MOBILE SOURCE EMISSIONS ANALYSIS FOR CALIFORNIA

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16. Abstract (Limit: 200 words)

This report, issued in two volumes, reviews mobile source emissions from California vehicles and updates the analytical basis for mobile source emissions modelling. The research effort addresses the following issues, among others:

1. Identifies the market penetration of emissions control systems for model years 1975-1982 vehicles and projects the penetration of the systems to 1990;
2. Reviews 1975 forward in-use vehicle emissions data to evaluate the performance of individual emissions control systems including an analysis of failure rates and the emissions impact of specific component failures;
3. Analyzes the influence of speed, temperature, misfueling and inspection/maintenance programs on emission control systems;
4. Derives new emission factors for heavy-duty trucks to incorporate the influence of component malfunction;
5. Analyzes current technical and regulatory mobile source emission issues, as assessment of light-duty vehicle compliance with a 0.4 g/m NOx standard and comments on methanol additive fuel waivers;
6. Develops a California I/M credits model; and
7. Determines the effect of maintenance practices and fuel quality on transit bus smoke and particulate emissions

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PREFACE

This report presents the results of a major research study on mobile source emissions from California vehicles. That effort was divided into four task areas:

Task 1: Analysis of Post-1979 Model Year Light-and-Medium Duty Vehicle Emissions

Task 2: Analysis of Post-1979 Model Year Light-Duty and Medium-Duty Vehicle Emissions

Task 3: Analysis of Heavy-Duty Vehicle Emissions

Task 4: Analysis of Regulatory Issues

A total of 14 separate reports were produced under the contract. This volume contains all of the reports produced under Task 4. They are:

Technology Assessment for Light-Duty Vehicle Compliance With 0.4 g/m NO_x Standard

Comments Regarding MVMA Petition for Reconsideration of Petrocoal 211(f) Waiver

Comments Regarding American Methyl Corporation's Request for Waiver of Clean Air Act Section 211(f) for "Methyl-10" Fuel Additive

Environmental Impacts of Methanol/Gasoline Blends

Development of California's I/M Credits Model

Maintenance and Fuel Quality Effects In Transit Bus Smoke and Particulate Emissions

Three of the above documents incorporate comments and revisions suggested by the California Air Resources Board. These documents were published by ARB and submitted to dockets of relevant EPA rulemakings. They are reproduced in this volume in the format published by ARB.

For an overview of all of the reports produced under the contract the reader is referred to:

Executive Summary of Work Produced Under ARB Contract
"Mobile Source Emissions Analysis for California

TECHNOLOGY ASSESSMENT FOR LIGHT-DUTY VEHICLE COMPLIANCE WITH A 0.4 G/M NOx STANDARD

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TABLE OF CONTENTS

	Page
Summary	1
Statistical Analysis	1
Engineering Analysis	10
Available NOx Control Techniques	11
Compensating for Increased HC and CO	22
Effects of a 0.4 NOx Standard on Fuel Economy	31
Estimates of Likely Hardware and Cost Changes	32
References	37

LIST OF TABLES

		Page
1.	Relationship Between Catalyst Loading and NOx Level	4
2.	Relationship Between Catalyst System Type and NOx Level	4
3.	Comparison of CO Emissions - Port Fuel Injection vs. Carbureted 3-Ways	7
4.	Fuel Economy Analysis of 1982 Model Cars	10
5.	Methods for Reducing NOx Emissions Without Fuel Economy Loss	11
6.	Effects of Converter Type on Emissions and Time for Exhaust Exiting Converter to Reach 600°F	28
7.	Effect of Start Catalyst on Composite Emissions	30
8.	System Changes to Achieve 0.4 NOx With Some 3-Way Catalyst Cars	34
9.	System Changes to Convert Oxidation Catalyst Cars to 3-Way Catalyst Systems	35
10.	System Changes to Convert 3-Way Plus Oxidation Catalyst Cars to 3-Way Catalyst Systems	36

LIST OF FIGURES

		Page
1.	NOx vs. EGR Rate for Nissan Fast-Burn Engine	16
2.	Fuel Consumption and Hydrocarbon Emissions vs. EGR Rate for Nissan Fast-Burn and Conventional Engines	18
3.	Catalyst NOx Efficiency vs. Mileage for Different Platinum/Rhodium Ratios.	20
4.	Texas Instruments Heater	24

SUMMARY

As is evident from the 1983 emissions certification results, many cars and light trucks have already been certified at 0.4 grams per mile NOx or less. However, some of these models may require additional emission control to maintain compliance with the assemblyline testing requirements. Other models need as much as 40% greater NOx control to achieve 0.4. Two different approaches, one based on statistical analysis and one based on engineering analysis, have been used to determine the feasibility of achieving the additional NOx control required without fuel economy penalties.

STATISTICAL ANALYSIS

One indication of the type of changes which can be made to reduce NOx emissions has been derived from a detailed analysis of the 1982 model year certification results. A computer analysis was performed using detailed information on the emissions, fuel economy, and control system design of each gasoline engine powered passenger car model certified by thirteen different manufacturers. These manufacturers account for approximately 90% of California car sales. They were selected because they represent a reasonable cross

section of the total California fleet. The thirteen manufacturers analyzed in detail were General Motors, Ford, Chrysler, Toyota, Nissan, Volvo, Saab, BMW, Mercedes-Benz, Toyo Kogyo (Mazda), Peugeot, Fiat, and Mitsubishi.

Information analyzed included the following:

1. type of catalyst system used
2. amount of active ingredients in the catalysts
3. volume of the catalysts
4. type of catalyst substrate used
5. type of EGR system used, if any
6. type of air injection system used, if any
7. type of fuel metering system used
8. HC, CO, and NOx emission levels
9. city cycle fuel economy
10. engine displacement
11. vehicle test weight
12. vehicle gearing
13. engine horsepower rating

A variety of analyses were conducted to see if any relationships exist between vehicle design characteristics and NOx emission level. Analyses were also conducted to determine whether any relationship exists between the NOx emission levels of the vehicles and the fuel efficiency of the vehicles.

It has previously been noted that most vehicles certified to very low NOx emission levels are equipped with "port-type" fuel injection systems (one fuel injector per cylinder located in the intake manifold port). However, the analysis of all of the data indicated that the apparent correlation between the type of fuel metering system used

and NOx level may be primarily due to other system characteristics typical of models which happen to use port-type fuel injection. It appears from the data that the NOx level achieved is dependent on two factors: (1) the amount of rhodium used in the catalyst system and (2) the type of catalyst system used.

