

**Evaluation of Automotive MTBE Combustion Byproducts
in California Reformulated Gasoline**

Report to California State Legislature under S.B. 521: Effects of MTBE

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Executive Summary

Governor Wilson signed Senate Bill S.B. 521 into law on October 8, 1997, enacting the MTBE Public Health and Environmental Protection Act of 1997. This legislation appropriates \$500,000 to the University of California for a study and assessment of the human health and environmental risks and benefits of methyl *tertiary*-butyl ether (MTBE). The state-funded effort consists of several different components, including “identification and quantification of all of the combustion byproducts of MTBE in California’s reformulated oxygenated fuel and the type of analytical methods used and their sensitivity.” Our study addresses this specific component of the state-funded study, including a review of existing literature studies and data sets evaluating byproducts of MTBE alone and MTBE in reformulated gasoline, from laboratory and vehicle measurements. Our study also includes results of our experimental work, evaluating combustion byproducts of MTBE and reformulated gasoline containing MTBE in a flow reactor.

A review of existing studies shows that MTBE is often a major component of reformulated gasoline (11 to 15% by volume). Reformulated gasoline, which differs in several key parameters from conventional gasoline, is designed to reduce exhaust and evaporative emissions of photochemical ozone precursors, especially volatile organic compounds, as well as toxic emissions such as benzene. Reformulated gasoline does not *necessarily* contain any oxygenated compounds, such as MTBE. Studies show that reformulated gasoline (with or without MTBE or any other oxygenate) reduces vehicle emissions of total hydrocarbons, air toxics, and carbon monoxide (CO). As an oxygenate, MTBE’s presence in fuel is linked to decreased CO emissions. However, when present in fuel, MTBE is emitted to the atmosphere as an unburned hydrocarbon, especially during cold engine starts. MTBE is present in ambient air throughout urban California areas at levels on the order of parts per billion (ppb). In the atmosphere, MTBE reacts with the OH radical to yield primarily tert-butyl formate (TBF) and formaldehyde (Japar et al., 1990; Tuazon et al., 1991; Smith et al., 1991; Carter et al., 1991).

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At elevated temperatures, the products of incomplete combustion of pure MTBE are primarily isobutene, methanol, and formaldehyde, with minor amounts of other species (Brocard et al., 1983; Norton and Dryer, 1990; Arif et al., 1997; Ciajolo et al., 1997; Dagaut et al., 1997). Studies of MTBE reaction at elevated temperatures in the presence of automotive catalysts find nearly complete conversion of MTBE and its byproducts. Few laboratory studies have examined MTBE combustion in the presence of other gasoline components; our comparative evaluation identifies those compounds whose presence in automotive engine exhaust is linked to the presence of MTBE in fuel. We conducted a series of tests in a flow reactor that simulates “worst-case” engine-out automotive emissions produced by incomplete combustion. We tested four fuels: pure MTBE, refinery-grade MTBE, California Phase 2 reformulated gasoline (CaRFG2) with MTBE, and CaRFG2 without MTBE. Our experimental results corroborate data reported in previous laboratory studies. Less than 30% destruction of MTBE occurs below 773K, but nearly complete destruction of MTBE occurs at 1073K. Methanol is formed from reaction of pure MTBE at temperatures above 950 K, but not from combustion of CaRFG2 with or without MTBE. Formaldehyde is measured from 550 to 1150 K from reaction of pure MTBE, CaRFG2 with MTBE, and non-oxygenated CaRFG2. TBF is not formed as a reaction byproduct at any temperature for either pure MTBE, CaRFG2 with MTBE, or CaRFG2 without MTBE. In general, the non-oxygenated CaRFG2 produces lower or non-detectable amounts of the key MTBE byproducts at each temperature, relative to the CaRFG2 with MTBE.

Reformulated fuels decrease vehicle exhaust emissions of CO, NO_x, VOCs, and toxics, as well as evaporative emissions, relative to conventional gasoline. The use of oxygenates in fuel is associated with decreased CO emissions. The major impact of adding MTBE to a reformulated gasoline is an increase in formaldehyde emissions. Analysis of speciated hydrocarbon emissions (both engine-out and exhaust) for different vehicle technologies and fuel formulations shows striking differences in emissions from fuels with and without MTBE (Auto/Oil, 1996). MTBE, isobutene, and formaldehyde emissions all increase with fuel containing MTBE in a study of 1994 model year vehicles (Auto/Oil, 1995; 1996; 1997). Vehicle dynamometer studies show reduced emissions of certain hydrocarbons for both reformulated fuel with MTBE and reformulated fuel without MTBE, including propene, acetylene, methane, ethane, 1,3-butadiene, and 2-methyl-2-butene (Auto/Oil, 1996). On-road vehicle measurements comparing reformulated fuel (containing MTBE) to conventional gasoline (without MTBE) find net decreases in VOC, benzene, NO_x, and CO emissions (Kirchstetter et al., 1996, 1998a). These findings are consistent with other dynamometer and tunnel measurements that have compared speciated emissions for fuels with and without MTBE.

The overall consensus of laboratory and vehicle studies is that the presence of MTBE in reformulated gasoline is associated with decreased CO emissions and increased emissions of formaldehyde, isobutene, and unburned MTBE. A key MTBE byproduct that is formed under *ambient* (e.g., atmospheric)

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conditions, TBF, is *not* formed under elevated temperatures such as occur in automotive engines. Through our review of the available information, we find that there is no significant additional air quality benefit to the use of MTBE in reformulated gasoline, relative to non-oxygenated CaRFG2 formulations. Using ethanol or other oxygenates in CaRFG2 may achieve similar benefits but may incur additional risks as well. Thus, while the benefits of reformulated gasoline for automotive emissions has been clearly demonstrated, it is not clear that the presence of MTBE as a component of RFG contributes significantly to the overall air quality benefits.

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Appendix A: Test Matrix

List of Abbreviations and Symbols

ϕ	Equivalence ratio
AL	Adaptive learning
atm	atmosphere
CAAA	1990 Clean Air Act Amendments
CaRFG2	California Phase 2 Reformulated Gasoline
CL	Closed-loop
CO	Carbon monoxide
DIPE	Di-isopropyl ether
EPA	U.S. Environmental Protection Agency
ETBE	Ethyl <i>tertiary</i> -butyl ether
FTIR	Fourier transform infrared
FTP	Federal Test Procedure
g/mi	Grams per mile
GC	Gas chromatography
GC-FID	Gas chromatography - flame ionization detector
K	Kelvin
m	meter
mg/L	Milligrams per liter (fuel)
mg/mi	Milligrams per mile
MMP	2-methoxy-2-methyl propanal
mol%	Mole percent
MTBE	Methyl <i>tertiary</i> -butyl ether
MY	Model year
NMOC	non-methane organic compounds
NO _x	Oxides of nitrogen
PFC	Pulse flame combustor
ppb	parts per billion
ppm	Parts per million
psi	pounds per square inch
RFG	Reformulated gasoline
RVP	Reid Vapor Pressure
s	seconds
SIP	State Implementation Plan
slpm	Standard liters per minute
SO _x	sulfur oxides
TAME	<i>Tertiary</i> -amyl methyl ether
TBF	<i>Tertiary</i> -butyl formate
TWC	Three-way catalyst
VOC	Volatile organic compound
vol%	Volume percent
wt%	Weight percent
τ	residence time

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Introduction

Methyl tertiary-butyl ether (MTBE) is an oxygenate that has been added to U.S. gasoline since 1979, primarily in premium grades of gasoline (at levels of 2 to 3% by volume) as an octane booster and replacement for lead in gasoline. Last year, over 90% of California gasoline contains 11% by volume (vol%) MTBE, corresponding to about 100,000 barrels of MTBE per day statewide. MTBE has been used at these levels since April 1996, when California Phase 2 Reformulated Gasoline (CaRFG2) requirements became effective. The use of MTBE in CaRFG2 is not mandated by state regulations, but MTBE has become the oxygenate of choice among the state's refiners. In about 40 urban areas across the country, including major cities in California such as Los Angeles, MTBE or another oxygenate is added to wintertime oxygenated fuel formulations at 2.7% by weight (wt%) oxygen (15 vol% MTBE). Our study focuses on the air-quality impact of MTBE use in reformulated gasoline (RFG), specifically on characterizing the combustion byproducts of MTBE, as part of the California state-funded effort under S.B. 521 to study the effects of MTBE.

Reformulated gasoline reduces automotive emissions of photochemical ozone precursors, especially hydrocarbons, as well as benzene and other toxic emissions. As a component of reformulated gasoline, MTBE is credited with helping reduce vehicle emissions of total hydrocarbons (which contribute to ozone formation), air toxics, and carbon monoxide (CO).

MTBE itself may escape the engine unburned and be emitted to the atmosphere. The vast majority of all MTBE emissions are from non-point sources, including automotive emissions, automotive evaporative losses, evaporative losses at gasoline stations, and accidental spills (NSTC, 1997). Especially during cold engine starts, emissions of unburned MTBE from the tailpipe are likely to be quite high. Total exhaust MTBE emissions are about 2.5% of total hydrocarbon emissions, and evaporative MTBE emissions are about 8 to 10% of the total evaporative hydrocarbon emissions (California EPA, 1998a). About 43 tons/day of MTBE were emitted in 1996 (California EPA, 1998a).

From a human and environmental health perspective, it is important to determine what combustion byproducts are formed from the complex reactions of reformulated gasoline containing MTBE. Characterizing these byproduct emissions allows species of potential concern to be identified. MTBE is classified as a possible human carcinogen and neurotoxicant. Use of MTBE in gasoline has sparked public health complaints in several cities (e.g., Anchorage and Milwaukee), although controlled experiments and toxicological studies of pure MTBE exposure have so far proven inconclusive. It may be that the byproducts of MTBE, or the synergistic effect of these byproducts with other gasoline

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byproducts, rather than MTBE alone, are responsible for some of the observed effects. Furthermore, comparing the reaction of MTBE alone and in a gasoline mixture may reveal the extent to which formation of byproducts is influenced by interactions with other components of gasoline.

In accordance with the mandate of S.B. 521, this study has two primary technical objectives:

- 1.□ To evaluate automotive combustion byproducts of MTBE as a component of reformulated gasoline, based on a review of existing literature and databases on MTBE combustion byproducts. These studies have evaluated atmospheric reactions, reactor studies of MTBE reaction at elevated temperatures, and vehicle emission studies that incorporate dynamometer and on-road tunnel measurements. This study focuses on hydrocarbon species formed as products of incomplete combustion.
- 2.□ To conduct experimental studies to investigate reaction byproducts of MTBE and California Phase 2 Reformulated Gasoline containing MTBE under conditions that simulate worst-case automotive engine exhaust.

This report first explains some of the relevant terminology used throughout, including “oxygenates,” “oxyfuels,” and “reformulated gasoline.” Subsequently, we summarize the literature reporting MTBE reaction byproducts, beginning with simple laboratory studies of pure MTBE at ambient and elevated temperatures. We then describe our own laboratory work, which evaluates the effect of MTBE as a component of reformulated gasoline on combustion byproducts formed under conditions similar to those in the automotive engine exhaust manifold. We also review studies that incorporate increased complexity in the form of additional variables and exogenous factors: engine dynamometer tests and on-road vehicle measurements. We conclude by summarizing the distinct impacts on air quality associated with reformulated gasoline and, specifically, MTBE as a component of reformulated gasoline.

Background: fuel formulations

To achieve emission reductions, different formulations of gasoline have been developed, targeting different air quality issues. As key provisions of the 1990 Clean Air Act Amendments (CAAA), these fuel formulations have been implemented nationwide.

“Oxygenates” are organic molecules that contain oxygen. Oxygenates are typically alcohols (such as ethanol) or ethers (such as MTBE). The main purpose for adding oxygenates to fuels is to promote more efficient combustion under adverse engine conditions. These conditions include cold starts

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or fuel-rich operations, when a substantial amount of fuel may escape the engine unburned. The extra oxygen in the fuel helps to convert CO (a product of incomplete combustion) to carbon dioxide. To a lesser extent, the extra fuel-bound oxygen may help to convert hydrocarbons, also formed as products of incomplete combustion, to carbon dioxide and water. Currently, the most widely used gasoline oxygenates in California are MTBE, ethanol, and *tert*-amyl methyl ether (TAME). In the San Francisco Bay Area in 1997, MTBE constituted about 95% of the oxygenates used in gasoline (Kirchstetter et al., 1998a). Other oxygenates used to a much lesser extent include other ethers, such as ethyl *tert*-butyl ether (ETBE) and di-isopropyl ether (DIPE).

Oxygenated fuels or “oxyfuels” are fuels that contain oxygenates as a major component, on the order of 10 to 15% by volume (vol%). Oxyfuels are used in urban areas during winter months to help reduce automotive CO emissions that cause ambient air quality problems. The 1990 CAAA mandate the use of oxygenated fuels during winter months in approximately 40 urban areas throughout the U.S. that do not meet ambient CO standards. In these designated “non-attainment” areas, gasoline sold in the winter months must contain at least 2.7% wt% oxygen, effective November 1992. California has obtained a waiver from this minimum oxygen level, because of concerns that this amount of oxygen would increase automotive emissions of oxides of nitrogen (NO_x), thus exacerbating state air quality problems. California’s oxyfuel requirement was amended to require 1.8 to 2.2 wt% oxygen.¹ The 1990 CAAA do not specify what type of oxygenate must be used in wintertime oxyfuels.

