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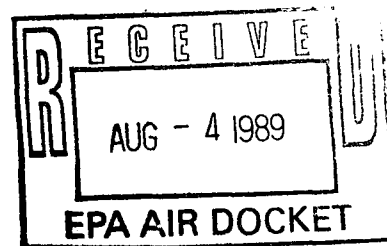
Motor Vehicle Emission Changes
With Use of Gasoline-Oxygenate Blends

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Craig A. Harvey and Jonathan Adler

Emission Control Technology Division
Office of Mobile Sources
Office of Air and Radiation
U. S. Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, MI 48105



ABSTRACT

Based on a large number of studies, the blending of gasoline with oxygenates such as alcohols or ether has been found to greatly reduce exhaust emissions of carbon monoxide (CO), for both non-catalyst and catalyst equipped vehicles. Smaller effects on exhaust hydrocarbons (HC) and oxides of nitrogen (NOx) have also been found. The effects on evaporative emissions depend largely on the volatility of the blend in question. These data are analyzed as a function of vehicle emission control technology, oxygen content, and fuel volatility. Based on this analysis, an example of fleet average effects of the use of such blends is presented.

INTRODUCTION

EPA has consolidated a large quantity of test data in an effort to clarify the potential benefits of gasoline-alcohol and gasoline-ether fuel blends on air quality. Specifically, exhaust HC, CO, and NOx data from 258 vehicles in 21 studies at both low and high altitudes have been analyzed to determine effects on ambient CO and ozone levels due to use of gasoline-oxygenate blends up to 3.7% oxygen by weight. In estimating ozone impacts, evaporative emissions were also considered, but these effects were modeled based on gasoline test data with adjustments to account for the various differences in fuel properties.

The fuels addressed here consist of ethanol blends up to 10 volume percent, methanol-cosolvent blends up to 5 percent methanol, and methyl tertiary butyl ether (MTBE) blends up to 15 volume percent.

This information is summarized mainly from EPA reports on the effects of fuel properties on vehicle emissions [1-3], and analyses conducted by the Colorado Department of Health for exhaust emissions of vehicles

at high altitude [4-6], and from statistical analyses of low altitude data performed by the EPA Office of Mobile Sources [7-9]. References 1 and 2 contain the details of the analysis presented here, along with a full list of the studies included and other pertinent references. Much of the information in the section on ethanol blends is applicable to methanol blends and, to a lesser extent, MTBE blends both of which are discussed later in the paper.

10% ETHANOL BLENDS (3.7% OXYGEN)

Exhaust HC, CO and NOx Emissions

The use of an oxygenated fuel blend such as gasoline with 10% ethanol (gasohol) results in an enleanment (i.e., more oxygen for fuel combustion) due to the oxygen contained in the blend itself. Fuel metering devices typically meter fuel and air volumetrically. Thus, the oxygen in the fuel results in less fuel and more total oxygen reaching the engine for fuel combustion, since the amount of air is not diminished. If the initial mixture when using gasoline is rich of stoichiometric, this enleanment results in reduced exhaust HC and CO but causes an increase in NOx emissions.

A closed-loop vehicle with an operating oxygen sensor in control of the engine will try to compensate for the oxygen present in the fuel by increasing the fuel flow until stoichiometry is achieved. If its fuel system has the necessary range of control authority, such a vehicle experiences little or no enleanment due to the blend for those portions of vehicle operation when the oxygen sensor is functioning and in control of the engine. Thus, one expects a smaller absolute reduction in exhaust HC and CO emissions from vehicles with oxygen sensors (generally 1981 and later model years) than earlier model year vehicles and perhaps a smaller proportional (percentage) reduction as well. It should be noted, however, that a

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closed-loop vehicle produces most of its CO during its occasional open-loop modes of operation.

HC and CO emissions are generally greater for vehicles at high altitude, since a given volume of air at high altitude has lower density and less oxygen. Open-loop vehicles operate richer more often and to a greater degree than they would at low altitude, which results in greater grams per mile emissions. The same holds for closed-loop vehicles during their open-loop modes unless there is some compensation for altitude in open-loop modes. One issue EPA has had to address is how these differences in operation between altitudes affects the reductions -- both absolute and relative -- that will occur with use of oxygenated blends. Analysis of the separate low and high altitude data bases indicates essentially the same effects of blends on a percent basis, while HC and CO reductions on an absolute basis are generally higher at high altitude.