Rhodium is the most effective element for catalytically reducing NOx in automotive catalysts. The effect of the catalyst rhodium loading is illustrated in Table 1. As can be seen from the table, cars which certified at or below 0.4 grams per mile NOx used, on the average, 0.392 total grams of rhodium and 0.125 grams of rhodium per thousand pounds of vehicle test weight. Vehicles which did not achieve 0.4 NOx used 58% less rhodium per car and 59% less rhodium per 1,000 pounds.

Table 2 indicates the possible significance of catalyst system type. None of the cars without catalytic NOx control certified at 0.4 grams per mile or less. In addition, of those cars which use catalytic NOx controls, cars which used only 3-way catalysts rather than 3-way catalysts followed by oxidation catalysts have significantly lower NOx emissions. 87% of the cars using only 3-way catalysts were certified at 0.4 NOx or less. Only 15% of the cars using 3-way plus oxidation catalysts met 0.4 NOx.

Table 1

Relationship Between Catalyst Loading and NOx Level

	NOx Certification Level	
	0.4 or less	above 0.4
Rhodium (grams)	0.392	0.166
Rhodium/1000 lbs. test weight	0.125	0.051

Table 2

Relationship Between Catalyst System Type and NOx Level

System Type	Grams Rhodium per 1000 lbs.	Fraction Certified @ 0.4 NOx or less
Oxidation Catalysts	0.0	0%
3-way plus oxidation catalyst	0.058	15%
3-way only	0.131	87%

Catalyst rhodium loading appears to be a significant factor contributing to the superior performance of the 3-way only systems. On the average, the 3-way only cars used over twice as much rhodium as the 3-way plus oxidation catalyst cars per pound of car weight. In addition, the 3-way cars at or below 0.4 NOx used 32% more rhodium than the 3-way cars above 0.4 NOx.

However, rhodium loading is not the only factor contributing to the superior performance of 3-way only systems. The presence of the oxidation catalyst itself diminishes NOx control. Oxidation catalysts are installed behind 3-way catalysts to achieve greater levels of HC and CO control. However, a disadvantage of this system configuration is that the oxidation catalyst converts some of the NOx that was reduced (to ammonia) in the 3-way catalyst back to NOx.

It is interesting to note that the cars equipped only with 3-way catalysts demonstrated <u>superior</u> CO control to the cars equipped with 3-ways plus oxidation catalysts. 94% of the 3-way only systems certified at or below the federal CO standard of 3.4 grams per mile. Only 69% of the 3-way plus oxidation catalyst cars met 3.4 CO.

The catalyst loadings of platinum (Pt) and palladium (Pd), the two ingredients which control hydrocarbon and carbon monoxide emissions most effectively, may explain the superior performance of 3-way only systems on CO. Total Pt and Pd usage for the 3-way only and 3-way plus oxidation catalyst systems is comparable. However, the 3-way plus oxidation catalyst systems use much less loading in the front catalyst (the 3-way). This may degrade the performance of the system during the critical warmup period which the engine has high CO emissions and the catalysts, especially the rear catalyst, are below normal operating temperature.

An additional explanation for the relatively worse performance of 3-way plus oxidation catalyst systems is that they are not generally used in conjunction with port-type fuel injection systems. Port fuel injection generally provides improved CO control during warmup. This effect is evident from the comparison of the CO emission levels for the 3-way catalyst cars with port-type fuel injection and carburetors. As shown in Table 3, 100% of the 3-way cars with port-type fuel injection certified at 3.4 grams per mile CO or less. Their average CO level was 1.8 grams per mile. By contrast 82% of the carbureted 3-way cars certified at 3.4 CO or less. Their average CO level of 2.6 grams per mile was 44% higher than the port-type fuel injection cars.

Table 3

Comparison of CO Emissions
Port Fuel Injection vs. Carbureted 3-Ways

	% of Cars @ 3.4 or less	Average CO Level
Port-type Fuel Injection	100%	1.8 grams/mile
Carburetors	82%	2.6 grams/mile

No significant difference in the NOx levels exists between the carbureted and port-type fuel injected cars. Average NOx levels were 0.299 grams per mile for carbureted cars and 0.292 grams per mile for injected cars. About 25% of the 3-way cars certified above 0.4 NOx used feedback controlled carburetors as did 26% of the cars at or below 0.4 NOx.

Fuel economy differences between the 1982 certification cars were analyzed with the aid of a predictive model developed by Bascunana[1]*. The model predicts fuel economy from the three most critical vehicle parameters which affect economy: test weight, engine size, and gearing. The form of the equation is as follows:

$$MPG = A[(TW)^a (CID)^b (N/V)^c]$$

where: A,a,b, and c are constants
TW = vehicle test weight in pounds
CID = engine displacement in cubic inches
N/V = engine rpm/vehicle speed in mile per hour when in high gear

*Superscripts denote references listed at end of text.

Constants used with the equation were developed by EPA using EPA's 1981 data base for city cycle fuel economy. The coefficient of determination (r-squared) for the equation was 0.9, indicating the model is a good predictor of fuel economy. With the use of the model it is possible to account for the differences in fuel economy between vehicles which are due to difference in weight, engine size, and gearing. Differences which are not explained by the equation can be assigned to other factors including engine calibration differences needed to achieve various emission levels with the specific emission control system used on the vehicle. If certain combinations of emission control systems and NOx levels are associated with engine calibrations which adversely affect fuel economy then such effects should become evident provided enough cars are available for comparison and they are similar in other respects.

City fuel economy data for every test car in the sample was first "normalized" by adjusting it to correct for differences between the characteristics of the specific test car and average car in the population as far as weight, engine size, and gearing were concerned. The following equation was used:

$$MPG_{norm.} = (MPG_{act.})(CMPG_{avg.})/(CMPG_{act.})$$

where: $MPG_{norm.}$ = fuel economy of the test car adjusted to the average weight, engine size, and gearing of all of the cars tested

$MPG_{act.}$ = actual measured fuel economy of the test car

$CMPG_{avg.}$ = predicted fuel economy of a car with average weight, engine size, and gearing

$CMPG_{act.}$ = predicted fuel economy of a car with the same weight, engine size and gearing as the test car

The results of the analysis are displayed in Table 4. Cars certified at or below 0.4 NOx were 0.5% more fuel efficient than the average car and 0.9% more efficient than cars certified with NOx levels above 0.4 grams per mile. 3-way only cars demonstrated 1.8% better economy than the average car and 4.5% better economy than 3-way plus oxidation catalyst cars.