“Conventional gasoline” refers to gasoline used nationwide before 1995. Conventional gasoline typically does not contain any oxygenates, except in quantities on the order of 2 to 3% by volume, when refiners have chosen to add them as octane boosters.

“Reformulated gasoline” (RFG) differs from conventional gasoline with respect to several fuel parameters. RFG is intended to reduce automotive pollutant formation, especially evaporative emissions and exhaust emissions of photochemical ozone precursors. The most important targeted ozone precursors are volatile organic compounds (VOCs). RFG is also intended to reduce air toxic emissions, specified in the 1990 CAAA as benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. Compared to conventional gasoline, RFG has lower vapor pressure (to reduce evaporative emissions), lower sulfur content (to prevent poisoning of catalytic converters), and lower aromatic and benzene content (to decrease evaporative and exhaust emissions of these compounds). *Reformulated fuel may or may not include oxygenated compounds; the term “reformulated gasoline” does NOT itself imply the presence of oxygenates.*

¹ 2.7 wt% oxygen corresponds to 15 vol% MTBE (or 7.3 vol% ethanol). 2.0 wt% oxygen corresponds to 11 vol% MTBE (or 5.4 vol% ethanol).

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There are two primary “flavors” of RFG: Federal RFG and California Phase 2 RFG. Requirements for Federal RFG are defined in the 1990 CAAA. Federal RFG specifies maximum limits on vapor pressure, benzene content, and aromatics content; it prohibits any lead content, requires detergents, and requires a minimum oxygen content of 2.0 wt%. Federal RFG does not specify what type of oxygenate must be used. Federal RFG also must produce a 15% reduction in air toxic² and VOC emissions compared to conventional gasoline; 25% emission reductions will be effective in the year 2000. Effective January 1, 1995, Federal RFG is required year-round in nine different areas in the U.S. with ozone levels classified as “severe” or “extreme.” In California, these areas include key population centers such as Los Angeles, San Diego, and Sacramento.

California Phase 2 RFG (CaRFG2, sometimes referred to as “Cleaner Burning Gasoline”) is required year-round, statewide, effective April 1, 1996. The California Air Resources Board (ARB) enacted this regulation as part of California’s State Implementation Plan (SIP) under the 1990 CAAA to meet California air quality goals.³ CaRFG2 contains stricter provisions than Federal RFG, including restrictions on maximum sulfur content, aromatics content, altered distillation profile (to reduce evaporative emissions), and reduced olefins content (to reduce the reactivity of the exhaust hydrocarbons). CaRFG2 must reduce automotive air toxic and VOC emissions by 25% compared to conventional gasoline. The “formula” for CaRFG2 specifies an oxygen content of 1.8 to 2.2 wt% (see discussion below). State regulations do not specify what type of oxygenate must be used (CARB, 1994).

Unlike the Federal RFG standard, the CaRFG2 standard may be met in one of two ways: (1) by meeting the prescriptive limits, or (2) by using a predictive model to show that emissions reductions achieved using a given fuel formulation are equivalent to, or greater than, those achieved using the prescriptive fuel formula. Thus, if a refiner can show that a particular gasoline formulation that contains no oxygenates achieves the mandated emission reductions, that fuel formulation is allowed under the “predictive modeling” rules. Evaluation of gasoline sold in the San Francisco Bay Area indicates that usage of MTBE in Bay Area gasoline dropped by over 20% from 1996 to 1997 (from an average of 10.7 volume % MTBE in 1996 to an average of 8.2% in 1997). At the same time, the average oxygen content decreased by 20%, suggesting a corresponding increase in the use of non-oxygenated CaRFG2 (Kirchstetter et al., 1998a). However, Federal RFG requirements, including the minimum (flat limit) 2.0

² The Clean Air Act Amendments of 1990 specifically targeted reductions in five “toxic air pollutants” from mobile sources: benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter (POM). Since POM emissions from gasoline-powered vehicles are very low (they are of more concern from diesel vehicles), they are usually neglected in studies of gasoline-powered vehicles. Thus, “total toxic emissions” often refer to the sum of emissions of benzene, 1,3-butadiene, formaldehyde, and acetaldehyde.

³ As part of its SIP, California implemented its own statewide program to reduce automotive pollution through reformulated fuels. California Phase 1 reformulated gasoline was required beginning in 1992. It reduced gasoline vapor pressure to 7.8 psi, prohibited the use of lead in gasoline, and required the use of certain detergents.

wt% oxygen content, supercede state requirements in federally-designated ozone nonattainment areas. Thus, the predictive model may not be used in Federal nonattainment areas to avoid oxygen content limits.

Literature review: MTBE reaction byproducts

This review summarizes studies of MTBE reaction byproducts under simulated atmospheric conditions as well as in laboratory combustion reactors. We focus on hydrocarbon species formed as products of incomplete combustion. The relatively simple laboratory reactor experiments allow us to differentiate between directly-formed MTBE byproducts and secondary byproduct formation. These studies provide insight into byproduct formation observed in the far more complex motor vehicle studies, in which multiple parameters are changed simultaneously.

Atmospheric chemistry studies

Several researchers have investigated the atmospheric reactions of MTBE in laboratory settings, including atmospheric chamber studies. The main atmospheric removal mechanism for MTBE is via reaction with the OH radical, primarily at the methoxy side of the MTBE molecule where the C-H bond of the methoxy group is significantly weaker than the C-H bonds of the tert-butyl group (Carter et al., 1991; Smith et al., 1991). Major products formed are tert-butyl formate (TBF) and formaldehyde, in an approximate 80:20 ratio (Carter et al., 1991). Other species formed are methyl acetate, acetone, and 2-methoxy-2 methyl propanal (MMP). Minor species sometimes observed are methanol, isobutene,⁴ and *tert*-butanol. Figure 1 illustrates the main reaction pathways of MTBE under atmospheric conditions, and Table 1 summarizes the different byproducts of MTBE reaction under ambient conditions.

In their study of the reaction of MTBE with OH radicals in the presence of NO_x, Cox and Goldstone (1982) tentatively identified TBF as the major product and acetone as the minor product. Their results were qualitative only, and their methods precluded detection of formaldehyde. Japar et al. (1990) used Fourier transform infrared (FTIR) absorption spectroscopy to measure products formed by the reaction of MTBE with OH radicals or Cl atoms in NO_x-air systems in a smog chamber. They also found TBF, a relatively inert species, to be the major product formed, with a yield of 60% when MTBE reacted with OH. They found some evidence that the highly reactive compound MMP is formed as an intermediate. Their experimental methods prevented the detection of formaldehyde.

⁴ Isobutene may also be referred to as isobutylene or 2-methylpropene.

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Tuazon et al. (1991) carried out a study of the gas phase reaction of MTBE with OH radicals in the presence of NO_x in a smog chamber. Using FTIR and gas chromatography–flame ionization detection (GC-FID) measurement techniques, they determined that the formation of TBF, formaldehyde, methyl acetate, and acetone account for 95 ± 8% of the carbon in MTBE. Theirs was the first study in which methyl acetate was observed as a product of MTBE with the OH radical. Recently, Arif et al. (1997) used a laser photolysis - laser-induced fluorescence technique to study reaction of MTBE with OH radicals. They determined the kinetic rate expression for this reaction between 293 K and 750 K. Under atmospheric conditions the major products formed are TBF, formaldehyde, and methyl acetate. The reaction of MTBE exhibits a stronger temperature dependence than previously reported. At higher temperatures (918 K), they observe a different product distribution (TBF, formaldehyde, and methyl acetate). They interpret this result to signify a shift in the reaction mechanism between ambient and elevated temperatures. At higher temperatures, they suggest that OH attack on the tert-butyl group (rather than on the methoxy group, as observed at lower temperatures) is the dominant initial reaction pathway.

Idriss et al. (1997) conducted a study of the photoreactions of MTBE on metal oxide particles in the troposphere. In their study, they observe that MTBE reacts homogeneously through a series of steps to yield MMP and TBF in a 40:60 ratio. When MTBE reacts photochemically with flyash at low concentrations, it exhibits a first order, linear reaction rate increase, while at higher concentrations it exhibits a zero order (saturation) concentration dependence. Idriss and coworkers identify the three product intermediates formed from MTBE reaction with flyash as isobutene, formaldehyde, and methanol. The ultimate products of MTBE reaction via all pathways are formaldehyde and acetone.

Reactor studies at elevated temperatures

Several laboratory studies have investigated the possible byproducts formed by the combustion of MTBE under elevated temperatures and pressures; these are summarized below in Table 2. Daly and Wentrup (1968) were among the first researchers to study the thermal decomposition of MTBE. They studied the kinetics of homogeneous MTBE reaction from 706 - 768 K. Choo et al. (1974) also studied homogeneous MTBE reaction at very low pressures (0.5 - 5.0 millitorr, in order to suppress secondary reactions), and temperatures from 888 - 1158 K. Both groups observed a first-order kinetic reaction in which MTBE decomposes via a four-center molecular elimination reaction, forming isobutene and methanol, in which the global reaction may be written:

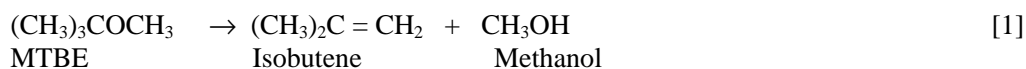


Table 1. Atmospheric MTBE byproduct formation (ambient temperatures and pressures)

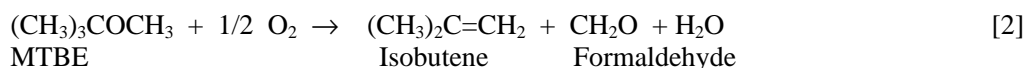
Compound	Comments	Reference
Tert-butyl formate (TBF)	Major product	Carter et al. (1991) Cox and Goldstone (1982) Japar et al. (1990) Tuazon et al. (1991) Arif et al. (1997) Idriss et al. (1997) ^(a)
Formaldehyde	Major product ^(b)	Carter et al. (1991) Tuazon et al. (1991) Arif et al. (1997) Idriss et al. (1997)
Methyl acetate		Tuazon et al. (1991) Arif et al. (1997)
Acetone		Cox and Goldstone (1982) Tuazon et al. (1991)
2-methoxy-2 methyl propanal	Highly reactive intermediate	Japar et al. (1990)
Methanol	Minor species	Idriss et al. (1997)
Isobutene	Minor species	Idriss et al. (1997)

(a) Idriss et al. observe that TBF in turn reacts to form tert-butyl alcohol (TBA).

(b) Some studies' techniques precluded measurement of formaldehyde.

Choo et al. (1974) also observed the formation of some formaldehyde, which they attribute to decomposition of methanol at the reactor walls.

Brocard et al. (1983) studied homogeneous reactions of equimolar MTBE and oxygen mixtures in a static reactor from 573 to 773 K, at pressures to 1 atm. The major products formed are isobutene and formaldehyde; some methanol is also formed. In this study, the MTBE was observed to either react slowly or ignite, with no cool flame region. As the authors noted, this behavior at relatively low temperature and pressure does not preclude the occurrence of cool flames under more severe conditions of higher pressure. The reaction of MTBE and oxygen mixtures at temperatures near 723 K appears to be more thermal degradation than true oxidation reaction. Thus, they postulate that two reactions occur in parallel: MTBE decomposition, according to global reaction (1), and oxygen-assisted decomposition, forming isobutene and formaldehyde according to global reaction (2):



The researchers postulate that the probable mechanism of MTBE reaction is OH attack on the C-H bond of the methoxy group, which is significantly weaker than the C-H bonds of the tert-butyl group. Thus,

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formation of the methoxy radical is favored; furthermore, decomposition of this radical to form the less active HO₂ radical is faster than all competing processes. The HO₂ radical cannot propagate fast chain reactions. The authors that these basic principles can be extrapolated to explain the antiknock effect of MTBE in motor vehicle engines, although the elementary reaction steps may be somewhat different under the high pressures in the internal combustion engine. The formation of products from MTBE decomposition under elevated temperatures is illustrated in Figure 2.

Dunphy and Simmie (1989, 1991) examined the ignition characteristics of MTBE and methanol/isobutene mixtures in a shock tube at temperatures from 1040 to 1850 K. Based on their observations, they speculate that at high oxygen concentrations direct oxidation of MTBE occurs. This pathway differs from reactions at stoichiometric or fuel-rich conditions, which occur via MTBE decomposition followed by oxidation of methanol and isobutene.

Norton and Dryer (1990) explored the homogeneous reaction of MTBE in a flow reactor at atmospheric pressure and initial temperatures of 1020 to 1120 K, under near-stoichiometric conditions. They found that MTBE decays in a unimolecular decay reaction, with isobutene and methanol the predominant species formed. Using gas chromatography (GC), they also detected the formation of acetylene, propyne, propene, methane, and propionaldehyde.

