x) emissions are not changed by low concentrations of oxygenates in fuel (Auto/Oil, 1997).

Reformulated gasoline compared to conventional gasoline. The Auto/Oil Air Quality Improvement Research Program (Auto/Oil) study highlights changes in fuel formulations that reduce automotive pollutants, especially photochemical ozone precursors and mobile air toxic emissions. One component of this study compares RFG to conventional fuel and concludes that California Phase 2 RFG (CaRFG2) reduces fleet average hydrocarbon emissions by 10–27% compared to industry average gasoline (Auto/Oil, 1995). Estimated reductions in total air toxics emissions from the use of CaRFG2 relative to conventional gasoline range from 9% to 32%, largely due to the reduced benzene and aromatic content of CaRFG2 (Auto/Oil, 1997). This gasoline is associated with significant decreases in benzene emissions and increases of formaldehyde emissions, as well as minor decreases in 1,3-butadiene and acetaldehyde emissions.

Reformulated gasoline with MTBE compared to non-oxygenated reformulated gasoline. Another component of the Auto/Oil study (1995, 1997) compares emissions from vehicles using non-oxygenated reformulated gasoline to vehicles using reformulated gasoline with 11 vol% MTBE. The study finds no statistically significant differences in emissions between CaRFG2 with MTBE and a similar, non-oxygenated reformulated fuel, except for a 13% decrease in formaldehyde tailpipe emissions with the oxygenate-free fuel.

The Auto/Oil study (1996) also evaluates engine-out and tailpipe (exhaust) emissions for 157 hydrocarbon species for different fuel formulations including CaRFG2 with MTBE, non-oxygenated CaRFG2 and a conventional non-oxygenated gasoline. Relative to non-oxygenated RFG, CaRFG2 with MTBE is associated with large increases in MTBE emissions, a lesser increase in isobutylene emissions and smaller increases in formaldehyde, acetone and propadiene emissions. For the remainder of compounds reported, MTBE-fuel produces either negligible emissions increases or even decreases.

Fig. 1 illustrates the change in the mass emission rates of certain hydrocarbon species between RFG containing MTBE and non-oxygenated RFG, based on engine-out vehicle dynamometer emission tests using FTP composite and Bag 1 results (Auto/Oil, 1996). Engine-out emissions measurements correspond to emissions when a catalytic converter is missing, non-operational or not fully warmed-up. As shown in the figure, when MTBE is included in the fuel, unburned MTBE, isobutylene and formaldehyde emissions all increase substantially. Other compounds with increased emissions associated with the presence of MTBE in gasoline in the Auto/Oil study include acetone, propadiene, acrolein, propyne and methacrolein. The largest observed decreases in mass emission rates associated with MTBE-fuel are for propene, acetylene, methane and ethane.
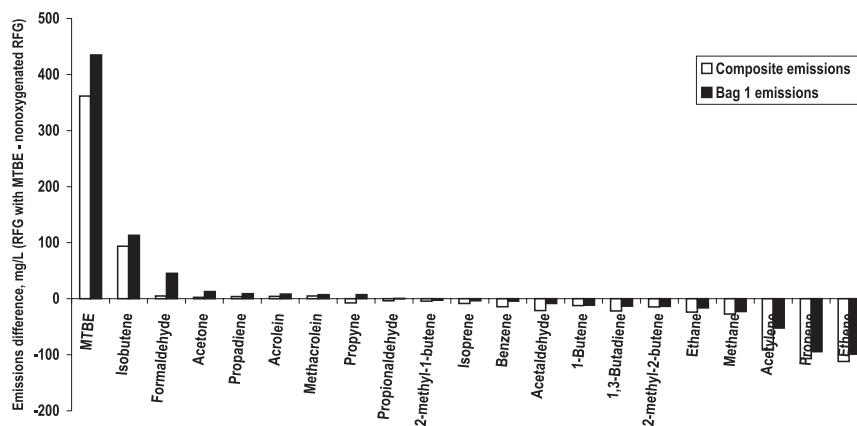