Table 4

Fuel Economy Analysis of
1982 Model Cars

	Normalized MPG	Difference from Average Car
All Cars	20.94	0%
Cars @ 0.4 NOx or Below	21.04	+0.5%
Cars Above 0.4 NOx	20.86	-0.4%
3-Way Only Cars	21.31	+1.8%
3-Way Plus Oxidation Catalyst Cars	20.40	-2.6%

ENGINEERING ANALYSIS

There are two fundamental approaches available for reducing the NOx emission levels of those models which have not yet demonstrated sufficient NOx emission control to meet the certification and assemblyline testing requirements under a 0.4 gram standard. The first approach is the reduction of "engine-out" emission levels through changes to the basic engine. The second approach is the improvement of catalyst efficiency. Both approaches can be taken using a variety of specific changes and both require consideration of the effects that changes to improve NOx control will have

on the control of HC and CO emissions, fuel economy, driveability, and cost.

AVAILABLE NOX CONTROL TECHNIQUES

The four most common approaches to the control of NOx emissions are (1) retarded spark timing, (2) richer air/fuel ratio, (3) exhaust gas recirculation (EGR), and (4) catalytic aftertreatment. The first three approaches involve changes to the basic engine which are commonly associated with reduced fuel economy. However, each of these approaches can be used to reduce NOx emissions without fuel economy loss provided other changes are also made. It is only when NOx controls are applied in a simplistic manner that fuel economy is less than optimum. The types of changes needed to incorporate these NOx control techniques without fuel economy loss are summarized in Table 5.

Table 5
Methods for Reducing NOx Emissions
Without Fuel Economy Loss

Technique	Changes Needed to Maintain Optimal Fuel Economy	Side Effects
spark retard	add "fast-burn" combustion chambers	reduced HC
richer air/fuel ratio	increase EGR rate to obtain best economy with richer mixture	increased HC and CO
EGR	advance spark timing and increase compression ratio	increased HC
catalytic control	none	none

As can be seen from Table 5, some NOx control techniques adversely affect other emissions. This is another reason why a "systems" approach should be taken to reducing NOx emissions. When the engine and emission control system are completely re-optimized, additional NOx control can be achieved without adverse consequences. As discussed below, the use of additional HC and CO controls in combination with more EGR, and catalysts with improved NOx conversion efficiency, offer the greatest potential for achieving additional NOx control without adverse consequences.

Exhaust Gas Recirculation - EGR has three principal effects on gasoline engines. First, it reduces NOx emissions. Second, it increases hydrocarbon emissions. And third, it reduces the octane requirement of the engine. All three of these effects are due to the reduced peak flame temperature and reduced oxygen concentration associated with the use of a diluent. The increased HC emissions and the reduced peak flame temperature in and of themselves would reduce fuel economy. However there are countervailing forces at work. EGR increases the ratio of specific heats of the intake mixture and thereby increases ideal air cycle thermal efficiency:

$$\text{thermal efficiency} = 1 - \frac{1}{r^{(k-1)}}$$

where:

r = compression ratio

k = $^{C}p/^{C}v$, ratio of specific heats.

This effect offsets the adverse effect on Carnot cycle efficiency due to the lowered flame temperature.

The reduction in fuel combustion efficiency as evidenced by increased HC emissions with EGR is insignificant because the portion of the total fuel not burned is insignificant.

Another factor affecting fuel economy with EGR is reduced pumping loss. Because the recirculated exhaust gas takes up space in the cylinder, a lower intake manifold vacuum is needed to deliver the same mass of air and fuel. The reduction in intake manifold vacuum increases the efficiency of the engine in the same manner that the use of a lean air/fuel ratio increases efficiency in an engine that does not use EGR. A side benefit of achieving a reduction in pumping loss without the use of lean mixtures is that the exhaust gas is compatible with catalysts which reduce NOx such as 3-way catalysts. Engines optimized for fuel economy without the use of EGR have excess oxygen in their exhaust gases which prevents the catalytic control of NOx for all practical purposes.

One reason EGR is so often linked to poor fuel economy is that before the availability of high efficiency catalysts, manufacturers used spark retard to offset the HC emission increase caused by EGR. This is no longer required. In addition, the first generation EGR systems used on automobiles in the early 1970's did a poor job of matching the EGR flow rate to the load on the engine. EGR flow-rate with unsophisticated systems is usually excessive at light load. This causes much greater HC emission increases and driveability degradation due to combustion stability problems. The increase in HC may be too large to be controlled adequately with a catalyst. More sophisticated EGR systems which are electronically controlled have minimized the HC emission increases associated with EGR, however, not all vehicles are yet equipped with sophisticated systems.

The NOx control achievable on conventional engines through the use of EGR in combination with advanced spark timing for retaining optimum fuel economy is approximately 80%, according to information published by General Motors[2] and others. Since uncontrolled conventional engines typically emit about 3-5 grams per mile of NOx, levels below 1.0 grams per mile are achievable through the use of EGR. Since typical 3-way catalysts have NOx conversion efficiencies of at least 60%, it is apparent that less than the maximum amount of EGR is used on those vehicles which are not yet certified at 0.4 grams per mile NOx.

Increased EGR rate is one of the most promising techniques available to those manufacturers who have not yet certified all of their models at 0.4 NOx. EGR rates of approximately 20% are needed to achieve 80% NOx control, however, conventional engines experience degraded driveability at rates above about 15%. Higher rates can be achieved without driveability problems provided more sophisticated EGR systems or "fast-burn" combustion chambers are used. A "fast-burn" combustion chamber is one that is designed to reduce the time required from the firing of the spark plug to the combustion of essentially all of the fuel in the cylinder. This can be accomplished through either increased turbulence or the addition of more than one spark plug.

The benefits of fast-burn combustion chambers is evident from information reported to EPA by Nissan[3]. As shown in Figure 1, the fast-burn combustion chamber extended the maximum EGR rate without combustion stability problems from about 19% to about 35%. This made it possible to improve NOx control efficiency from about 80% to over 95%. This level of NOx control is sufficient to achieve 0.4 grams per mile with no catalytic control of NOx.