Arif et al. (1997) observed the reaction of MTBE in a slow flow reactor at elevated temperatures. Under stoichiometric conditions at 918 K, the major reaction products are isobutene and methanol, with minor formation of ethane, propene, 1,2-propadiene, acetone, 1,1-dimethylcyclopropane, and a C₄ oxygenate. They did not detect the major products formed under atmospheric conditions (TBF, formaldehyde, or methyl acetate). The researchers suggest that at higher temperatures, differences in the C-H bond strengths between the methoxy and tert-butyl groups are less important, and formation of tert-butyl radicals becomes a dominant initial reaction pathway at these elevated temperatures, followed by C-O bond cleavage to yield isobutene and methoxy radicals. Arif and coworkers suggest that because there is no detection of 3- or 4- member ring compounds, molecular oxygen may not play an important role in reacting with the initial radicals.

Table 2. Byproducts of pure MTBE reaction at elevated temperatures observed in reactor studies

Compound	Comments	Reference
Isobutene	Major product	Daly and Wentrup (1968) Choo et al. (1974) Brocard et al. (1983) Norton and Dryer (1990) Arif et al. (1997) Ciajolo et al. (1997) Dagaut et al. (1997)
Methanol	Major product	Daly and Wentrup (1968) Choo et al. (1974) Brocard et al. (1983) Norton and Dryer (1990) Arif et al. (1997) Ciajolo et al. (1997) Dagaut et al. (1997)
Formaldehyde	Formed to lesser extent than isobutene and methanol	Choo et al. (1974) Brocard et al. (1983) Ciajolo et al. (1997) Cathonnet et al. (1995) as cited in Dagaut et al. (1997) Dagaut et al. (1997)
1,1-Dimethylcyclopropane	Minor product	Arif et al. (1997)
1,3-Butadiene	Minor product	Dagaut et al. (1997)
1-Butene	Minor product	Dagaut et al. (1997)
2,2-Dimethyloxiran	Minor product	Dagaut et al. (1997)
2-Methyl-1-butene	Minor product	Dagaut et al. (1997)
2-Methyl-2-butene	Minor product	Dagaut et al. (1997)
2-Methyl-2-propen-1-ol	Minor product	Dagaut et al. (1997)
2-Methylpropanal	Minor product	Dagaut et al. (1997)
4,4-Dimethyl 1,3-dioxolane	Minor product	Ciajolo et al. (1997)
Acetaldehyde	Minor product	Dagaut et al. (1997)
Acetone	Minor product	Arif et al. (1997) Ciajolo et al. (1997) Dagaut et al. (1997)
Acetylene (Ethyne)	Minor product	Norton and Dryer (1990) Dagaut et al. (1997)
Acrolein	Minor product	Dagaut et al. (1997)
Ethane	Minor product	Norton and Dryer (1990) Arif et al. (1997)
Isobutenal	Minor product	Ciajolo et al. (1997)
Isoprene (2-methyl-1,3-butadiene)	Minor product	Dagaut et al. (1997)
Methacrolein	Minor product	Dagaut et al. (1997)
Methane	Minor product	Norton and Dryer (1990) Ciajolo et al. (1997) Dagaut et al. (1997)
Propadiene (Allene)	Minor product	Arif et al. (1997)
Propene	Minor product	Norton and Dryer (1990) Arif et al. (1997) Dagaut et al. (1997)
Propionaldehyde	Minor product	Norton and Dryer (1990)
Propyne	Minor product	Norton and Dryer (1990)

Siegl et al. (1992) studied reaction of pure MTBE in a pulse flame combustor (PFC) near atmospheric pressure at a temperature of 1073 K at a slightly fuel-rich equivalence ratio (ϕ). Using GC-FID, they evaluated speciated hydrocarbon emissions, but their technique precluded measurement of formaldehyde. The major species formed from MTBE combustion measured in their study are summarized in Table 3. The authors note that their observed products are consistent with the mechanism of initial H-abstraction followed by β -scission, leading to relatively high formation of isobutene for branched compounds such as MTBE.

Ciajalo et al. (1997) evaluated products of pure MTBE decomposition in a jet-stirred flow reactor at high pressure, at conditions similar to those of the exhaust gases from spark ignition engines. Confirming the findings of Norton and Dryer's study (1990), they found that MTBE reaction under these conditions produces mostly isobutene and methanol. They propose a four-center molecular elimination reaction mechanism. In disagreement with the work of Brocard et al. (1983), they observed little formaldehyde formation, which they attribute to preferential formation of radicals on the tert-butyl, rather than the methoxy, position. For both isobutene and methanol, the maximum yield occurred at 600 K and decreased thereafter. Formation of several other minor product species occurred between 630 and 670 K: 4,4-dimethyl 1,3-dioxolane; acetone; formaldehyde; isobutenal; and methane.

Dagaut et al. (1997) have also conducted a study of the oxidation of n-heptane and mixtures of n-heptane with MTBE as well as ETBE in a high pressure jet-stirred reactor. Their experiments were conducted at an equivalence ratio (ϕ) of 1, with temperatures between 570 and 1150 K. Cool flame chemistry predominates at low temperatures (650 to 770 K) as reaction of MTBE inhibits chain branching. They argue that this evidence supports an anti-engine-knock mechanism driven by low-temperature chemistry. Dagaut and coworkers compare formation of products from combustion of three fuels: n-heptane alone; a mixture of n-heptane and MTBE; and MTBE alone. At temperatures above 800 K, the oxidation of MTBE produces large amounts of methanol and isobutene as intermediates. The reaction of the n-heptane/MTBE mixture produces increased formation of formaldehyde and reduces acetaldehyde and 1,3-butadiene formation relative to n-heptane. The results indicate that MTBE oxidation is responsible for the formation or increased production of the following compounds: methanol; acrolein; methacrolein; acetone; isobutene; isoprene; 2,2-dimethyloxiran; 2-methylpropanal; 2-methyl-2-propen-1-ol; 2-methyl-1-butene; and 2-methyl-2-butene. Table 4 summarizes the maximum mole fraction observed for selected species for combustion of MTBE, n-heptane, and a mixture of MTBE

Table 3. Major species formed from MTBE combustion in post-flame combustor

Compound (% of total HC)*	Pre-catalyst * (Siegl et al., 1992)	Post -catalyst (McCabe et al., 1992)
Total HC	1320 ± 260 ppm	440 ± 230 ppm
Isobutene	27.9 %	10.6 %
Methane	23.9	72.6
Ethene	20.7	9.9
Propene	11.6	2.5
Acetylene	4.3	n.d. ¹
MTBE	3.2	N.D.
Methacrolein	1.6	N.D.
Ethane	1.31	3.1
Propadiene	1.1	N.D.
2-Butyne	1.0	N.D.
1,3-butadiene	N.D.	N.D.
Benzene	N.D.	N.D.

¹N.D. = Not detected.

* Listed in decreasing order as percentage of total hydrocarbons, for pre-catalyst exhaust.

Table 4. Maximum mole fraction of major byproducts formed in jet-stirred reactor (Dagaut et al., 1997).

Species formed *	MTBE	n-heptane	n-heptane / MTBE
Acetylene	1.27×10^{-4}	6.24×10^{-4}	3.75×10^{-4}
Formaldehyde	3.12×10^{-4}	1.75×10^{-4}	2.14×10^{-4}
Isobutene	3.67×10^{-4}	---	1.94×10^{-4}
Methanol	2.70×10^{-4}	---	1.67×10^{-4}
Methane	2.51×10^{-4}	1.22×10^{-4}	1.55×10^{-4}
Propene	8.27×10^{-5}	2.06×10^{-4}	1.27×10^{-4}
Acetaldehyde	2.05×10^{-5}	1.32×10^{-4}	6.10×10^{-5}
1-Butene	1.70×10^{-6}	7.78×10^{-5}	4.00×10^{-5}
1,3-Butadiene	6.70×10^{-7}	1.93×10^{-5}	9.5×10^{-6}

* Compound listed in order of decreasing prevalence formed based on n-heptane / MTBE mixture.

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and n-heptane in a jet-stirred reactor under the following conditions: $\phi = 1$, 10 atm pressure, residence time (τ) = 0.5 s, and temperatures from 800 to 1200 K.

Several studies have examined the effect of catalysts on destruction of MTBE and on the formation of intermediate byproducts. McCabe et al. (1992), in a follow-up study to that of Siegl et al. (1992), observe the reaction products of MTBE after a pulse flame combustor (PFC) and a three-way automotive Pt/Rh catalyst. Their reactant conditions replicate those of Siegl et al. (1992), with the addition of secondary air so 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 near 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 increases dramatically. Within detection limits, no new hydrocarbon species were identified in the post-catalyst exhaust. Unburned MTBE and methacrolein are converted by the catalyst with such high efficiency that they are 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 3.

Fields et al. (1998) have 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 is present (0.42 mol% MTBE in nitrogen), isobutene and methanol are the primary products of catalytic decomposition. At temperatures below 530 K, the ratio of isobutene to methanol formation is close to 1, suggesting that unimolecular decomposition is the only significant reaction occurring. A catalyst light-off temperature of 580 K is required to achieve 50% conversion; at 767 K, 96.8% conversion of MTBE is achieved. At higher inlet temperatures (around 620 K), dimethyl ether appears as a reaction product, presumably as a byproduct of methanol.

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

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and CO₂. Methanol and isobutene concentrations decline with increasing temperatures, with isobutene 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) find MTBE conversions at inlet temperatures above 600 K to be nearly 100%, suggesting that MTBE decomposes in the high temperature catalyst exhaust. Small quantities of formaldehyde (about 40 parts per million, ppm) and methacrolein (a few ppm) are also detected. These compounds may form from partial oxidation of methanol and isobutene, respectively.

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

Recently, Taylor et al. (1998) have 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 postulate that these aromatic compounds are likely formed from the decomposition of isobutene through propargyl radical intermediates.

Thus, a number of laboratory studies of MTBE reaction byproducts 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 byproducts formed at elevated temperatures are methanol and isobutene. The studies differ in their findings of the relative amount of formaldehyde produced. 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 byproducts; no new compounds are formed over the catalyst.

Experimental study

Few of the experimental studies have explicitly addressed the reaction byproducts of MTBE in the presence of other gasoline components. Our experimental study evaluates reaction byproducts of pure MTBE as well as MTBE as a component of reformulated gasoline, focusing on hydrocarbon species formed as products of incomplete combustion. We also evaluate combustion byproducts formed from reformulated gasoline that does not contain any MTBE or other oxygenates. This comparison identifies those compounds whose presence in automotive engine exhaust from reformulated gasoline is linked to

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the presence of MTBE in fuel. We compare our results with MTBE combustion byproduct laboratory reactor studies of MTBE reaction at elevated temperatures and vehicle emission studies from both dynamometer and on-road tunnel measurements.

Our laboratory study evaluates non-ideal automotive combustion conditions that result in byproduct formation. These “worst-case” conditions simulate non-ideal engine operating conditions, such as cold-starts and engines running fuel-rich, when unburned fuel escapes from the engine and the catalytic converter is ineffective in fully oxidizing the exhaust gases.

Experimental methodology

Our laboratory study utilizes a flow reactor with post-flame fuel injection to study a range of temperatures and air/fuel ratios. Our reactor, shown schematically in Figure 3, is described in detail in Thomson (1994). We evaluate combustion byproducts from four fuels: pure MTBE, refinery-grade MTBE, reformulated gasoline with MTBE (CaRFG2 with MTBE), and non-oxygenated reformulated gasoline (CaRFG2 without MTBE).

In our combustion-driven flow reactor, we use a methane-air flame burning at equivalence ratios varying from fuel-lean ($\phi = 0.9$) to fuel-rich ($\phi = 1.1$). Appendix A includes a matrix showing the conditions tested. We moderate temperatures by changing the total flowrate through the reactor and by changing the downstream location of the fuel injection. To achieve lower post-flame temperature variations, nitrogen is injected immediately downstream of the flame holder. The experimental reactor configuration produces a decreasing axial temperature gradient, with the injected fuel experiencing the highest temperature at the fuel injection point. The fuel flowrate into the reactor is controlled using a nitrogen-pressurized flow regulated by a rotameter. To facilitate vaporization, the fuel is co-injected with nitrogen, and this mixture is pre-heated in a hot oil bath. The fuel/nitrogen stream is injected into the reactor centerline through an upstream-facing injector to provide mixing with the post-combustion gas stream flow. The fuel is added at concentrations ranging from about 1000 ppm to 2900 ppm (pure MTBE); from 900 to 2000 ppm (CaRFG2 with MTBE, corresponding to about 100 to 240 ppm MTBE injected); and from 1000 to 2900 ppm (CaRFG2 without MTBE). Total flowrates were varied by adjusting the methane and air flowrates proportionately (ranging from 79 to 210 standard liters per minute, slpm).

The conditions in the flow reactor are comparable to characteristic conditions of engine exhaust, where unburned fuel that has escaped the primary flame zone may react to form combustion byproducts. Pressure in the reactor is atmospheric, and temperatures in the fuel-injection region range from 599 to 1159 K. The fuel residence time (from fuel injection to exhaust gas sampling) ranges from 0.6 to 2.0 seconds.

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Exhaust products are extracted from the centerline at the end of the reactor using a quartz capillary probe. Exhaust gases are transferred through a heated Teflon line at a pressure of 71 torr to a Fourier transform infrared (FTIR) spectrometer. The spectrometer is a Biorad Digilab model FTS-40 with a 60-cm long multi-pass infrared optical cell. The FTIR uses an ultra-low noise, liquid nitrogen-cooled, mercury-cadmium-telluride (MCT) detector. Calibrations of pure species are measured in the spectrometer cell under the same conditions used in the experimental test runs, using chemical purity-grade specimens obtained from Aldrich Chemical Co.