Fig. 1. Comparison of engine-out emissions (FTP) for RFG with MTBE and non-oxygenated RFG for Federal Tier 1 (1994 MY) cars, emissions in mg/l fuel (data from Auto/Oil, 1996). Both composite and Bag 1 (cold-start) emissions are shown.
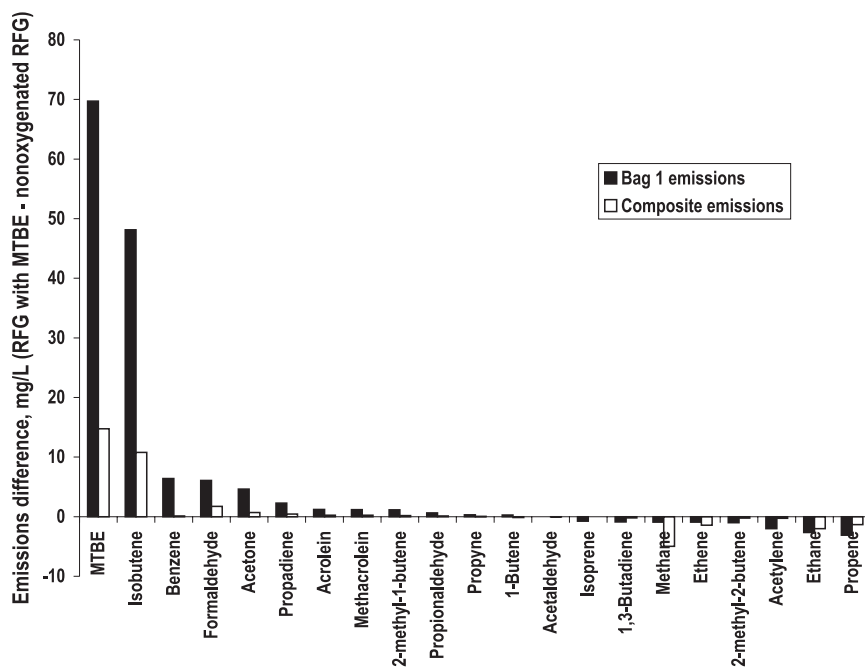
Fig. 2. Comparison of exhaust emissions (FTP) for RFG with MTBE and non-oxygenated RFG for Federal Tier 1 (1994 MY) cars, emissions in mg/l fuel (data from Auto/Oil, 1996). Both composite and Bag 1 (cold-start) emissions are shown.

Fig. 2 shows a similar comparison between vehicle emissions for RFG with MTBE relative to non-oxygenated RFG, in this case for vehicle exhaust (tailpipe) emissions for Federal Tier 1 (1994 MY) vehicles. The exhaust measurements include the effects of vehicle emission control systems, especially the catalytic converter. The similarity between the emission trends for engine-out and exhaust measurements (Figs. 1 and 2) suggests that vehicle emission control systems do not dramatically alter the relative composition of the emission by-product profile with respect to the key MTBE by-products formed.

2.5. On-road – tunnel studies

Another method of measuring actual on-road vehicle emissions is through tunnel measurements, which allow for the collective analysis of the exhaust from many vehicles. The main limitation of tunnel measurements is the limited range of operating conditions observed: typically warmed-up engines in stable mode during a slight uphill gradient (slightly fuel-rich conditions). Thus, cold-start emissions and stop-and-go driving conditions are not observed. Since tunnel measurements are based on tunnel air, rather than in situ tailpipe exhaust, some evaporative (running loss) emissions are incorporated in these measurements, but these emissions are small relative to the dominant exhaust emissions. As vehicle fleets turn over and become cleaner, tailpipe

emissions decrease but running loss emissions are relatively unaffected. Thus, over time, running loss emissions increase as a percentage of total on-road emissions.

Kirchstetter et al. (1996) compare on-road speciated VOC emissions from light-duty vehicles in the Caldecott tunnel (Oakland, California) for low-oxygenated fuel (1994 summertime fuel, containing on average 0.3 wt% oxygen) [1] to those from vehicles using high-oxygenate fuel (a 1994 "wintertime" oxyfuel, containing on average 2.0 wt% oxygen). [2] Both fuels are conventional rather than reformulated. The dramatic difference in oxygen levels within a relatively short period of time (August and October) highlight vehicle emission changes that may be attributed to the presence of oxygenate in the gasoline, rather than vehicle fleet turnover that is a confounding factor when measurements are taken over a longer period of time. The oxygenate used in the "high oxygenate" gasoline in approximately 80% of the vehicles was MTBE; the other 20% of oxygenates used was mostly ethanol. [3] The high-oxygenate fuel is associated with a 21% decrease in CO

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[1] 0.3 wt% oxygen corresponds to 1.65 vol% MTBE.

[2] 2.0 wt% oxygen corresponds to 11 vol% MTBE or 5.7 vol% ethanol.

[3] The authors made this determination based on fuel sampling from gasoline stations in the area.

emissions and an 18% decrease in VOC emissions, but NO_x emissions are not significantly different for the two fuels. The high-oxygenate fuel is associated with higher emissions of formaldehyde (13% increase), MTBE and isobutylene. The high-oxygenate gasoline reduces total aromatic hydrocarbon emissions, with a 25% reduction in benzene emissions. Individual hydrocarbon species that are reduced by the high oxygenate fuel include methane, propene, acetylene, ethane and 1-butene.