Another issue is the relative effects of different oxygenates, such as methanol and ethanol. An analysis of emission tests of a group of vehicles tested with ethanol and methanol gasoline blends shows similar results for both fuels when the results are adjusted for RVP differences using the extensive emission data base obtained by EPA. This suggests that the most important factor is fuel oxygen content rather than the type of alcohol. Accordingly, EPA has pooled exhaust emission data from different types of oxygenated blends, using percent oxygen content and RVP as the only important variables influencing exhaust emission reductions.

Table 1 lists EPA's conclusions on the exhaust emission changes with oxygenated blends for fuels with 3.7% oxygen (gasohol or methanol blends) and 2% oxygen (an 11% MTBE blend). Both CO and exhaust volatile organic compounds (VOC) decrease while NO_x increases. VOC, in effect, are the non-methane hydrocarbons with adjustments made to account for the mix of true hydrocarbons, alcohols, and aldehydes that is expected with each blend. Because vehicle exhaust emissions with oxygenated fuels are still primarily true hydrocarbons, the adjustment is small. Specifically, EPA assumes that the effects of slightly increased alcohol and aldehyde emissions

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One important point to note is that some, but not all, newer closed-loop vehicles are equipped with "adaptive learning." Properly functioning vehicles with adaptive learning continuously adjust their open-loop fuel calibrations based on the most recent period of closed-loop operation. Thus, they can in theory compensate at least partially for fuel-caused enrichment even when the oxygen sensor is not in control, such as during cold starts and heavy accelerations. They may also not run as rich in failure modes as simpler closed-loop vehicles. These vehicles have been expected by some to have lower exhaust CO (and HC) reductions from oxygenated blends than earlier closed-loop vehicles. These lower reductions expected for the adaptive learning vehicles are not reflected in the test data available. Thus, for the purposes of this analysis, the same emission reduction is applied to all closed-loop vehicles regardless of model year.

Also, increases in RVP can cause an increase in exhaust emissions. For example, an increase in RVP of 1 psi results in carbon monoxide increases of about 3.1% for pre-1981 vehicles and about 7.6% for 1981 and newer vehicles for 75° ambient temperatures. Also, a 1 psi RVP increase results in exhaust hydrocarbon increases of about 1.8% from pre-1981 vehicles and 3.7% from 1981 and newer vehicles for 75° ambient temperatures. The adjustments for 75° are reflected in the "+0.76 psi" columns of Table 1 which give the emission changes with higher RVP ethanol blends based on an average increase in volatility for ethanol blends of 0.76 psi.

10% Ethanol - Evaporative HC Emissions

Evaporative emissions consist of hot soak and diurnal emissions. Hot soak emissions occur during the period immediately following engine shut-down (i.e., at the end of each vehicle trip). These losses will originate from both the fuel metering system and from the fuel tank. These emissions are greater for carbureted vehicles than for vehicles with fuel injection. Diurnal emissions consist of hydrocarbons both evaporated and displaced from the vehicle's fuel tank as the vehicle tracks the daily swing in ambient temperatures.

The EPA vehicle emission model, MOBILE3, determines an evaporative emission rate in

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makes 3.05 daily trips totalling 31.1 miles per day, so that there are 3.05 incidences of hot soak emissions for every diurnal emission.

Fuel volatility varies by season and from one part of the country to another. For example, in most areas of the country, the recommended ASTM RVP level during the summer months is generally 11.5 psi, although some areas have lower ASTM RVP limits but higher temperatures and/or higher altitude. This paper gives data on evaporative emissions with both low and high volatility fuel, of 9 and 11.5 psi RVP respectively. The correct case to use should be selected carefully. For the purposes of this analysis, the percent reduction values given under the 11.5 psi RVP headings should be used whenever local RVP is about equal to the local ASTM limit, i.e., nearly everywhere at present. The 9.0 psi RVP values are provided because EPA has proposed a new limit of 9.0 psi that would apply in areas now having an 11.5 psi ASTM limit. These two cases are evaluated separately because evaporative emissions are a non-linear function of RVP. Thus, the percentage reduction effects of oxygenated fuels at one RVP level could not be easily evaluated based on the effects at the other level.

Test data indicate that evaporative emissions from a 10% ethanol blend consist mostly of gasoline vapor with only about 15% ethanol. It is important to note that gasohol of equal RVP to the gasoline it displaces is assumed to result in equal moles of diurnal emissions; the lower molecular weight of ethanol (46) versus the typical evaporative hydrocarbon (64) results in slightly lower mass emissions. This factor has been accounted for in the analysis.