In this study, FTIR instrument parameters are chosen to maximize sensitivity of the compounds measured, by using a pathlength of 13.68 m and a resolution of 0.25 wavenumber (cm^{-1}). To increase the signal to noise ratio, 64 single beam scans are taken for each sample. This system is estimated to allow detection for most species in the range of 1 to 10 ppm, with an error on absolute quantification of $\pm 20\%$. Relative error between measurements is approximately 1 to 5% (Fisher, 1990).

Experimental results

The destruction of MTBE as a function of the fuel injection temperature for different fuels and equivalence ratios is shown in Figure 4. Very little destruction ($< 30\%$) is observed at temperatures below 773 K, while there is nearly complete destruction of MTBE at 1073 K. The destruction of MTBE as a function of temperature is very similar for pure MTBE and for MTBE in reformulated gasoline. This result suggests that there is no significant inhibitory mechanism (with respect to MTBE destruction) associated with either the presence or reactions of other compounds in the RFG.

In our study, reaction of pure MTBE yields primarily isobutene, methanol, and formaldehyde as byproducts. This result agrees with previously reported results of pure MTBE reaction at elevated temperatures in benchscale laboratory studies. In our study, isobutene formation increases as temperature increases from about 633 K to about 973 K, after which it decreases with increasing temperature. Methanol is formed only at temperatures above 950 K. Formaldehyde is observed over the full temperature range studied (575 to 1150 K), but there is no apparent trend for formaldehyde formation as a function of temperature. No TBF formation is observed.

The CaRFG2 with MTBE used in our study contains about 11.6 vol% MTBE; no TAME is measured in this gasoline. Isobutene is observed only at temperatures above 973 K. In contrast to the pure MTBE case, no methanol is produced over the range of temperatures studied. As with the case of pure MTBE, formaldehyde is observed over the entire range of temperatures studied, with no apparent trend as a function of temperature. Again, no TBF formation is observed.

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The non-oxygenated CaRFG2 does not produce methanol over this temperature range. Isobutene is formed only above 973 K. Formaldehyde is formed over the entire range of temperatures studied, with no apparent trend as a function of temperature. No TBF formation is observed over this temperature range.

Other species observed as byproducts from either pure MTBE or CaRFG2 with MTBE include benzene, methacrolein, acrolein, formic acid, ethylene, propene, acetylene, methane, and ethane (Tables 5 and 6). Table 5 describes the formation of key MTBE byproducts from pure MTBE, CaRFG2 with MTBE, and CaRFG2 without MTBE. The formation of isobutene, formaldehyde, and benzene, normalized based on the amount of MTBE reacted, is shown as a function of temperature in Figures 5 to 7. The formation of these byproducts, normalized based on fuel injected (CaRFG2 with and without MTBE), is shown in Figures 8 to 10.

Table 6 summarizes the observed presence of compounds at temperatures where nearly complete destruction (>90%) of MTBE occurs. This temperature range should predict an upper limit on the temperature at which these primary products are formed. As temperature increases above this point, the byproducts themselves react, ultimately forming carbon dioxide and water.

Discussion

In this study, flame stoichiometry has a significant effect on post-flame fuel injection byproduct formation. The fuel-rich methane-air ($\phi = 1.1$) post-flame conditions generally yield lower formation of MTBE byproducts at each temperature, compared to stoichiometric ($\phi = 1.0$) post-flame conditions.

At temperatures where nearly complete destruction (>90%) of MTBE occurs (roughly 1070 to 1090 K), there are observable differences in the formation of MTBE byproducts between pure MTBE and CaRFG2 with MTBE, in terms of product quantity formed and the temperature range of byproduct formation. The most prevalent byproducts from pure MTBE observed at this temperature are methanol, isobutene, and formaldehyde. Minor species formed include methacrolein, acrolein, acetaldehyde, and formic acid. In contrast, reaction of CaRFG2 with MTBE at this temperature does not produce measurable quantities of methanol or methacrolein but does produce a minor amount of benzene. Since benzene is a component of the fuel itself and may also be formed as a byproduct from other precursors in gasoline, this result is not surprising.

No significant differences are observed in formation of byproducts between chemical-grade (“pure”) and refinery-grade MTBE. The refinery-grade MTBE evaluated in this study, produced by ARCO Chemical Company, contained no traces of TAME. In practice, however, “refinery-grade” MTBE may contain up to 3-4 % TAME, which could affect byproduct formation.

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The non-oxygenated CaRFG2 produces lower (non-detect, in many cases) amounts of the key MTBE byproducts than the CaRFG2 containing MTBE. One exception to this observation is (somewhat surprisingly) formaldehyde, where the amount formed on a per-fuel basis is roughly comparable for the two gasoline formulations at any given temperature.

Table 5. Summary of MTBE byproduct formation in flow reactor experiments.

Compound	MTBE	CaRFG2 with MTBE	Non-oxygenated CaRFG2
Isobutene	<ul style="list-style-type: none"> •□ Formation increases with temperature from ~ 600 to 1000 K, then decreases •□ Max: 0.9 – 1.1 ppm/ppm MTBE * 	<ul style="list-style-type: none"> •□ Only formed above ~ 1000 K •□ Max: at ~ 1050 K •□ Max: ~1.3 ppm / ppm MTBE •□ Max: 0.15 ppm/ppm fuel 	<ul style="list-style-type: none"> •□ Only formed above 950 K •□ Max at 1050 K •□ Max: ~0.04 ppm / ppm fuel
Methanol	<ul style="list-style-type: none"> •□ Only formed above ~ 950 K •□ Max. at ~ 1000 K •□ Max: 1.5 – 1.6 ppm / ppm MTBE 	<ul style="list-style-type: none"> •□ None measured 	<ul style="list-style-type: none"> •□ None measured
Formaldehyde	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature •□ Max. at ~ 1050 – 1100 K •□ Max: ranges from 0.8 – 1.2 ppm / ppm MTBE 	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature. •□ Max. between ~ 800 – 900 K •□ Max: 2.3 – 2.7 ppm / ppm MTBE •□ Max: ~ 0.3 ppm / ppm fuel 	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature. •□ Max at 1100 K. •□ Max: ~ 0.3 ppm / ppm fuel
Tert-butyl formate (TBF)	<ul style="list-style-type: none"> •□ None measured. 	<ul style="list-style-type: none"> •□ None measured. 	<ul style="list-style-type: none"> •□ None measured.
Tert-amyl methyl ether (TAME)	<ul style="list-style-type: none"> •□ None measured. 	<ul style="list-style-type: none"> •□ None measured. 	<ul style="list-style-type: none"> •□ None measured.
Tert-butyl alcohol	<ul style="list-style-type: none"> •□ Virtually none formed above ~ 900 K (Outlier at 1100 K) •□ Max. at ~ 650 – 750 K •□ Max: ~ 0.0035 ppm / ppm MTBE 	<ul style="list-style-type: none"> •□ Formed from 600 to 1150 K. •□ Max. at ~ 800 – 850 K •□ Max. ~ 0.01 ppm / ppm MTBE (Outlier at 0.045 ppm / ppm MTBE) •□ Max: 1 to 5 x 10⁻⁵ ppm / ppm fuel 	<ul style="list-style-type: none"> •□ None measured.
Benzene	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature. •□ Formed from ~ 600 - 1150 K. •□ Max. ranges from 950 – 1100 K •□ Max. ~ 0.011 – 0.025 ppm / ppm MTBE 	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature. •□ Formed from ~ 550 – 1150 K. •□ Max. at ~ 1100 K •□ Max: ~ 0.12 ppm / ppm MTBE (Outlier at ~ 0.5 ppm/ppm MTBE) •□ Max. ~ 1.2 x 10⁻⁴ – 4.2 x 10⁻⁴ ppm / ppm fuel 	<ul style="list-style-type: none"> •□ None measured.
Methacrolein	<ul style="list-style-type: none"> •□ Formed from ~ 625 – 1150 K. •□ Max: 1050 – 1100 K •□ Max (pure): 0.005 ppm / ppm MTBE •□ Max (refinery-grade): 0.011 ppm / ppm MTBE 	<ul style="list-style-type: none"> •□ One “hit” at 700 K •□ ~ 0.004 ppm / ppm MTBE •□ ~ 2.2 x 10⁻⁶ ppm / ppm fuel 	<ul style="list-style-type: none"> •□ None measured.
Acrolein	<ul style="list-style-type: none"> •□ No clear trend as a function of temperature •□ Formed from 625 – 1150 K. •□ Max at ~ 1100 K 	<ul style="list-style-type: none"> •□ Only measured above ~ 800 K •□ Max at ~ 1100 K 	<ul style="list-style-type: none"> •□ None measured.

Compound	MTBE	CaRFG2 with MTBE	Non-oxygenated CaRFG2
	<ul style="list-style-type: none"> • Max. ~ 0.001 ppm / ppm MTBE (refinery) • Max. ~ 0.007 ppm / ppm MTBE (pure) 	<ul style="list-style-type: none"> • Max: ~ 0.06 ppm / ppm MTBE • Max: ~ 4.7×10^{-5} ppm / ppm fuel 	
Acetaldehyde	<ul style="list-style-type: none"> • No clear trend as a function of temperature; only a few “hits” • (Pure): max at 750 K, ~ 0.011 ppm / ppm MTBE • (Refinery): max at 1100 K, ~ 0.09 ppm / ppm MTBE 	<ul style="list-style-type: none"> • $\phi = 1$: max. at ~ 850 K, then decreases • Not observed for $\phi = 1.1$ • Max: 0.14 ppm / ppm MTBE • Max: 1.2×10^{-4} ppm / ppm fuel 	<ul style="list-style-type: none"> • None measured.
Formic acid	<ul style="list-style-type: none"> • Formed from 800 – 1150 K. • Max: 1000 K (refinery) - 1100 K (pure) • Max: ~ 0.01 ppm / ppm MTBE (refinery) • Max: ~ 0.037 ppm / ppm MTBE (pure) 	<ul style="list-style-type: none"> • Formed from 600 – 1100 K. • Max at ~ 825 K • Max: ~ 0.03 ppm / ppm MTBE • Max ~ 2.5×10^{-5} ppm / ppm fuel 	<ul style="list-style-type: none"> • None measured.

* Maximum temperature, formation are for $\phi = 1.0$ unless otherwise noted.

Table 6. Formation of species at temperatures sufficient for destruction of nearly all MTBE.

Compound	Pure MTBE $\phi = 1.0$ T = 1092 K MTBE destruction = 91.2%	CaRFG2 with MTBE $\phi = 1.0$ T = 1073 K MTBE destruction = 91.3%		Non-oxygenated CaRFG2 $\phi = 1.0$ T = 1052 K MTBE destruction = N/A
	Formation (ppm / ppm MTBE)	Formation (ppm / ppm MTBE)	Formation (ppm / ppm fuel)	Formation (ppm / ppm fuel)
Isobutene	0.8	1.3	0.15	0.04
Methanol	1.5	0	0	0
Formaldehyde	0.8	2.2	0.25	0.2
Tert-butyl formate (TBF)	0	0	0	0
Tert-amyl methyl ether (TAME)	0	0	0	0
Tert-butyl alcohol	0	0	0	0
Benzene	0	0.013	8.5×10^{-6}	0
Methacrolein	0.005	0	0	0
Acrolein	0.007	0.06	4×10^{-5}	0
Acetaldehyde	0.005	0.06	4×10^{-5}	0
Formic acid	0.04	0.02	1×10^{-5}	0
Ethylene	Observed *	Observed *		Observed *
Propene	Observed *	Observed *		Observed *
Acetylene	Observed *	Observed *		Observed *
Methane	Observed *	Observed *		Observed *
Ethane	Observed *	Observed *		Observed *
Isoprene	Not identified	Not identified		Not identified
2-methyl-1-butene	Not identified	Not identified		Not identified
2-methyl-2-butene	Not identified	Not identified		Not identified
Acetone	Not identified	Not identified		Not identified

* Not quantified in the present study.

Vehicle studies evaluating MTBE combustion byproducts

Vehicle emission studies are several degrees more complex than laboratory studies. Evaluating the implications of these studies to determine the significance of MTBE byproduct formation is also more complex. First, the evaluation is no longer based on combustion of a single pure compound (MTBE), but rather on gasoline, a complex fuel mixture that contains hundreds of individual species. Furthermore, the internal combustion engine is vastly more complex than simple flow reactors in terms of its dynamic, variable physical operating properties, including temperature, pressure, and air/fuel ratio. In addition, vehicle emission control technologies (such as catalytic converters, fuel injection systems, and feedback control systems) dramatically impact exhaust (tailpipe-out) emissions. Thus, it is difficult to isolate the effect of a change in a single fuel parameter, namely MTBE content, on exhaust emissions.