Fig. 3 illustrates emission differences (mg/l fuel) for select hydrocarbon species, comparing the high-oxygenate and low-oxygenate fuels based on these tunnel measurements from Kirchstetter et al. (1996). These data are distinct from those shown in the previous Figs. 1 and 2 in one important regard: the Auto/Oil study data shown are based on reformulated fuels (with or without MTBE), while the tunnel study data shown in Fig. 3 are based upon non-reformulated gasoline with high and low amounts of oxygenate (predominantly MTBE). Nonetheless, this comparison elucidates the emissions differences associated with the presence or absence of MTBE in gasoline. This figure shows that the largest emission increases associated with high levels of MTBE in fuel are unburned MTBE emissions, followed by lesser amounts of isobutylene and formaldehyde. This

finding corresponds to previous comparisons of reformulated gasoline with and without MTBE.

In a subsequent study, Kirchstetter et al. (1999a,b) compare on-road emissions associated with CaRFG2 and a previous gasoline formulation, California Phase 1 RFG. They made this comparison by measuring tunnel emissions for two sequential years when different statewide gasoline formulation standards were in effect. The two gasoline formulations (Phase 1 and Phase 2 RFG) are significantly different from each other. Phase 1 RFG is very similar to conventional gasoline, except that it eliminates lead and has slightly reduced sulfur levels and vapor pressure. As noted earlier, Phase 2 RFG has significantly different properties than conventional gasoline (Table 1). Based on representative sampling of service stations, CaRFG2 contained, on average, 10.7 vol% MTBE in the summer of 1996, compared to 1.0 vol% MTBE for the Phase 1 formulation in the summer of 1995. Thus, though the oxygen content differs appreciably from one year to the next as a result of the fuel formulation requirements, the differences in fuel oxygen content are only one factor among many affecting vehicle emissions.

Kirchstetter et al. (1999a,b) observe an 18% reduction in CO emissions, a 22% reduction in non-methane organic carbon emissions and a 6% decrease in NO_x

Fig. 3. Comparison of on-road emissions (Caldecott tunnel measurements) for high-oxygenate (October 1994) and low-oxygenate (August 1994) fuels. Note that both fuels are non-reformulated. Data from Kirchstetter et al. (1996). Emissions are in mg/l fuel. Again, bars above the axis indicate increases in emissions which are associated with the high-MTBE fuel compared to the low-MTBE fuel.

emissions from the summer of 1995 (California Phase 1 RFG) to the summer of 1996 (CaRFG2). The authors note that, due to fleet turnover effects, not all of these decreases can be attributed simply to the use of CaRFG2. MTBE emissions increase dramatically with the use of CaRFG2, with a lesser increase in isobutylene emissions. Minor increases in ethane and formaldehyde emissions are also observed. Hydrocarbon emissions reduced by the use of CaRFG2 include isoprene, propionaldehyde, acrolein, methacrolein and acetone.

Gertler et al. (1999) performed a tunnel study, comparing real-world vehicle emissions in the Sepulveda Tunnel in Los Angeles in October 1995 (Phase 1 California RFG) and July 1996 (Phase 2 California RFG). They find significant decreases in CO and NO$_x$ vehicle emissions, but not total non-methane hydrocarbons, for the 1996 Phase 2 RFG compared to the Phase 1 RFG measurements in 1995. In their study, the most important change in the hydrocarbons measured from the two years is a nearly 50% increase in the fraction of MTBE emissions. The ethene-to-acetylene ratio was the same in their two data sets, suggesting that the overall catalyst conversion efficiency did not change significantly between the two measurements.

Table 3 compares the formation of select hydrocarbon species associated with reformulated gasoline with MTBE to reformulated gasoline that does not contain any oxygenate. This comparison includes dynamometer engine-out emissions (Auto/Oil, 1996) and on-road vehicle emissions from tunnel measurements (Kirchstetter et al., 1999a,b). To facilitate this comparison, all emission measurements have been converted to units of grams of pollutant per liter of fuel consumed. There are striking correlations in the relative amounts of the major by-products formed.