If no adjustments are made to compensate for it, use of alcohol increases RVP compared to the base gasoline. Since a blend of 10% ethanol in gasoline presently is not subject to ASTM or any federal RVP limits, the final blend will average about 0.76 psi higher in RVP. However, state or federal regulations could establish the same RVP limit for gasohol as for gasoline, so the tables contain separate columns to reflect both cases.

Addition of ethanol to gasoline also changes the distillation curve of the fuel and, in

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at 160°F. The increase in the 160° point has been shown to result in an increase in hot soak evaporative emissions even if the RVP of the gasohol is kept at the same level as the displaced gasoline [8].

Another potentially important phenomenon to consider with ethanol blends is "commingling" which refers to the mixing of gasoline-alcohol blends with non-oxygenated gasolines in vehicle fuel tanks whenever consumers switch from one fuel type to the other when refueling their vehicles at different service stations. The resultant commingled blend consisting of a mixture of gasohol and gasoline will have a higher RVP level than the simple volume weighted average of the gasohol and gasoline. The analysis presented in this paper considers only cases of 100% market share of each blend, thus avoiding any cases where commingling would be an issue. Detailed information on the effects of commingling can be found in Reference 1.

A final factor has been raised for ethanol blends concerning the relative contribution of ethanol emissions to ozone formation compared to hydrocarbons in either exhaust or evaporative emissions. Some smog chamber data have indicated that on a mass basis ethanol may be less reactive than the typical hydrocarbon compounds in exhaust and evaporative emissions [10]. This lower reactivity in effect has been incorporated into the evaporative VOC adjustment factors by ignoring the mass of oxygen in the ethanol. The issue of relative reactivity of ethanol on a per-carbon atom basis is much less clear-cut and no further adjustment has been used in this paper [11].

METHANOL-COSOLVENT BLENDS WITH 3.7% OXYGEN

Exhaust HC, CO and NOx Emissions

As mentioned before, the exhaust emission effect depends on the fuel oxygen level and RVP. Therefore, Table 1 also applies to methanol blends.

As was done with ethanol blends, the potential increase in exhaust aldehydes has been accounted for by assuming it would increase exhaust ozone potential to the same degree as the presence of exhaust alcohol would decrease the ozone potential (i.e., the net effect of increases in exhaust aldehydes

Methanol-Cosolvent Blends -- Evaporative HC

Table 2 contains the evaporative emission effects of methanol blends. Addition of methanol to a base gasoline generally results in an increase of 2-3 psi RVP. However, the resultant blend is subject to ASTM volatility parameters unlike gasohol. Thus, the volatility of the blend is adjusted (e.g., by prior butane removal) to decrease the volatility. Therefore, this paper assumes that the RVP of a methanol blend will be the same as that of the gasoline it displaces in the market place.

The lower molecular weight of methanol versus gasoline evaporative hydrocarbons (32 versus 64) reduces the mass of diurnal evaporative emissions. Evaporative emissions from a vehicle using a methanol blend consist of about 15% methanol, so the molecular weight adjustment (for diurnal emissions) has been applied to this fraction of the evaporative emissions in Table 2. Methanol, like ethanol, increases the percentage of fuel evaporated at 160°F. This has also been accounted for in the values shown in Table 2. Molecular differences between methanol and true hydrocarbons with respect to ozone formation are also reflected in the tables.

11% MTBE BLENDS (2% OXYGEN)

Exhaust HC, CO, and NO_x Emissions

It is assumed that the changes in exhaust emissions from use of 11% MTBE with a 2% oxygen level will be directly proportional to the amount of oxygen present. Thus, the values are a linear proportion of the earlier values for ethanol and methanol blends as shown in Table 1. The basis for this assumption is as follows.

An 11% MTBE blend has less oxygen and, therefore, less potential for enrichment of the air/fuel mixture. Among a large group of vehicles, the actual reductions should logically show a trend of diminishing returns from higher and higher oxygen levels as more and more cars are pushed into the lean region for more of their operation, so that further oxygen has less or no effect. Most of the existing data on oxygenated blends is for fuels in the 3.5% - 3.7% oxygen range, and if a linear effect is assumed from zero up to 3.7%, it will provide a conservative estimate

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issue is whether a substantially greater than linear emission reduction occurs at 2.0% oxygen. EPA has reviewed the data on vehicles tested with both 2.0% and 3.7% oxygen fuels, and its judgment is that the available data are currently neither extensive enough, consistent enough, nor dramatic enough, in showing a clear departure from linearity to risk overestimating the benefits at this time. Therefore, EPA assumes a linear relationship between exhaust emissions and oxygen content in the zero to 3.7% range of fuel oxygen. This issue is being investigated further in EPA and industry programs designed to obtain more data with both fuels.