Figure 1

NOx vs. EGR Rate for
Nissan Fast-Burn Engine

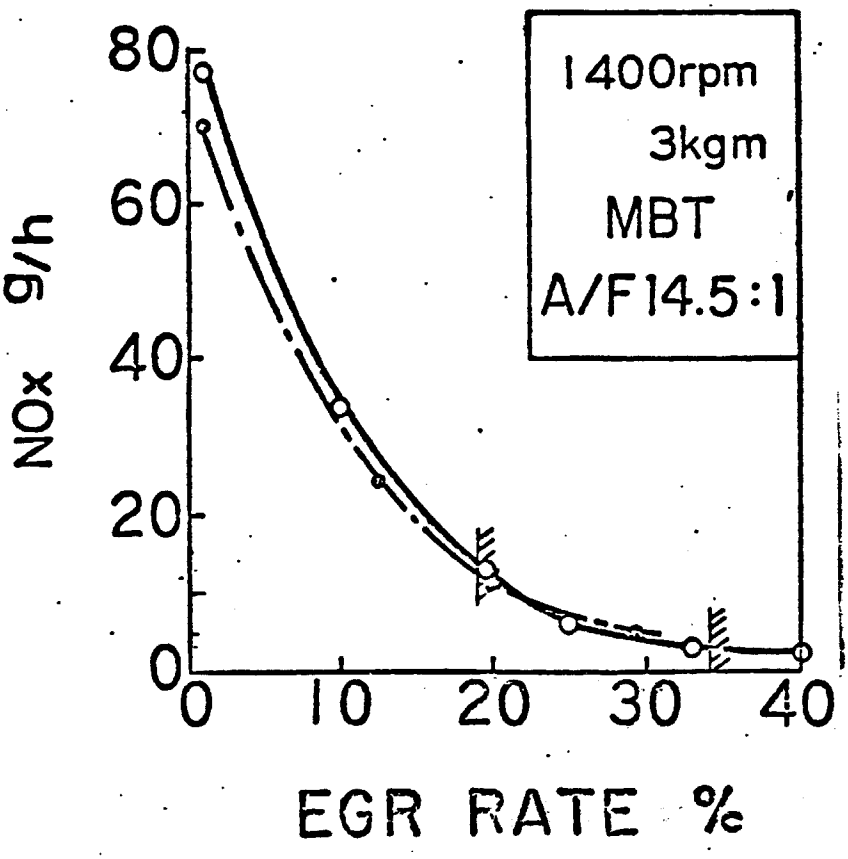


Figure 2 shows that the fast-burn engine also emits less hydrocarbons and has 9% better fuel efficiency at an EGR rate of about 20%. As can be seen from the figure, the fast-burn engine achieves optimum fuel efficiency at 20% EGR. Test data provided by Nissan indicate that when the engine is calibrated for 0.6-0.8 grams per mile NOx it achieves almost 10% better fuel economy than the average 1982 car of equivalent weight. The Nissan data indicate that with the use of fast-burn combustion chambers, EGR, and a 3-way catalyst it is possible to easily achieve the 0.4 gram NOx standard with a fuel economy improvement.

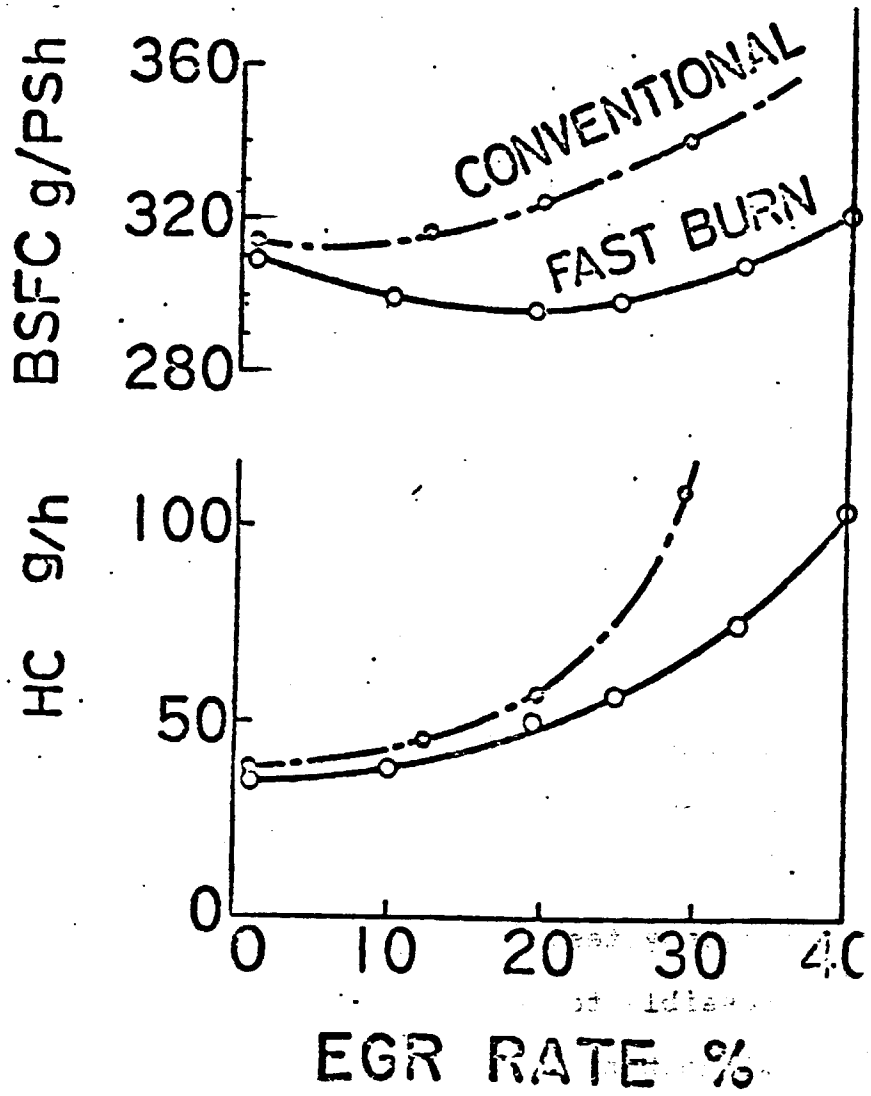
Improved Catalytic Control of NOx - Many different approaches can be taken to increase the efficiency of HC and CO control with catalytic converters. Two of the most straightforward approaches are increased catalyst loading and the elimination of clean-up oxidation catalysts.