2.6. Impact of MTBE on formation of individual toxic species

As would be expected, automotive MTBE emissions increase as a result of MTBE in RFG. Because MTBE

Table 3
Speciated combustion byproducts of reformulated gasoline with and without MTBE: comparison of dynamometer and on-road vehicle emission measurements

Compound fuel	Compound formation, mg/l fuel Reformulated gasoline with 11.0 vol% MTBE		Reformulated gasoline without oxygenate
Type of measurement	Engine-out, vehicle dynamometer[a]	On-road vehicle emissions[b]	Engine-out, vehicle dynamometer
1,3-Butadiene	77	14.0	98
1-Butene	68	13.7	80
2-Methyl-1-butene	42	7.7	46
2-methyl-2-butene	52	13.4	67
Acetaldehyde	64	10.3	85
Acetone	48	6.3	45
Acetylene	421	83.2	512
Acrolein	21	2.3	17
Benzene	262	242	276
Ethane	110	28.8	134
Ethylene	654	178.0	766
Formaldehyde	414	62.4	410
Formic acid	NQ[c,d]	NQ	NQ
Isobutylene	434	94.3	340
Isoprene	34	0.9	42
Methacrolein	26.0	2.6	21
Methanol	NQ	NQ	NQ
MTBE	373	155.9	11
Propadiene	10	NQ	23
Propene	514	104.9	620
Propionaldehyde	10	1.4	14
Propyne	40	NQ	47
Tert-butyl alcohol	NQ	NQ	NQ
Tert-butyl formate	NQ	NQ	NQ

[a] Auto/Oil (1996). Conversion based on an assumed 20 mile per gallon fuel economy. Composite emissions from Federal Test Procedure measurements on Federal Tier 1 (1994 MY) cars.
[b] Kirchstetter et al. (1999a,b).
[c] ND = Not detected (below method detection limit).
[d] NQ = Not quantified.

destruction efficiency is a function of reaction temperature, emissions of unburned MTBE from the tailpipe are likely to be quite high during cold engine starts. Automotive exhaust MTBE emissions are about 2.5% of total exhaust hydrocarbon emissions and 8–10% of evaporative hydrocarbon emissions (California EPA, 1998). Kirchstetter et al. (1999a) found a sixfold increase in on-road automotive MTBE emissions associated with CaRFG2 containing MTBE.

Automotive formaldehyde emissions increase with the addition of MTBE to reformulated gasoline. Previous studies indicate that formaldehyde is a key by-product of pure MTBE reaction at elevated temperatures, such as those in the automotive engine exhaust system. Formaldehyde is also a key reaction by-product of MTBE reaction at ambient temperatures from atmospheric oxidation of evaporative emissions or tailpipe emissions of unburned fuel. Engine studies indicate that an increase in formaldehyde emissions of 13% is the only statistically significant difference between CaRFG2 with MTBE and CaRFG2 without any oxygenate (Auto/Oil, 1995). Similarly, Kirchstetter et al. (1999a) found a 12% increase in on-road formaldehyde emissions associated with the use of CaRFG2 containing MTBE.

Laboratory studies indicate that isobutylene is a key by-product of pure MTBE reaction at elevated temperatures, such as those in the automotive engine. Both vehicle dynamometer and on-road measurements confirm increased isobutylene emissions associated with the presence of MTBE in gasoline. Isobutylene appears to be effectively destroyed in the catalytic converter.

Methanol is also a key by-product of pure MTBE reaction at elevated temperatures in laboratory studies and in the laboratory spark ignition engine (Zervas et al., 1999). Vehicle and on-road studies have not evaluated or reported methanol in automotive exhaust.

TBF is a key atmospheric reaction by-product of MTBE. Laboratory study results suggest that TBF is not a product of MTBE reaction at elevated temperatures. Vehicle and on-road studies have not reported TBF in automotive exhaust.

Benzene emissions decrease with the use of CaRFG2; vehicle dynamometer tests show benzene emission decreases ranging from 34% to 47% depending on vehicle technology (Auto/Oil, 1995). A tunnel study found a 52% decrease in benzene associated with the use of RFG (Kirchstetter et al., 1999b).

3. Conclusions

The presence of MTBE in reformulated gasoline increases the formation of formaldehyde, methanol and isobutylene, all major MTBE by-products at elevated temperatures. Formation of other MTBE by-products such as methacrolein and ethylene are also increased, including emissions of unburned MTBE.

There is substantial consistency among laboratory studies, vehicle dynamometer studies and on-road vehicle measurements with respect to the overall impact of MTBE in gasoline on exhaust emissions. In terms of the impact of MTBE-fuel on automotive emission by-products, the post-combustion region before the catalytic converter plays the most critical role. The high temperature flame processes in the cylinder itself are relatively unaffected by adding oxygenates to fuel. Neither are catalytic converter reactions significantly affected by fuel composition. However, a significant fraction of total automotive emissions are attributed to emissions that are uncontrolled by catalytic converter systems, either because older vehicles miss control systems entirely, vehicle emission systems malfunction or vehicles operate in cold-start or fuel-rich modes that overwhelm the catalytic converter capacity. Thus, in order to promote further understanding of fuel-related changes in emissions, it is important to more fully understand changes in the post-flame reaction conditions in the automobile.

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