The extensive Auto/Oil industry study (summarized below) is the most comprehensive evaluation to date of the impact of various fuel parameters on vehicle emissions. Only a limited number of additional studies have evaluated engine-out or exhaust products of incomplete combustion of MTBE in reformulated gasoline, by comparing speciated vehicle hydrocarbon emissions for fuels with and without MTBE (Howard et al., 1997; Hood and Farina, 1995; Koehl et al., 1993). 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). Two major types of vehicle studies have been conducted: dynamometer studies and tunnel studies.⁵

Dynamometer studies

Dynamometer studies are generally conducted in a controlled laboratory environment at 75° F using a standard format prescribed by the U.S. EPA, the Federal Test Procedure (FTP). The FTP incorporates cold start, stable running, and hot start emissions (referred to as “Bag 1,” “Bag 2,” and “Bag 3” emissions, respectively).⁶ “Composite” emissions are averaged over the entire test cycle. The key advantage of dynamometer vehicle testing is that it is a highly replicable, standardized test conducted under controlled conditions, so that individual fuel parameters can be varied under uniform test conditions, keeping other variables constant. A major drawback of dynamometer testing is that it does not accurately reflect the range of real-world driving conditions. Furthermore, the vehicles selected for testing may not be reflective of the actual on-road fleet of vehicles (e.g., the tested vehicles are generally in good operating condition and therefore under-represent emissions from malfunctioning vehicles).

⁵ A vehicle study currently being completed by CARB is not summarized here: *Comparison of the effects of a fully complying gasoline blend and a high-RVP ethanol gasoline blend on exhaust and evaporative emissions*. Draft Report, October 1998.

⁶ Unless specifically denoted “engine-out,” dynamometer emissions are presumed to be exhaust emissions.

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Hoekman (1992) characterizes FTP exhaust emissions from 19 vehicles (model years 1970 - 1990), comparing a Los Angeles premium gasoline with a reformulated gasoline containing 11% by volume MTBE. The reformulated fuel differs from the conventional fuel with respect to several parameters besides MTBE content: Reid vapor pressure (RVP), sulfur content, aromatic content, and distillation profile. The author compares speciated organic emissions for the two fuels for different vehicle control technologies (nuncatalyst, oxidation catalyst, three-way catalyst, and three-way catalyst with adaptive learning). Reformulated fuel containing MTBE reduces total VOC emissions from all vehicles by 6%. Reformulated fuel with MTBE increases MTBE and formaldehyde emissions, and reduces acetylene, 1,3-butadiene, total aromatic, and benzene emissions relative to the non-reformulated, non-oxygenated (conventional) fuel. Certain emission increases are attributed largely to the presence of MTBE in the reformulated fuel, especially isobutene emissions and total carbonyl emissions. Furthermore, as a percentage of total VOCs, isobutene emissions increased by 76% with the use of reformulated fuel for all vehicle categories. There were no significant differences in the normalized reactivity of the emissions from reformulated fuel compared to conventional fuel.

Hoekman (1992) also finds that vehicle control technologies play an important role in emissions; Table 7 summarizes some of the key hydrocarbon emissions reported in this study. The effect of vehicle technology appears particularly significant in the case of the four regulated toxic emissions. Large differences in exhaust toxic emissions are observed among vehicle categories; smaller differences are apparent when comparing the effects of reformulated versus conventional fuels. For example, reformulated fuel reduced total toxic emissions from three-way catalyst vehicles by 12%, but increased total toxic emissions from oxidative catalyst and adaptive-learning vehicles by 10% and 18%, respectively. Not surprisingly, emissions of MTBE from nuncatalyst vehicles are much higher than from other vehicle types. Otherwise, however, there is very little difference between the two fuels in toxic emissions from nuncatalyst vehicles. Figure 11, created from data collected by Hoekman, illustrates the range of emission differences (mg/mi) in select hydrocarbon emissions from nuncatalyst vehicles, comparing reformulated fuel with MTBE to a reference fuel. The hydrocarbon compounds selected for this graph are compounds observed as MTBE combustion byproducts at elevated temperatures, based on literature studies of flow reactors (see Table 2). Not surprisingly, pure (unburned) MTBE emissions are greatly increased from the fuel containing MTBE. Formaldehyde emissions are also increased, but to a much lesser extent. There are minor changes in emissions of most of the other hydrocarbon species of interest. For comparison, emissions difference data for the reformulated fuel with MTBE and the conventional fuel, for vehicles equipped with adaptive-learning catalyst systems, are shown in Figure 12. The absolute differences observed are dramatically decreased (note the scale difference for the two

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graphs), reflecting the decrease in emissions for the advanced technology vehicles. Qualitatively, the effects are similar; the greatest emissions increases are observed for formaldehyde and MTBE.

Table 7. Selected speciated mass emissions (FTP), mg/mi for different vehicle technologies for reference and reformulated fuels (data from Hoekman, 1992)

Species *	Noncatalyst		Oxidation catalyst		3-way catalyst		Adaptive learning	
	Reference fuel	Reform. fuel *	Reference fuel	Reform. fuel	Reference fuel	Reform. fuel	Reference fuel	Reform. fuel
Acetylene	209.69	177.10	15.37	13.36	7.38	4.21	2.84	3.01
Methane	188.07	156.04	66.70	57.70	73.42	66.67	65.72	67.64
MTBE	10.50	130.30	2.43	11.83	1.42	4.59	0.84	3.16
Propene	110.06	97.74	17.39	16.50	11.01	8.85	8.72	8.06
Formaldehyde	73.25	85.24	28.50	35.83	7.27	7.61	4.87	8.43
Acetaldehyde	19.74	21.72	11.15	11.76	4.43	3.64	3.07	4.71
Ethane	21.35	20.28	13.24	12.05	15.50	13.82	11.59	11.37
Propyne plus allene	19.21	20.25	0.88	1.22	0.69	0.53	0.38	0.31
Acrolein	11.62	13.20	3.74	3.75	1.11	0.74	0.81	1.16
1,3-Butadiene	2.96	1.81	0.02	0.33	0.07	0.05	0.00	0.14

* Species listed in order of decreasing prevalence in emissions from noncatalyst vehicles with reformulated fuel.

Several studies compare emissions of the four air toxics targeted in the 1990 CAAA: benzene, formaldehyde, acetaldehyde, and 1,3-butadiene. Reuter et al. (1992) measure exhaust emissions from twenty 1989 model year vehicles using the FTP for different fuels, including fuels with and without MTBE. Adding MTBE to fuel results in a statistically significant reduction in benzene emissions, with insignificant changes in the three other toxics measured.

Sawyer (1992) compares the change in emission levels of these four pollutants using a reformulated gasoline with 14.9 vol% MTBE with emissions from vehicles using conventional gasoline. ARCO, which developed this particular reformulated fuel, reports significant decreases in benzene, 1,3-butadiene, and acetaldehyde emissions and increases in formaldehyde emissions for 1990 vehicles equipped with three way catalysts (DeJovine et al. (1991) as cited in Sawyer (1992)).

Similarly, Mayotte et al. (1994a, 1994b) measures these four pollutant emissions from 1987 - 1990 model year vehicles, characterized as either “normal” or “high” emitters, using fuels with and without MTBE. They find decreased benzene, 1,3-butadiene, and acetaldehyde emissions for fuel containing MTBE relative to a reference fuel. Formaldehyde emissions are somewhat elevated for the MTBE fuel.

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Several studies report speciated emissions from vehicles using conventional gasoline containing no MTBE. These studies are useful as a baseline for comparison to measured emissions from fuels with MTBE. For instance, Sigsby et al. (1987) measure speciated VOC emissions from 46 in-use passenger cars (model years 1975 - 1982).

Auto/Oil Studies

The Auto/Oil Air Quality Improvement Research Program (Auto/Oil) has been conducted by a consortium of three domestic automobile manufacturers and 14 oil companies. The study highlights changes in fuel formulations that would reduce automotive pollutants, especially photochemical ozone precursors and mobile air toxic emissions. The Auto/Oil research and testing program has collected data on potential improvements in vehicle emissions and air quality associated with reformulated gasoline, alternative fuels, and developments in automotive technology. The study evaluates the effect on automotive emissions of multiple fuel variables: fuel composition (aromatics, MTBE, olefins, and T_{90} ⁷); RVP and oxygenates; methanol; and sulfur content.⁸ The study vehicles include 1983-1985 model year (MY) vehicles (“older” fleet), 1989 MY vehicles (“current” fleet), a “Federal Tier 1” fleet of 1994 vehicles, an “Advanced technology” fleet of prototype vehicles, and vehicles meeting 1993 California emissions standards.

One component of the Auto/Oil study evaluates vehicle emission effects of California Phase 2 RFG with MTBE compared to non-oxygenated, conventional gasoline (Auto/Oil, 1995, 1997). The study

⁷ T_{90} signifies the 90% distillation temperature.

⁸ The key findings of the Auto/Oil study with respect to toxic emissions and fuel composition are summarized below:

- Benzene was the most prevalent air toxic found. Decreasing the total aromatic content of gasoline reduced benzene emissions.
- Decreasing T_{90} reduced all measured toxics in newer cars but only some toxics in older cars.
- Decreasing the sulfur content of gasoline reduced exhaust toxics by 10%.
- Methanol (M85) reduced benzene emissions but increased formaldehyde emissions relative to gasoline.
- The aromatic content of fuel had the largest impact on total toxic emissions, mainly due to its effect on benzene emissions.
- Oxygenate addition increased aldehyde emissions in all cars. MTBE and other oxygenates (ETBE and TAME) had insignificant effects on total exhaust toxics. The oxygenates decreased benzene emissions and increased formaldehyde emissions.
- Reducing the olefin content of gasoline did not significantly reduce total exhaust toxic levels, but lowered 1,3-butadiene emissions by 30%.

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finds that average exhaust hydrocarbon emissions are reduced by 10 to 27%, CO emissions are reduced by 21-28%, and NO_x is reduced by 7 to 16%. Total toxic emissions are reduced by 9 to 32%.

Another component of the Auto / Oil study (1995, 1997) compares the four regulated toxic emissions from vehicles using reformulated gasoline without oxygenate to vehicles using reformulated gasoline with MTBE. For this component of the study, the vehicle fleets include 1989 MY, Federal Tier I, and advanced technology vehicles. Adding MTBE to fuel (at a level of 2.7 wt% oxygen, or 15% by volume MTBE) reduces total hydrocarbon emissions by 5 to 9%. The addition of MTBE is associated with decreased benzene emissions and increased aldehyde emissions. In general, oxygenates have no significant effect on emissions from Federal Tier 1 and advanced technology vehicles. California Phase 2 RFG reduces fleet average hydrocarbon emissions by 10 to 27% compared to industry average gasoline (Auto/Oil, 1995). This gasoline is associated with significant decreases in benzene emissions and smaller increases of formaldehyde emissions, as well as minor decreases in 1,3-butadiene and acetaldehyde emissions. The study finds no statistically significant differences in emissions between California Phase 2 RFG with MTBE ("C2" fuel) and a similar reformulated fuel without oxygenate ("C1" fuel), except for a 13% decrease in formaldehyde emissions with the oxygenate-free fuel.

Thus, in general, vehicle studies find that reformulated gasoline reduces emissions of CO and hydrocarbons, with lesser reductions in NO_x. Specific hydrocarbon emissions that have been shown to increase as a result of the presence of MTBE in gasoline include MTBE, isobutene, and formaldehyde. Other hydrocarbon emissions generally decrease when MTBE is used in gasoline, including propene, methane, and acetylene. However, because gasoline formulations differ widely (particularly conventional versus reformulated fuels), it is difficult to determine whether specific emission changes are due only to the presence of MTBE.

Analysis of Auto / Oil database

The extensive Auto/Oil database includes speciated engine-out and tailpipe (exhaust) emissions, comparing industry average gasoline with a gasoline blend containing 15 volume % MTBE, as well as speciated tailpipe emissions from different vehicle technologies with varying fuel compositions. The database speciation has 157 different exhaust components, including 12 aldehydes and ketones.

Table 8 is a matrix of measurements included in the database for engine-out and exhaust emissions for different vehicle fleets for three fuels of interest in our study. These fuels are a gasoline meeting CaRFG2 specifications with 11% by volume MTBE ("C2"); a gasoline meeting CaRFG2 specifications without MTBE or other oxygenates ("C1"); and an industry-average, nonreformulated

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gasoline (“A”). As shown in this matrix, the database contains the most data for Federal Tier I (1994 MY) vehicles for these three fuels for both engine-out and exhaust emissions.⁹

Table 8. Summary of Auto/Oil data points for hydrocarbon speciation emissions

Vehicle fleet technology	Fuel “A” Industry average, non-reformulated, no MTBE	Fuel “C1” CaRFG2, no MTBE	Fuel “C2” CaRFG2, 11 vol% MTBE
	Engine out / exhaust	Engine out / exhaust	Engine out / exhaust
“Older” fleet, 1983-85 MY	0 / 5	0 / 0	0 / 5
“Current” fleet, 1989 MY	0 / 14	0 / 8	0 / 16
Federal Tier I vehicles, 1994 MY	10 / 8	5 / 5	11 / 9
Advanced Technology vehicles	0 / 0	5 / 4	10 / 10
California 1993 MY	0 / 0	0 / 0	0 / 7

The hydrocarbon speciation emissions information from the Auto/Oil database for Federal Tier I vehicles (cars only) is compared with the literature studies of pure MTBE combustion byproducts at elevated temperatures. The emissions data for these compounds are shown in Tables 9 and 10. For purposes of this analysis, the Bag 1 (cold start) and composite emissions (average over whole cycle) are the most relevant. Tables 9 and 10 show average of emission data points for Federal Tier 1 cars for these three fuels. The selected species shown are a subset of the 157 species measured in the Auto/Oil study; they represent those compounds observed in laboratory studies of combustion byproducts of pure MTBE at elevated temperatures (Table 2).