Loading - The active ingredients of 3-way catalysts are platinum and rhodium. Platinum is the ingredient which is principally responsible for the control of hydrocarbons and carbon monoxide. Rhodium is the ingredient which is principally responsible for the control of NOx.

The amount of rhodium used in 3-way catalysts has a significant effect on the ability of the catalyst to eliminate NOx. This effect was apparent from the analysis

Figure 2

Fuel Consumption and Hydrocarbon Emissions vs. EGR Rate for Nissan Fast-Burn and Conventional Engines



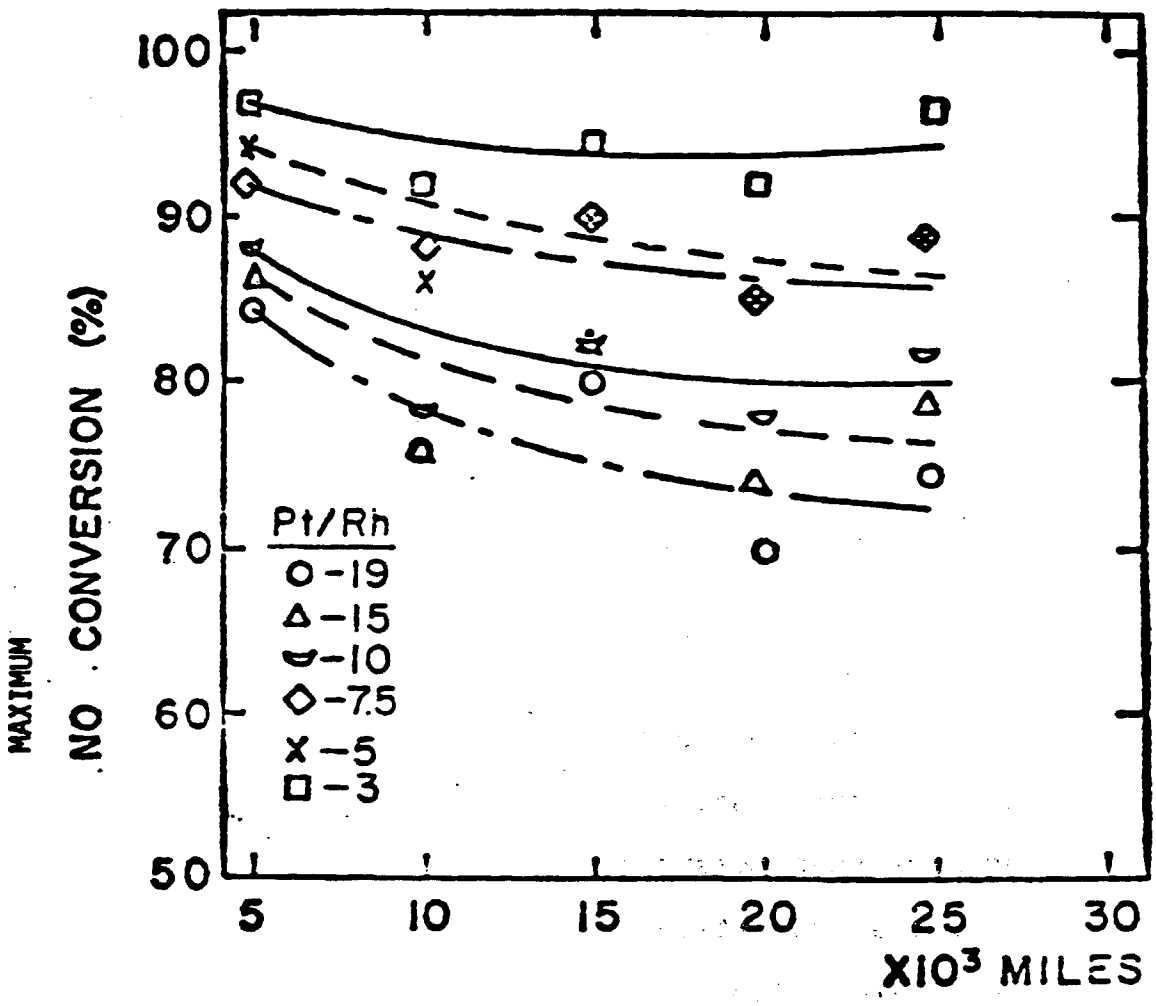
of the 1982 certification data, however, it is more clearly illustrated in Figure 3. This figure shows the reported[4] effect of different ratios of platinum and rhodium on NOx conversion efficiency as a function of mileage accumulation. Since the total amount of platinum and rhodium combined was held constant during the tests, those catalysts with the lower ratios of platinum to rhodium contained the most rhodium.

As can be seen from Figure 3, NOx conversion efficiency increased significantly as the ratio of platinum to rhodium decreased and the total amount of rhodium increased. A catalyst with a platinum/rhodium ratio of 3:1 controlled NOx with about 95% efficiency. In addition, no significant loss of conversion efficiency was measured as mileage was accumulated. A catalyst with a platinum/rhodium ratio of 19:1 initially achieved about 84% efficiency. Conversion efficiency degraded to about 73% after 25,000 miles.

Catalyst efficiency tests such as those reported in Figure 3 make it possible to see the effect of changes in catalyst loading without the effect of the many other variables which effect the NOx emission level of a particular car. A comparison of two specific cars using catalysts with different rhodium content may not show the effect illustrated in Figure 3 because of numerous other differences

Figure 3

Catalyst NOx Efficiency vs. Mileage
for Different Platinum/Rhodium Ratios



between the vehicles which may exist such as EGR flow rate, spark timing, etc.

Based on Figure 3, it appears that the 43% reductions in NOx emission levels needed to bring the highest emission level 1983 models into compliance with the 0.4 NOx standard could be accomplished through increases in rhodium usage of approximately a factor of two. Since the average car that does not achieve 0.4 NOx is currently using just under 0.2 grams of rhodium, a total of 0.4 grams may be needed for these cars. Interestingly, 0.4 grams per car is almost precisely the average level of rhodium used in those cars which have already certified to 0.4 NOx or less.

Deletion of Oxidation Catalysts - It appears from the certification data that the use of oxidation catalysts in conjunction with 3-way catalysts may adversely affect the degree of NOx control achievable. This phenomenon has been documented in numerous tests where significant increases in NOx emissions have been measured between the inlet and the outlet of the oxidation catalyst. Ford has reported[5] numerous tests wherein the oxidation catalyst increased the NOx emissions by about 100%. The specific benefits of eliminating oxidation catalysts will vary from car to car due to differences in fuel metering and catalyst formulations.