11% MTBE Blends -- Evaporative HC

Addition of MTBE to gasoline does not result in increased RVP; in fact, some limited evidence indicates that there may be a slight decrease in RVP. However, 11% MTBE will increase the 160°F distillation point. This is expected to result in increased evaporative emissions as mentioned above. Values for this emission impact are given in Table 2.

FLEET AVERAGE EFFECTS

The general approach for calculating emission changes due to use of alternative fuels is based on MOBILE3, which calculates emissions from in-use motor vehicles for the calendar year of interest. Using the default MOBILE3 inputs as an example, fleet effects in calendar year 1990 are shown in Table 3. The estimated CO reduction with the use of oxygenated blends ranges from -14.6% to -26.9%, which is a substantial effect. These values are based on the specific conditions of the default case of MOBILE3, but details of how to determine appropriate estimates for specific areas can be found in Reference 1.

CONCLUSIONS

Based on a large quantity of vehicle test data, the use of gasoline-oxygenate blends can result in substantial reductions in exhaust CO emissions. The impact of these blends on ozone formation potential is less clear, since the exhaust and evaporative effects can be different, and they depend on a number of variables that would need to be

REFERENCES

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- 10 "Reactivity/Volatility Classification of Selected Organic Chemicals: Existing Data," EPA Report 600/3-84-082, H. B. Singh, et al, 1984.
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Table 1

Exhaust Emissions
Technology-Specific Effects of Blends
Percent Change from Gasoline

Technology	3.7% Oxygen (10% Ethanol or 5% Methanol/Cosolvent Blends)						2.0% Oxygen (11% MTBE Blends)	
	CO		NOx	VOC		RVP	CO	VOC
	Same	+0.76		Same	+0.76		Same	Same
	RVP	PSI		RVP	PSI		RVP	RVP
Non-Catalyst	-24.5%	-22.8%	+3.8%	-5.5%	-4.2%	-13.2%	+2.1%	-3.0%
Open-Loop Catalyst	-34.9	-33.4	+4.0	-15.6	-14.5%	-18.9	+2.2	-8.4
Closed-Loop	-21.4	-17.2	+8.1	-5.1	-2.4%	-11.6	+4.4	-2.8%

Table 2

Evaporative VOC
Technology-Specific Effects of Blends^a
Percent Change From Gasoline

	10% Ethanol				3.7% Oxygen Methanol-Cosolvent				11% MTBE
	11.5 RVP Base		9.0 RVP Base		11.5 RVP Base		9.0 RVP Base		Matched
	Match	+ 0.76	Match	+ 0.76	Match	+ 0.76	Match	+ 0.76	To Any RVP
<u>Diurnal</u>									
Carb	-9.66	+80.1	-9.66	+41.13	-18.79	+61.89	-18.79	+26.88	+1.78
F.I.	-9.66	+122.2	-9.66	+42.67	-18.79	+99.76	-18.79	+28.26	+1.78
<u>Hot Soak</u>									
Carb	+14.85	+35.28	+14.85	+25.52	-3.19	+12.45	-3.19	+3.37	+12.82
F.I.	-5.70	+20.18	-5.70	+34.01	-12.20	+11.90	-12.20	+24.77	-1.90

^a These effects include adjustments for lower molecular weight of the alcohols and different number of carbons/gram relative to gasoline vapor. For hot soak, adjustments for molecular weight are not used, but for carbureted vehicles an adjustment for distillation (% evap @160°F) is included. These adjustments assume 100% market share of the blend in question, with no commingling effects.

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Table 3

Fleet Average Effects of Blends in 1990

(With an Inspection/Maintenance Program)

	<u>CO</u>	<u>VOC</u>
Base Gasoline	18.2 g/mi	2.54 g/mi
Unadjusted 10% Ethanol	-24.6%	+15.0%
11% MTBE	-14.6%	- 0.8%
5% Methanol + Cosolvent	-26.9%	- 9.8%
Adjusted 10% Ethanol	-26.9%	- 5.1%