Exhaust emissions are generally much lower than engine-out emissions because the catalytic converter achieves high conversion rates. This result agrees with laboratory studies of MTBE and other fuel reaction over catalysts. Bag 1 (cold-start) emissions are generally higher than composite emissions

⁹ These vehicles all have closed-loop fuel injection systems, with either sequential, throttle body, or port fuel injection.

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for all species. This is true for both engine-out and exhaust emissions, but the effect is more pronounced for exhaust emissions because the catalyst must warm up before it is fully effective.

Key combustion byproducts are common to all three fuels, as the complex mixture of hydrocarbons in gasoline produces numerous different products of incomplete combustion. Thus, the presence of MTBE is perhaps most markedly manifest in the differences (increases or decreases) in key combustion byproducts comparing fuels with MTBE (C2) to those without (C1 or A). Figure 13 illustrates emission differences (mg/mi) for select hydrocarbon species of interest for Bag 1 engine-out emissions, comparing CaRFG2 with and without MTBE (fuels C2 and C1). Figure 14 compares exhaust emissions for CaRFG2 with and without MTBE (C2 and C1). The absolute differences in emissions for the exhaust emissions are much lower than for the engine-out emissions, because the catalytic converter reduces overall emissions greatly. However, the directional changes are very similar for the engine-out and exhaust emissions: CaRFG2 with MTBE (C2) is associated with large increases in MTBE emissions, a lesser increase in isobutene emissions, and smaller increases in formaldehyde, acetone, and propadiene emissions. There are very small increases or even decreases in the remainder of compounds reported here.

Similarly, Figures 15 and 16 compare emission differences (mg/mi) for engine-out and exhaust emissions, respectively, between CaRFG2 with MTBE (C2) and conventional fuel (A). Again, the absolute differences in emissions are much lower for exhaust emissions because of the presence of the catalyst. There are a few interesting qualitative differences in comparing the difference between CaRFG2 with MTBE (C2) and conventional gasoline (A). In this case, the difference in exhaust emissions of isobutene and MTBE are about equivalent. In addition, there is a larger relative increase in propene emissions than there was between the two reformulated fuels.

The data set indicates that trace amounts of unburned MTBE are measured even from fuels that are supposedly oxygenate free, such as CaRFG2 without MTBE (C1) and conventional gasoline (A). This may be an artifact of measurement techniques or the result of carryover / residual from sequential testing with different fuels.

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Table 9. Engine-out emissions of MTBE reaction byproducts (mg/mi) (Auto / Oil, 1996)

Compound *	Fuel C2		Fuel C1		Fuel A Industry average, non-reformulated fuel without MTBE	
	CaRFG2 with MTBE		CaRFG2 without MTBE		Bag 1	Composite
	Bag 1 *	Composite	Bag 1	Composite		
Propene	104.1	97.2	122.0	117.4	88.9	83.5
Isobutene	86.2	82.1	64.8	64.4	30.8	29.9
MTBE	84.3	70.5	2.0	2.1	1.3	1.3
Acetylene (Ethyne)	83.3	79.6	93.2	96.9	84.5	82.3
Formaldehyde	73.7	78.4	65.1	77.5	57.2	63.9
Methane	65.5	58.7	69.8	63.9	55.7	51.0
Ethane	22.9	20.9	26.0	25.4	19.9	18.7
1,3-Butadiene	15.5	14.5	18.0	18.6	19.5	18.2
1-Butene	13.0	12.8	15.2	15.1	15.4	14.5
Acetaldehyde	12.1	12.1	13.7	16.1	12.0	13.1
2-methyl-2-butene	10.1	9.8	12.7	12.6	10.8	9.8
Acetone	9.1	9.1	6.7	8.6	4.6	4.5
2-methyl-1-butene	8.2	7.9	8.7	8.7	7.1	6.7
Propyne	7.7	7.5	6.3	8.9	5.6	5.7
Isoprene ¹⁰	6.2	6.4	6.9	8.0	8.1	7.4
Propadiene (Allene)	6.0	5.1	4.3	4.4	3.3	3.0
Methacrolein	4.8	4.9	3.4	4.0	2.2	2.5
Acrolein	3.7	4.0	2.1	3.2	3.2	3.7
Propionaldehyde	2.1	1.9	2.0	2.6	2.2	2.2

* Compounds listed in order of decreasing prevalence from Bag 1 emissions with C2 fuel.

¹⁰ Also referred to as 2-methyl-1,3-butadiene.

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Table 10. Exhaust emissions of MTBE reaction byproducts (mg/mi) (Auto / Oil, 1996)

Compound*	Fuel C2		Fuel C1		Fuel A Industry average, non-reformulated fuel without MTBE	
	CaRFG2 with MTBE		CaRFG2 without MTBE		Bag 1	Composite
	Bag 1*	Composite	Bag 1	Composite		
Methane	33.31	18.6	33.48	19.6	33.13	23.1
Isobutene	19.17	4.4	10.06	2.4	5.51	1.4
Propene	18.84	4.2	19.43	4.4	16.49	4.1
MTBE	13.40	2.9	0.204	0.1	0.105	0.05
Acetylene (Ethyne)	11.83	2.52	12.21	2.57	9.82	2.12
Ethane	8.36	3.4	8.86	3.8	9.25	5.0
Formaldehyde	6.72	2.1	5.57	1.7	5.82	1.8
1-Butene	2.75	0.59	2.70	0.618	3.19	0.771
1,3-Butadiene	2.43	0.53	2.60	0.568	3.12	0.705
2-methyl-2-butene	2.25	0.5	2.44	0.6	2.74	0.7
Acetaldehyde	2.08	0.59	2.08	0.604	2.28	0.640
Acetone	1.95	0.5	1.07	0.4	1.07	0.3
2-methyl-1-butene	1.40	0.3	1.23	0.3	1.19	0.3
Isoprene ¹¹	1.28	0.3	1.42	0.3	1.55	0.3
Propyne	0.896	0.2	0.839	0.2	0.497	0.1
Propadiene (Allene)	0.829	0.2	0.400	0.1	0.352	0.07
Methacrolein	0.629	0.1	0.403	0.1	0.327	0.07
Acrolein	0.368	0.1	0.137	0.03	0.434	0.09
Propionaldehyde	0.211	0.04	0.093	0.02	0.382	0.08

* Compounds listed in order of decreasing prevalence from Bag 1 emissions with C2 fuel.

Studies of other oxygenates

One component of the Auto/Oil study (1991) evaluates the emissions effects of oxygenated gasoline in twenty 1989 model year vehicles using the FTP. The oxygenates evaluated are MTBE, ethanol, and ETBE. Within a 95% confidence interval, the three oxygenates produced similar exhaust effects for criteria pollutants. The average effect of any of the oxygenates is to reduce total hydrocarbons by about 5%, reduce non-methane hydrocarbons by about 6%, reduce CO by about 13%, and increase NOx by about 5%. Emissions effects of the three oxygenates studied are summarized in Table 11.

¹¹ Also referred to as 2-methyl-1,3-butadiene.

Table 11. Effects on vehicle emissions from adding oxygenates for 1989 MY vehicles (Auto/Oil, 1991).

Emission constituent	Ethanol (a)	MTBE (b)	ETBE (c)
Exhaust (based on g/mi)	% changes*		
Total hydrocarbon	-4.9 ± 2.6	-6.5 ± 3.4	-5.2 ± 3.7
Non-methane hydrocarbons	- 5.9 ± 2.7	-7.0 ± 3.6	-6.3 ± 3.9
CO	-13.4 ± 4.9	-9.3 ± 6.7	-14.6 ± 7.4
NOx	5.1 ± 4.1	N.S.	N.S.
Benzene	-11.5 ± 6.0	-11.1 ± 8.0	-9.5 ± 8.2
1,3-Butadiene	-5.8 ± 5.7	N.S.	N.S.
Formaldehyde	N.S.	N.S.	N.S.
Acetaldehyde	159.0 ± 43.6	N.S.	256.6 ± 67.9
Evaporative (based on g/test)			
Diurnal (total)	30.3 ± 11.3	N.S.	N.S.
Diurnal (benzene)	27.7 ± 15.4	N.S.	N.S.
Hot soak (total)	50.1 ± 8.7	13.0 ± 9.9	N.S.
Hot soak (benzene)	45.4 ± 12.0	N.S.	N.S.

* Statistically significant values within 95% confidence interval.

N.S. Not statistically significant.

(a) □ Adding 10% by volume ethanol (2 wt% oxygen).

(b) □ Adding 15% by volume MTBE (2 wt% oxygen).

(c) □ Adding 17% by volume ETBE (2 wt% oxygen).

A subsequent Auto/Oil study (1992) compares vehicle emissions with fuels containing MTBE and TAME, using a fleet of ten 1989 model year vehicles. The fuels studied consist of a base fuel plus added oxygenate, forming approximately 2 wt% oxygen in the oxyfuel. At the 95% confidence level, there are no statistically significant differences in emissions from MTBE or TAME fuels for exhaust emissions of total hydrocarbons, non-methane hydrocarbons, CO, and NOx. Hot soak evaporative emissions are not different for the two fuels; neither are exhaust or evaporative emissions of benzene, 1,3-butadiene, or acetaldehyde. There is no significant difference between the two fuels in terms of ozone-forming potential or specific reactivity of the exhaust or hot soak evaporative emissions. The only significant differences in the emissions associated with the two fuels is that the TAME fuel has 28% higher formaldehyde emissions, and 24% lower ozone-forming potential of its diurnal evaporative emissions. Table 12 summarizes the emissions associated with the two fuels.

Table 12. FTP Vehicle emissions from fuels containing MTBE and TAME, 1989 model year vehicles (Auto/Oil, 1992)

Pollutant	Fuel with 11.5 vol% MTBE	Fuel with 12.7 vol% TAME
Exhaust emissions:		
Hydrocarbons, g/mi	0.21	0.21
Non-methane hydrocarbons, g/mi	0.17	0.17
CO, g/mi	2.48	2.57
NOx, g/mi	0.63	0.64
Benzene, mg/mi	6.6	6.5
1,3-Butadiene, mg/mi	0.7	0.7
Formaldehyde, mg/mi	1.5*	1.9*
Evaporative hydrocarbons, g/test		
Diurnal	0.54*	0.41*
Hot soak	0.37	0.39
Evaporative benzene, mg/test		
Diurnal	2.2	2.5
Hot soak	3.8	4.1

* Indicates statistically significant at 95% confidence level.

Tunnel studies

Tunnel measurements are ideal for isolating motor vehicle emissions. Tunnel air sampling allows for the collective analysis of the exhaust from many vehicles. The key advantage of tunnel studies is their ability to directly measure on-road performance of in-use vehicles. The main limitation of tunnel measurements is the limited range of operating conditions, typically warmed-up engines in a stable mode during an uphill gradient (slightly fuel-rich conditions). Thus, cold-start emissions and stop-and-go driving conditions are not observed. Since tunnel air, rather than *in situ* tailpipe exhaust, is measured, some evaporative (running loss) emissions are incorporated in tunnel measurements, but these emissions are small relative to the dominant exhaust emissions.

Kirchstetter et al. (1996) compare on-road speciated VOC emissions from light duty vehicles in the Caldecott tunnel (Oakland, California) for low-oxygenate fuel (0.3 wt% oxygen) to those from vehicles using high oxygenate fuel (2.0 wt% oxygen). 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 (based on sampling of service stations in the area). The high oxygenate fuel is associated with a 21% decrease in CO emissions and an 18% decrease in VOC emissions. NOx emissions are not changed significantly. The higher oxygenate fuel is associated with higher emissions of formaldehyde (13% increase), MTBE, and isobutene. The high-oxygenate gasoline reduced emissions of benzene by 25%, and

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also reduced total aromatic hydrocarbon emissions. Other individual hydrocarbon species that were reduced by the high oxygenate fuel include methane, propene, acetylene, ethane, and 1-butene. Table 13 summarizes key emissions data (as they pertain to MTBE and reformulated fuel combustion products) from Kirchstetter et al. (1996). Figure 17a illustrates emission differences (mg/L fuel) for select hydrocarbon species, comparing the high oxygenate and low-oxygenate fuels. Figure 17b shows these data, converted to units of mg/mi (assuming an average fuel economy of 20 miles per gallon), to facilitate comparison to data collected by other authors. These graphs show that the largest emissions increases associated with high levels of MTBE in fuel are MTBE, followed by lesser amounts of isobutene and formaldehyde. There are minor changes in the emissions of the remaining hydrocarbon species between the two fuels.