If done properly, a change from a 3-way plus oxidation catalyst system to a 3-way only system will not significantly affect HC and CO control. Loss of control can be prevented by retaining the same total volume of catalyst. In other words, two relatively small catalysts should be replaced by one relatively large catalyst.

COMPENSATING FOR INCREASED HC AND CO

Although no significant additional HC and CO control is likely to be required due to the imposition of a 0.4 gpm NOx standard, a small fraction of the different models could require some additional control. The further control over HC or CO emissions that may be needed with some 0.4 NOx systems can also be accomplished thorough changes to either the basic engine or the catalytic aftertreatment system. Two of the most effective basic approaches to reducing HC and CO emissions without increasing NOx emissions are reduced cold start enrichment and increased catalyst efficiency.

Reduced Cold Start Enrichment - It has long been recognized that warmed up gasoline engines emit much less HC and CO than engines which are cold when started. The area of the engine that is most temperature sensitive is the intake manifold. A warm intake system improves fuel

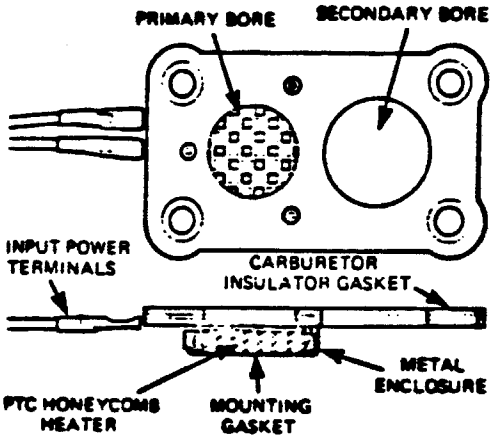
vaporization and atomization and reduces the mixture enrichment required to obtain a combustible air/fuel mixture in the cylinder.

Directing exhaust gas through the intake manifold during warmup operation is one technique that has been employed on many production vehicles. Such systems are commonly referred to as Early Fuel Evaporation (EFE) systems. EFE systems are beneficial in reducing warmup time and therefore they make it possible to reduce the time during which the engine must be operated with fuel enrichment. However, because of thermal inertia, EFE systems do not provide heat to the intake manifold during startup and immediately thereafter when it is needed most.

An extremely successful technique for providing heat to the intake manifold immediately during cold starting and warmup operation has been developed by the Control Products Division of Texas Instruments, Inc. (T.I.). T.I. reports[6] that the basic concept involves the use of electrical resistance heating of a grid mounted directly under the carburetor. The grid is made of a "positive temperature coefficient" (PTC) ceramic. T.I. refers to the device as either a "PTC Honeycomb Heater" or an "EFE Heater". A schematic of the heater is shown in Figure 4.

Figure 4

Texas Instruments Heater



Maximum power consumption for the T.I. heater is approximately 350 watts. Power consumption decreases when the grid temperature at which resistance increase occurs is reached. According to T.I., the heater reaches operating temperature in just a few seconds after it is energized. Fuel atomization is enhanced even before the engine fires during a low temperature cold start. Therefore, leaner choke settings are feasible. Current to the heater is switched off when the engine coolant temperature reaches approximately 150°F. With the use of the heater, T.I. reports that CO emission reductions of 30% to 60% are possible under standard test conditions.

The atomization improvement associated with the T.I. heater is probably due to three mechanisms:

1. Convective heating of the intake charge passing through the grid
2. Conductive heating of fuel droplets which impact the grid
3. Improved mixing due to the presence of the grid

According to T.I. representatives, the device has already been mass produced as an original equipment part for several engines including:

1. Chevrolet Chevette 1.6L
2. GM 2.8L V-6
3. GM "J-Car" 1.8L
4. GM 3.8L V-6
5. Ford Escort 1.6L
6. Datsun 510 & Stanza
7. Chevy (Isuzu) Luv Truck

T.I. reports that other applications may also be produced by T.I.'s subsidiary in Japan. In addition, T.I. says that Sylvania is producing an almost identical heater for every application T.I. covers. Sylvania is also reportedly producing a heater for the turbocharged Buick 3.8L V-6 which uses a Rochester Quadrajet carburetor.

In addition to the grid heater, T.I. also manufactures another device which is called the "Hedgehog Heater". The Hedgehog uses similar technology as far as the use of the PTC ceramic is concerned. However, rather than the use of a grid suspended under the carburetor, the Hedgehog is bolted to the floor of the intake manifold. Metal spines are attached to the ceramic which extend upwards into the plenum chamber of the manifold. These spines conduct heat from the ceramic to the intake charge.

T.I. reports that the Hedgehog device is already in production for all inline engines manufactured by American Motors. T.I. says the Hedgehog has also been sold to Volkswagen.

First production of the T.I. grid heaters did not occur until very recently. GM was the only U.S. manufacturer using the device (and on just two engines) prior to the 1983 model year. It has been reported that numerous other applications are under consideration by the automobile manufacturers. The extent of the heater's future use will depend in large part on whether additional CO control is needed as a result of the elimination of oxidation catalysts from behind 3-way catalysts in order to improve NOx emission control.

Improved Catalytic Control of HC and CO - As discussed earlier, there are a variety of approaches that can be taken to improve catalyst efficiency. The use of higher noble metal loadings and increased catalyst volumes will benefit HC and CO control as well as NOx control. However, since HC and CO emissions are highest during engine warmup, the most effective approach to achieving improved catalytic control of HC and CO is through techniques designed to reduce the time required to achieve catalyst light-off.

Most catalysts must be heated to approximately 500°F before they are effective in reducing emissions. Rapid catalyst warmup is particularly difficult to achieve with "pelletized" catalysts. Since the pellet must be large enough to be held within the catalyst container by supporting grids, it has a lower surface to volume ratio than the catalyst washcoat which is applied in a very thin coat on a monolithic substrate. Therefore, when the catalyst is supported by a pellet, rather than a monolithic honeycomb, the weight of the catalyst is higher for the same amount of active surface area. This higher weight gives the pelletized catalyst more thermal inertia and it therefore

rises to operating temperature more slowly. Table 6 shows test results obtained by GM and reported by EPA[4] which demonstrate this effect.

Table 6

Effects of Converter Type on Emissions and Time For Exhaust Exiting Converter to Reach 600°F

Converter	-- grams/mile --- HC	CO	NOx	seconds to reach 600°F
260 CID pellet	0.35	3.11	1.40	338
160 CID pellet	0.37	2.82	1.44	224
150 CID monolith	0.24	2.11	1.45	165

The emissions data shown in Table 6 indicate that the 150 cubic inch monolith was superior in performance to the 260 CID pelletized catalyst. Much of this advantage for the monolith is associated with the fact that it warmed up in 51% less time.

Although Ford, Chrysler, and most foreign manufacturers have relied primarily on monolithic catalysts, the largest manufacturer, General Motors, has relied primarily on pelletized catalysts. Use of more monolithic catalyst by GM is one approach that could be taken to reduce HC and CO emissions. Fuel economy is unaffected by the choice of catalyst substrate.

Another means of solving the catalyst warmup problem is through the addition of a small volume "close-coupled" catalyst. Small catalysts located as close as possible to the outlet of the exhaust manifold are referred to as "start catalysts", "pre-catalysts", or "warmup catalysts". The concept is straightforward:

- locate a catalyst as close to the exhaust valve as possible to minimize heat loss
- use a monolithic design to minimize warmup time
- make the size of the catalyst only as large as is necessary to handle the exhaust volume that occurs under warmup conditions to minimize thermal inertia

Although start catalysts would be most effective when added to vehicles equipped with pelletized catalysts, they will also reduce cold start emissions when added to vehicles which are already equipped with larger monoliths located under the vehicle floor or in the "toe-board" location.

The effectiveness of a start catalyst installation depends several factors:

- the light-off characteristics of the main catalyst
- the light-off characteristics of the start catalyst
- adequate oxygen for efficient oxidation to occur in the bed of the start catalyst

Data from tests run by Chrysler and previously reported by EPA[7] demonstrate the potential of start catalyst installations. The data are displayed in Table 7.

Start catalysts have not been used on very many production vehicles for the simple reason that emission control technology has progressed to the point where start catalysts are not needed to comply with either California or federal emission standards.

Table 7

Effect of Start Catalyst
on Composite Emissions

Chrysler 400 CID, C Body

	grams per mile		
	HC	CO	NOx
Two Test Average Without Start Catalyst	0.37	2.7	1.35
Three Test Average With Start Catalyst	0.20	1.4	1.35
Change With Start Catalyst	-46%	-48%	0%

Johnson Matthey has reported[8] that they have recently completed the development of a new oxidation catalyst formulation which is specifically designed for high temperature applications such as heavy duty truck exhausts or start catalysts for light duty vehicles. It appears that this new catalyst would perform well in a start catalyst application.

The addition of start catalysts is one of the most effective changes to the typical car that could be made to restore any HC or CO emission control lost through the deletion of oxidation catalysts. No fuel economy change is associated with the use of start catalysts.

EFFECTS OF A 0.4 NOX STANDARD ON FUEL ECONOMY

The net effect on passenger car fuel economy associated with a requirement for all manufacturers to certify at 0.4 NOx will depend on the approach to reducing NOx emissions selected by each manufacturer. It is conceivable that some manufacturers will elect to merely retard spark timing in order to reduce NOx emission levels without making any changes to the emission control system design. However, those manufacturers who have already certified at 0.4 NOx did so with the use of technology that offers about 1% better fuel economy to the cars certified at higher emission levels. As discussed in the preceeding sections of this report, the technology is clearly available to allow substantial reductions in NOx emissions without fuel economy penalties for those models which have not yet been certified at the 0.4 NOx level.

ESTIMATES OF LIKELY HARDWARE AND COST CHANGES

The cost impact of a 0.4 NOx standard was calculated based on the modifications that could be used to reduce the NOx emission levels of those cars not already certified at 0.4 without adverse fuel economy impacts. While a zero cost increase could be achieved through the use of spark retard, it is unlikely that this will be the approach taken by manufacturers for two reasons. First, such an approach would degrade fuel economy and thereby adversely affect sales. Since so many models are already certified at 0.4 NOx using systems that provide excellent fuel economy, market forces will encourage the use of modifications which retain competitive fuel economy levels. Second, the cost of the modifications which reduce NOx without adversely affecting fuel economy are modest.

Based on the analysis of the 1982 certification data from thirteen manufacturers, about 54% of the models will need reduced NOx emissions in order to certify at 0.4 NOx. 68% of these cars used 3-way plus oxidation catalyst systems. 23% used oxidation catalyst only systems. 11% used 3-way only systems.

Although expanded use of port-type fuel injection systems may provide some benefits in terms of achieving reduced

NOx emission levels without increases in HC or CO emissions, the conversion to fuel injection is relatively expensive (estimated sticker price increase of about $150) and unnecessary. Changes needed for each type of control system (3-way plus oxidation catalyst, 3-way only, and oxidation catalyst only) were therefore estimated based on the assumption that fuel metering system changes would not be employed.

Projected 3-way Only System Changes - The 11% of the cars above 0.4 NOx that use 3-way only systems represent only 13% of all of the 3-way catalyst systems that were certified. On the average, these cars were different from the 3-way only cars that certified at 0.4 NOx or less. 20% of these higher NOx level cars did not use feedback control of fuel metering. The other 80% of these high NOx 3-way cars used, on the average, 30% less rhodium than the 3-way cars certified at 0.4 NOx. It also should be noted that the 3-way car with the highest NOx emissions needs only 27% lower NOx emissions to certify at 0.4 grams per mile.

It is estimated that most 3-way only cars can be brought into compliance with no change in fuel economy if two basic changes are made. First, the cars which do not employ feedback control of fuel metering will achieve additional control if feedback control is added. Second, catalyst rhodium loadings could be increased by about .2 grams to improve conversion efficiency.

Cost associated with these changes are shown in Table 8. The cost values were based on estimated manufacturing and materials costs marked up 40% for the component vendor, 40% for the vehicle manufacturer, and 20% for the car dealer.

Table 8
System Changes to Achieve 0.4 NOx
With Some 3-way Catalyst Cars

Change	Estimated Sticker Price Increase
add feedback control to carburetor	$10
electronic control unit	$37
oxygen sensor	$4
add .2 grams rhodium	$8

Based on the estimates from Table 8, those few 3-way only models which do not employ feedback controls are projected to have a sticker price increase of $59 associated with the imposition of a 0.4 NOx standard. Most 3-way only cars that do not already comply are estimated to increase in price by only $8.