In a subsequent study, Kirchstetter et al. (1998a, 1998b) compare on-road emissions associated with California Phase 2 RFG and California Phase 1 RFG by comparing tunnel emissions for two sequential years when different statewide gasoline formulation standards were in effect. The authors find that Phase 2 RFG contained on average 10.7% by volume MTBE in the summer of 1996, compared to 1.0% by volume MTBE for Phase 1 RFG in the summer of 1995. Figures 18a and 18b, created from data in Kirchstetter et al. (1998a, 1998b), show the relative emission changes from onroad vehicles for California Phase 1 and Phase 2 RFG. They observe an 18% reduction in CO emissions, a 22% reduction in non-methane organic carbon emissions, and a 6% decrease in NO_x emissions from the summer of 1995 to the summer of 1996.¹² Figure 18a illustrates the change in emissions (mg/L fuel) reported by the authors for select hydrocarbon species. Consistent with other studies, MTBE emissions increase dramatically with the use of Phase 2 RFG, with a lesser increase in isobutene 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. Figure 18b shows the same data, converted to units of mg/mi (presuming a fuel economy of 20 miles per gallon), for ease of comparison with reported results from other studies. Table 14 summarizes key emissions data from Kirchstetter et al. (1998a, 1998b).

¹² The authors note that due to fleet turnover effects, not all of these decreases can be attributed simply to the use of Phase 2 RFG.

Table 13. Selected speciated emissions comparing on-road (tunnel) vehicle emissions for high-oxygenate fuel and low-oxygenate fuel (data from Kirchstetter et al., 1996)

Species *	High oxygenate fuel, Emissions, g/L fuel *	Low oxygenate fuel, Emissions, g/L fuel
Methane	0.375	0.413
MTBE	0.113	0.000
Propene	0.113	0.146
Acetylene	0.089	0.117
Isobutene	0.089	0.058
Formaldehyde	0.067	0.059
Ethane	0.041	0.054
2-methyl-2-butene	0.016	0.018
1-Butene	0.015	0.020
Acetaldehyde	0.015	0.014
1,3-Butadiene	0.012	0.014
2-methyl-1-butene	0.012	0.0096
Acetone	0.0065	0.0054
Propionaldehyde	0.0041	0.0017
Acrolein	0.0034	0.0033
Methacrolein	0.0031	0.0025

* Species listed in order of decreasing prevalence in emissions from high-oxygenate fuel.

The authors note that a large fraction of emissions in the Caldecott Tunnel is likely to come from high-emitting vehicles with reduced catalytic converter activity, evidenced by the high emissions of ethene and acetylene in the tunnel. Formaldehyde emissions increased between 1995 and 1996 (corresponding to the switch from California Phase 1 to Phase 2 RFG) despite the overall increase in non-methane hydrocarbon emissions, implicating the MTBE component of CaRFG2. Taking into account the fleet turnover effect,¹³ the California Phase 2 RFG is estimated to have an effective 12% increase in formaldehyde emissions. Kirchstetter et al (1998a, 1998b) find that MTBE emissions increased from 26 ± 4 mg/L (California Phase 1 RFG, summer 1995) to 160 ± 20 mg/L in 1996 (California Phase 2 RFG). They estimate, however, that only about 0.2% of the MTBE in gasoline escaped combustion under tunnel driving conditions. Table 15 shows the authors' reported data on percent changes in vehicle emissions from the summers of 1995 to 1996 (reflecting the shift from California Phase 1 RFG to Phase 2 RFG) for several pollutants (Kirchstetter et al., 1998a). Changes in measured emissions for previous and subsequent years (when there were not dramatic changes in fuel parameters) are listed for comparison.

¹³ Each year of the four-year tunnel measurements reported in Kirchstetter et al. (1998a, 1998b) found a one-year increase in the average model year vehicle, suggesting that some older, higher-emitting vehicles are continually replaced with newer, more advanced technology, cleaner vehicles. This "turnover" effect in and of itself should result in gradual improvements in vehicle emissions over time as vehicle technology improves.

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Table 14. Selected speciated emissions comparing on-road (tunnel) vehicle emissions for California Phase 1 and Phase 2 RFG (data from Kirchstetter et al., 1998a, 1998b)

Compound	California Phase I RFG			California Phase 2 RFG		
	Summer 1995			Summer 1996		
	wt% of NMOOC emissions (b)	mg/L emissions (b)	mg/mi emissions (c)	wt% of NMOOC emissions (b)	mg/L emissions (b,d)	mg/mi emissions (c)
Total NMOOC (a)		3,680	696		2,850	539
MTBE	0.70	25.8	4.88	5.47	155.90	29.50
Propene	3.36	123.6	23.40	3.68	104.88	19.85
Isobutene (2-methyl-propene)	1.38	50.8	9.61	3.31	94.34	17.85
Acetylene	3.07	113.0	21.38	2.92	83.22	15.75
Formaldehyde	1.60	58.9	11.14	2.19	62.42	11.81
Ethane	0.54	19.9	3.76	1.01	28.79	5.45
1,3-butadiene	0.63	23.2	4.39	0.49	13.97	2.64
1-butene	0.47	17.3	3.27	0.48	13.68	2.59
2-me-2-butene	0.59	21.7	4.11	0.47	13.40	2.54
Acetaldehyde	0.33	12.1	2.30	0.36	10.26	1.94
2-me-1-butene	0.39	14.4	2.72	0.27	7.70	1.46
Acetone	0.15	5.5	1.04	0.22	6.27	1.19
Methacrolein	0.05	1.8	0.35	0.09	2.57	0.49
Acrolein (propenal)	0.06	2.2	0.42	0.08	2.28	0.43
Propionaldehyde	0.03	1.1	0.21	0.05	1.43	0.27
Isoprene (2-methyl-1,3-butadiene)	0.10	3.7	0.70	0.03	0.86	0.16

- (a) □ Based on data from Kirchstetter et al. (1998a)
- (b) □ Based on data from Kirchstetter et al. (1998b)
- (c) □ Conversion based on presumed fuel economy of 20 miles per gallon.
- (d) □ Compounds listed in descending order of prevalence based on mg/L emissions from CaRFG2.

Table 15. Percent change in vehicle emissions, from tunnel studies (Kirchstetter et al., 1998a).

Pollutant	% change in vehicle emissions		
	1994-1995	1995-1996	1996-1997
CO	-17 ± 4	-18 ± 2	+1 ± 4
Non-methane hydrocarbons	-9 ± 8	-22 ± 7	-19 ± 8
NOx	-10 ± 4	-6 ± 4	-2 ± 3
Benzene	-22 ± 11	-52 ± 5	-10 ± 7
1,3-Butadiene	N/A	-39 ± 17	+21 ± 10
Formaldehyde	-8 ± 5	+4 ± 8	-41 ± 10
Acetaldehyde	-18 ± 7	-15 ± 9	-23 ± 13

N/A = Not available

Comparison of different vehicle studies evaluating MTBE byproducts

Both qualitatively and quantitatively, the Auto/Oil data are strikingly consistent with results of vehicle emission studies, such as Hoekman (1992) and Kirchstetter (1996, 1998a, 1998b). The prevalence of increased emissions of isobutene and formaldehyde associated with use of MTBE in fuel is consistent with the observations of these compounds as key products of incomplete combustion of MTBE at elevated temperatures in laboratory studies.

Table 16 summarizes the findings of key studies as well as the experimental work conducted in the present study. It compares observed byproducts of pure MTBE combustion and byproducts associated with MTBE as a component of CaRFG2.

Table 16. MTBE combustion byproducts observed in different studies^(a)

Compound	Ambient conditions (laboratory studies)	Elevated temperatures (laboratory studies)	Post-catalyst (laboratory studies)	Vehicle studies (engine-out) CaRFG2 with MTBE	Pure MTBE (This study)	CaRFG2 with MTBE (This study)
Tert-butyl formate	Major product	(b)			Not detected	Not detected
Formaldehyde	Major product	Major product		Major product	Measured at all temperature ranges	Measured at all temperature ranges
Isobutene	Minor product	Major product	Minor product	Major product	Major product	Major product
Methanol	Minor product	Major product			Major product, only above ~ 950 K	Not detected
Acetone	Minor product	Minor product		Minor product	Not identified	Not identified
Methane		Minor product	Major product	Major product	Major product	Major product
Acetylene		Minor product	Not detected	Major product	Major product	Major product
Propene		Minor product	Minor product	Major product	Minor product	Minor product
Acrolein		Minor product		Minor product	Minor product	Minor product, only above 800 K
Methacrolein		Minor product	Not detected	Minor product	Minor product	Minor product
Ethylene			Minor product	Minor product	Minor product	Minor product
Ethane			Minor product	Minor product	Minor product	Minor product
Acetaldehyde				Minor product	Trace product	Minor product

(a) Results cited in this table are compiled from multiple studies, as summarized in Tables 1, 2, 5, and 9.

(b) Blank indicates not reported in literature.

Summary: Automobile-generated air pollution

Thus far, our report has addressed specific hydrocarbon compounds associated with combustion of pure MTBE in laboratory settings, as well as the byproducts of reformulated gasoline containing MTBE from internal combustion engines. It is important to address the overall pollution emissions associated with the use of oxyfuels and RFG in motor vehicles. It is critical to distinguish the effect of these fuel formulations from the effects associated specifically with the presence of MTBE in the fuel. We begin, therefore, with a brief summary of the key factors that affect automotive emissions.

Air pollution from automobiles consists of both evaporative emissions and exhaust (tailpipe) emissions. Evaporative emissions of unburned gasoline occur during refueling or from fuel spills, as well as directly from the automobile itself. Automotive evaporative emissions include diurnal (breathing) losses caused by expansion and contraction of vapors in the fuel tank due to daily temperature variations, and running losses associated with evaporation from the fuel system at elevated temperatures during operation. Evaporative emissions are linked primarily to the gasoline volatility.

Exhaust emissions consist primarily of the criteria pollutants CO, VOCs,¹⁴ and NOx.¹⁵ Hydrocarbons and NOx together are precursors critical in the formation of photochemical ozone (smog). While it is difficult to make exact correlations between automotive emissions and ambient pollutant concentrations, particularly of secondary pollutants such as ozone, it is certain that automobile emissions have a tremendous impact on air quality.¹⁶

Under ideal conditions, gasoline combusts completely in the automotive internal combustion engine, producing carbon dioxide and water. Undesired compounds, such as hydrocarbons, CO, or NOx, are formed in the engine when local conditions (pressure, temperature, residence time, or oxygen concentration) do not permit complete combustion. Modern vehicles are equipped with emission control systems (catalytic converters with feedback control and fuel injection systems) intended to oxidize or reduce these compounds to reduce tailpipe emissions to below regulatory limits. In older vehicles, there is no catalyst present at all. Even when a catalyst is present, it may fail to fully convert the engine-out

¹⁴ VOCs are also referred to as reactive hydrocarbons or non-methane organic compounds (NMOCs).

¹⁵ While gasoline-powered automobiles emit some sulfur oxides (SOx) and particulates, they are generally considered negligible sources of these pollutants.

¹⁶ It is difficult to translate predictions of vehicle tailpipe emission reductions to ambient air quality changes. For one, predictive tests used to estimate vehicle emission reductions may not be representative of the actual on-road fleet; in actuality, a small percentage of vehicles contribute disproportionately to motor vehicle air pollution. In addition, stationary sources as well as "off-road" mobile sources contribute significantly to the formation of secondary pollutants such as ozone. Emission inventories from these other sources are often very uncertain. Furthermore, the complexities of meteorology confound many modeling efforts.

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emissions under a number of circumstances. For instance, it may not be functioning properly, or it may not have reached its light-off temperature (as in “cold starts”). Under certain fuel-rich operating conditions (e.g., under a heavy load, travelling uphill, or accelerating) the catalytic converter may be incapable of fully converting the engine-out emissions.

Historically, the approach to reducing automotive exhaust emissions was to change the mechanics of the automobile itself, by adjusting engine parameters such as spark plug timing or adding exhaust gas recirculation. Subsequently, emission control technologies were added, including catalytic converters, fuel injection systems, and feedback control loops. More recently, changes in fuel formulation have been investigated as a means of achieving lower automotive emissions, both evaporative and exhaust.

Air Quality Effects of Oxygenates and Oxyfuels

It is important to distinguish the automotive emission reduction benefits that are associated with the use of oxygenated fuels from those associated with reformulated fuels.

Effect of oxyfuels on CO

The most prominent effect of oxygenated fuels is on CO emissions. Key studies of the effect of oxyfuels on automotive CO emissions are summarized below and in Table 17. Oxygenated fuels were originally introduced into certain northern cities with high levels of wintertime CO (e.g., Denver) in the late 1980s. Federal oxyfuel requirements for CO nonattainment areas were effective in the winter of 1992-1993.

The Auto/Oil study (1997) found that adding oxygenate at 2.7 wt% oxygen reduces CO emissions by 11 to 14% in 1989 MY and “older” (1983-1985 MY) vehicles. The different oxygenates tested (MTBE, ETBE, ethanol, and TAME) had equivalent effects. In general, adding oxygenates had no significant effect on emissions from Federal Tier I and Advanced Technology vehicles (Auto/Oil, 1997).

In tests conducted using the EPA Federal Test Procedure (FTP), vehicle exhaust CO emissions (at ambient temperatures of 50°F and higher) are reduced by about 2 to 10% per wt% oxygen in fuel; for most vehicles, these reductions are in the range of 3 to 6%. CO emission reductions are generally smaller in more advanced technology vehicles, such as those with fuel injection, adaptive learning, and closed-loop, 3-way catalysts, and greater in older technology vehicles with carburetors and oxidative catalysts. High-emitting vehicles (malfunctioning or operating in a fuel-rich mode) generally also have larger CO reduction benefits from oxyfuels (NSTC, 1997).¹⁷

¹⁷ A study comparing the emissions benefit of 15% MTBE fuel in two different age vehicle fleets finds reduced CO emissions (about 4 to 5% reduction per wt% oxygen in the fuel); decreased hydrocarbon emissions (2 to 3% reduction per wt % oxygen); and a slight increase in NOx emissions (Hochhauser et al., 1991). The emission

Table 17. Summary of effect of MTBE on oxyfuel CO reductions.

Vehicle tested	Fuel tested (a)	Change in CO emissions, per wt% oxygen (b, c, d)	Reference
1989 MY	15 vol% MTBE	-3.4 ± 2.4	Reuter et al., 1992
1989 MY	15 vol% MTBE	-4.1 ± 1.3	Hochhauser et al., 1991
1983-85 MY	15 vol% MTBE	-5.2 ± 1.4	Hochhauser et al., 1991
High-emitters	15 vol% MTBE	-12 ± 7	Knepper et al., 1993
Normal emitters	11 vol% MTBE	-2.4 ± 4.0 (e) -4.4 ± 2.7 (e)	Mayotte et al., 1994a
High emitters	11 vol% MTBE	-8.0 ± 2.3 (e) -3.9 ± 2.1 (e)	Mayotte et al., 1994b
CL/AL/TWC (f)	11 vol% MTBE	35°F: -2.8 50°F: -5.1 75°F: -4.1	Most (1989), <i>cited in Hood and Farina (1995)</i>
CL/TWC	11 vol% MTBE	35°F: -1.8 50°F: +1.4 75°F: -3.8	Most (1989), <i>cited in Hood and Farina (1995)</i>

- (a) 15% by volume MTBE corresponds to 2.7 wt% oxygen; 11% by volume MTBE corresponds to 2.0 wt% oxygen.
- (b) Exhaust, measured in FTP, at ambient conditions unless otherwise noted.
- (c) Uncertainties represent 95% confidence intervals unless otherwise noted.
- (d) Relative to non-oxygenated (conventional) gasoline.
- (e) 90% confidence interval.
- (f) CL = closed loop; AL = adaptive learning; TWC = three-way catalyst.

The effects of oxyfuels on CO reductions appear to decrease at lower temperatures (20 to 55°F); very few data below 20°F are available (Hood and Farina, 1995). The reason for the decreasing effectiveness of oxygenates at low temperatures (even negative effects, increasing CO emissions) is not well understood (NSTC, 1997).

On-road measurements support these observed reductions in CO emissions. Field studies in Denver (Bishop and Stedman, 1989, 1990; PRC, 1992) found CO reductions between 8 and 10% per wt%

reductions are greater in the older vehicles than in the newer vehicles. A study of high-emitting vehicles (Knepper et al., 1993) indicates that benefits of oxyfuels on vehicle emission reductions may be greater than for normally operating vehicles. This study finds that oxyfuels produce increased reductions in both CO and hydrocarbon emissions (about 10% and 9% reductions, respectively, per wt% oxygen). NOx emissions increase by about 9% per wt% oxygen for these vehicles. A study by Most (1989, *cited in Hood and Farina, 1995*) compares CO emissions associated with oxyfuels for different vehicle technologies at different ambient temperatures. The older vehicles (carbureted, oxidative catalyst vehicles) have the largest, most consistent CO reductions at all temperatures (9% reduction per wt% oxygen). Vehicles with closed-loop, three-way catalysts show CO reductions of about 3% per wt% oxygen, while the most advanced technology vehicles (adaptive learning, three-way catalysts) had mixed effects on CO emissions from oxyfuels (in some cases oxyfuels even increase CO emissions).

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oxygen in the fuel. Both studies found that about 10% of the on-road vehicles contribute more than 50% of the total CO emissions; these vehicles account for most of the CO reductions achieved by oxyfuel use. Similarly, a tunnel study in California finds an approximate 10 % reduction in CO emissions per wt% oxygen associated with oxyfuel (Kirchstetter et al., 1996).¹⁸

Other studies have attempted to correlate vehicle CO emissions reductions associated with use of oxyfuels to changes in ambient CO levels. These studies have reached divergent conclusions about the effects of oxyfuels on the ambient urban CO concentrations: some studies found no quantifiable effect, while others attributed a 10% decrease in ambient CO levels to the use of oxyfuels (NSTC, 1997). Measuring ambient effects of this relatively small magnitude is problematic because of meteorological variability. Based on EPA predictive models, the observed CO reductions may represent upper limits of the effectiveness of oxyfuels. Urban CO concentrations have been declining for the last two decades, attributed largely to vehicle emission standards (fleet turnover) and improved vehicle emission control technology. The benefit of oxyfuels on ambient air quality has not been established for cold climate areas, and the effect of oxyfuels on ambient levels of other pollutants such as toxics and particulates is uncertain (NSTC, 1997).

Effects of oxyfuels on other pollutants

NO_x. In general, studies show that vehicle NO_x exhaust emissions are not changed significantly by low concentrations of oxygenates in fuel (Auto/Oil, 1997). In certain low-aromatic fuels, adding MTBE or another oxygenate increases NO_x emissions by about 5% (Auto/Oil, 1997). Some studies show increased NO_x emissions with oxygen concentrations at more than 2% by weight (NSTC, 1997). Based on a study of relatively “clean” 1989 model year vehicles, automotive NO_x emissions generally increase with the addition of fuel oxygenate, but are less affected by oxygenates at low temperatures (Hood and Farina, 1995). Increased NO_x emissions are expected, since adding oxygenate effectively increases the air/fuel ratio, contributing to increased NO_x formation.

Hydrocarbons. Studies indicate that vehicle hydrocarbon exhaust emissions are reduced by 1 to 7 % per wt% oxygen in oxyfuels (NSTC, 1997). In general, the reductions are larger in older, higher-emitting vehicles than in newer technology vehicles. The presence of oxygenate at 2.7 wt% oxygen produced a 5 to 9% reduction in hydrocarbon emissions in 1989 MY and “older” (1983-1985 MY) vehicles (Auto/Oil, 1997).

¹⁸ Kirchstetter et al. (1996) found a decrease of $21 \pm 7\%$ in CO emissions; the average oxygen content in gasoline was 2.0 wt%.

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Air Quality Effects of Reformulated gasoline (RFG)

Both dynamometer and on-road studies indicate that RFG results in significant reductions in automotive pollutant emissions relative to conventional gasoline, including hydrocarbons, CO, NO_x, and toxics. RFG also decreases the reactivity of vehicle emission, thereby reducing the subsequent ozone formation (Auto/Oil, 1995, 1997). Vehicle technology also has an important impact on emissions. Newer vehicles, which emit at lower levels than older technology vehicles, experience larger percentage reductions from using reformulated fuels (Auto/Oil, 1997). Furthermore, “Advanced” technology vehicles are designed to operate on CaRFG2, with its lower sulfur content (Auto/Oil, 1997).

Effect on CO emissions

CO emissions are reduced as a result of using RFG. Dynamometer tests have shown reductions of 21 to 28% associated with CaRFG2 (Auto / Oil, 1995; 1997). Actual on-road emission reductions are estimated to be 11% (California EPA, 1998). An on-road study found an 18% decrease in CO emissions associated with RFG (Kirchstetter et al., 1998a).

Effect on NO_x emissions

NO_x emissions are reduced by RFG. The Auto/Oil study (1997) found a 7 to 16 % reduction in NO_x emissions associated with CaRFG2. Estimates of on-road NO_x emission reductions range from 11% (California EPA, 1998) to a 6% decrease in NO_x measured in a tunnel study (Kirchstetter et al., 1998a, 1998b).

Effect on VOC emissions

VOCs in automotive exhaust are reduced from 10 to 27% by using CaRFG2 compared to conventional gasoline, according to FTP tests (Auto/Oil, 1997). On-road measurements have found reductions in VOCs of 17% (California EPA, 1998) and 13-31% (Kirchstetter et al., 1998a). Refueling and automotive evaporative emissions are expected to decrease in proportion to the decrease in vapor pressure associated with RFG, about 20% (Kirchstetter et al., 1998b). Based on on-road vehicle (tunnel) studies, Kirchstetter et al. (1998a) found that RFG was more effective in reducing VOC emissions than in reducing NO_x emissions.¹⁹

Effect on toxic emissions

¹⁹ CaRFG2 is projected to decrease the contribution of light-duty vehicles to peak ozone levels in New York by 28 to 39% for the years 2000 and 2010 (Auto/Oil, 1997).

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Benzene emissions are decreased 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., 1998b).

Total air toxics emissions are reduced by the use of CaRFG2 by 9 to 32% in dynamometer tests, largely due to the reduced benzene and aromatic content of the CaRFG2. (Auto/Oil, 1997). Total on-road toxic emission reductions are estimated to be 30% (California EPA, 1998).

Air Quality Benefits of MTBE as a Component of Gasoline

As noted above, it is critical to distinguish the effects associated with use of reformulated gasoline with effects associated purely with the presence of MTBE in reformulated gasoline. No significant difference was observed in exhaust emissions between CaRFG2 with and without oxygenates (Auto/Oil, 1995, 1997). Specifically, automotive CO, NO_x, VOC, benzene, and total exhaust toxic emissions are not significantly affected by including MTBE in CaRFG2, based on dynamometer tests (Auto/Oil, 1995).

Automotive formaldehyde emissions increase with the addition of MTBE to reformulated gasoline. 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 in advanced technology vehicles (Auto/Oil, 1995). Laboratory studies indicate that formaldehyde is a key byproduct of pure MTBE reaction at elevated temperatures, such as those in the automotive engine. Formaldehyde is also a key reaction byproduct of MTBE reaction at ambient temperatures (as in the case of evaporation or emissions of unburned fuel containing MTBE). Our laboratory study confirms the production of formaldehyde from both pure MTBE and CaRFG2 containing MTBE at elevated temperatures (570 to 1070 K). Similarly, Kirchstetter et al. (1998a) find a 12% increase in on-road formaldehyde emissions associated with the use of CaRFG2 containing MTBE.

As would be expected, automotive MTBE emissions also increase as a result of MTBE in RFG. Previous laboratory studies and our own measurements indicate that MTBE destruction efficiency increases as a function of reaction temperature. Especially during cold engine starts, emissions of unburned MTBE from the tailpipe are likely to be quite high. Automotive MTBE emissions are about 2.5% of total exhaust HC emissions; evaporative MTBE emissions are 8 to 10% of the total evaporative hydrocarbon emissions (California EPA, 1998). Kirchstetter et al. (1998a) found a six-fold increase in on-road automotive MTBE emissions associated with MTBE containing CaRFG2.

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Our laboratory studies confirm the findings of previous laboratory studies, vehicle studies, and on-road measurements that isobutene and formaldehyde are key byproducts of pure MTBE reaction at elevated temperatures, such as those in the automotive engine.

Methanol is also a key byproduct of pure MTBE reaction at elevated temperatures, as reported in previous laboratory studies and in our own study. However, we do not observe methanol production from reaction of CaRFG2 containing MTBE. This result suggests that methanol reacts quickly in the presence of the other hydrocarbons in gasoline. Vehicle and on-road studies have not reported methanol in automotive exhaust.

TBF is a key reaction byproduct of MTBE at ambient temperatures (e.g., in the case of evaporation or emissions of unburned fuel containing MTBE). Previous laboratory studies and our own observations confirm that TBF is not a product of MTBE reaction at elevated temperatures. Vehicle and on-road studies have not reported TBF in automotive exhaust.

Other compounds formed as byproducts of reaction of CaRFG2 containing MTBE include tertiary butyl alcohol, benzene, methacrolein, acrolein, acetaldehyde, and formic acid.

Conclusions

Compared to conventional gasoline, use of CaRFG2 significantly reduces automotive pollutant emissions of CO, VOCs, and toxics, as shown in both dynamometer and on-road (tunnel) studies. Vehicle technology also has an important impact on emissions; RFG has more pronounced emissions benefits in older, higher-emitting vehicles.

It is critical to distinguish the effects associated with use of reformulated gasoline from the effects associated purely with the presence of MTBE in reformulated gasoline. MTBE and other oxygenates have been found to have no significant effect on exhaust emissions of CO, NO_x, and VOC from advanced technology vehicles using reformulated fuel. The presence of MTBE in reformulated fuel is associated with an increase in formaldehyde emissions, relative to a non-oxygenated reformulated fuel.

Through our review of the available information, we find that there is no significant additional air quality benefit to the use of MTBE in reformulated gasoline, relative to non-oxygenated CaRFG2 formulations. Using ethanol or other oxygenates in CaRFG2 may achieve similar benefits but may incur additional risks as well.

Thus, there is strong evidence indicating that significant air quality benefits are associated with the use of reformulated gasoline. These benefits, primarily associated with reductions in exhaust and

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evaporative emissions of ozone precursors and air toxics, may be achieved without the use of oxygenates in RFG. The benefits from RFG are particularly effective for older vehicle technologies. Because newer vehicle technologies are designed to operate on RFG, reformulated fuel is critical for continued emissions reductions from the entire vehicle fleet. Despite its clear benefits, reformulated gasoline should not be viewed as a panacea for solving automotive air quality problems, but rather as one factor that can contribute to improved air quality. Achieving air quality goals will be achieved most effectively by specifying performance standards, rather than prescriptive fuel formulations, maintaining maximum flexibility for continued technological advances.

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