Projected Oxidation Catalyst Only System Changes - The 23% of the cars which failed to meet 0.4 NOx and which used oxidation catalyst only systems account for 100% of the

oxidation catalyst systems. There are a variety of approaches that could be used to achieve 0.4 NOx with these cars while retaining oxidation catalysts (such as the use of high EGR rates and fast-burn combustion chambers), however, the simplest approach would be to convert to 3-way catalyst systems. Estimated changes and associated costs for conversion to 3-way catalysts are shown in Table 9. Total sticker price increase for the conversion to a 3-way system is estimated at $115.

Table 9
System Changes to Convert Oxidation Catalyst Cars
To 3-way Catalyst Systems

Change	Estimated Sticker Price Increase
add feedback control to carburetor	$10
electronic control unit	$37
oxygen sensor	$4
replace oxidation catalyst with 3-way catalyst	$64

Projected Changes to 3-way Plus Oxidation Catalyst Systems - The 68% of the cars above 0.4 NOx which were equipped with 3-way plus oxidation catalyst systems represent 85% of all 3-way plus oxidation catalyst equipped

models. The most straightforward approach to achieving 0.4 NOx with these cars would be to convert to 3-way only systems using relatively higher rhodium loadings. However, deletion of the oxidation catalyst will not result in a cost savings. Most 3-way plus oxidation catalyst cars use relatively small 3-way catalysts compared to the typical 3-way only car. It will be necessary to retain the same total volume of catalyst when converting the system to 3-way only. In addition, the cost of the catalyst system will be increased by approximately $8 due to the increase in rhodium usage that will be needed to obtain adequate NOx conversion efficiency.

Estimated changes and associated costs for conversion to 3-way catalysts are shown in Table 10.

Table 10
System Changes to Convert
3-way Plus Oxidation Catalyst Cars
To 3-way Catalyst Systems

Change	Estimated Sticker Price Increase
replace 3-way plus oxidation catalyst with 3-way catalyst	$0
increase rhodium use	$8

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COMMENTS REGARDING AMERICAN METHYL CORPORATION'S REQUEST FOR WAIVER OF CLEAN AIR ACT SECTION 211(f) FOR "METHYL-10" FUEL ADDITIVE

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REQUEST FOR WAIVER OF CLEAN AIR ACT SECTION 211(f)
FOR "METHYL-10" FUEL ADDITIVE

Submitted to: U.S. Environmental Protection Agency
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Summary - Methyl-10 Will Cause and Contribute to Emission Standard Violations

Our analysis of the effects of Methyl-10, a methanol-based fuel additive, indicates that its use would substantially increase evaporative emissions regardless of whether the volatility of blends of Methyl-10 and gasoline is controlled to the same Reid Vapor Pressure (RVP) or Front End Volatility Index (FEVI) of straight gasoline. Conclusions reached by ARCO and DuPont that methanol addition will not increase evaporative emissions at constant FEVI were based on the use of statistical techniques that are incapable of recognizing the effect of methanol addition.

We estimate that as many as 60% of 1981 and later model vehicles would fail to meet evaporative emission standards in customer service due to the use of fuels containing Methyl-10. In addition, vehicles which already exceed the standards would exhibit even higher emissions.

Another problem associated with the use of Methyl-10 will be increased NOx emissions of 27%. We estimate that as many as 45% of 1981 and later model vehicles would fail to meet NOx emission standards in customer service due to the use of fuels containing Methyl-10.

Increases in all three regulated exhaust emissions will be associated with the tampering that will be induced by the degraded driveability that Methyl-10 causes. The applicant has also failed to demonstrate that Methyl-10 will not cause additional emissions increases associated with materials compatibility problems.

The Clean Air Act authorizes waivers for fuel additives only if the additive, "...will not cause or contribute to a failure... ...to achieve compliance by the vehicle with the emission standards...." However, the available data indicate that Methyl-10 will substantially increase the number of vehicles in customer service which fail the standards for evaporative emissions and NOx, regardless of what conditions might be placed on the use of Methyl-10. The statute therefore requires denial of the waiver request.

Background

Section 211(f) of the Clean Air Act prohibits the introduction of new fuels and fuel additives unless it is demonstrated that "...such fuel or fuel additive... will not cause or contribute to a failure of any emission control device or system (over the useful life of any vehicle in which such device or system is used) to achieve compliance by the vehicle with the emission standards...." American Methyl Corporation has requested a waiver of Section 211(f) for a fuel additive known as "Methyl-10".

According to the applicant, Methyl-10 consists of methanol and cosolvent alcohols combined with a proprietary corrosion inhibitor called American Methyl 1A-7. Maximum alcohol content is controlled by a 5% upper limit on oxygen content of the blend. This limit allows about 10% methanol without cosolvents and about 14% total alcohol for a 50/50 mixture of methanol and butanol. Even higher alcohol content would be permissible with a greater proportion of butanol. By Federal Register notice of July 6, 1983, EPA announced a comment period on the waiver request for Methyl-10 ending on August 22, 1983.

Based on our review of the waiver request, it appears that Methyl-10 covers a wide range of methanol, higher alcohol, and corrosion inhibitor blends, many of which have never been tested. Except for any possible differences in the proprietary corrosion inhibitor used, Methyl-10 appears to be very similar to the "Petrocoal" additive for which American Methyl (formerly Anafuel Unlimited) has already received a waiver which is currently the subject of reconsideration.

American Methyl has requested a waiver based on the submission of data which purportedly reflects the effect of "worst case" blends containing 10% methanol. In addition, American Methyl has suggested a number of "conditions" for the requested waiver which purportedly will eliminate driveability and materials compatibility problems associated with water contamination and phase separation. These conditions put the onus on the user of the additive for eliminating water contamination problems through the use of such techniques as emptying and drying all underground service station tanks in which blends containing Methyl-10 additive will be stored.

American Methyl Has Underestimated the Evaporative Emissions Increase Associated With Methyl-10

Evaporative Emissions data developed by American Methyl was limited to an analysis of the alcohol fraction of the vapor formed by blends of methanol or methanol plus four carbon alcohols with gasoline in test tubes. American Methyl

asserts that such data are representative of the alcohol fraction of total evaporative emissions from motor vehicles using such blends and that the typical alcohol fraction for a wide range of Methyl-10/gasoline blends is about 7.5%. American Methyl also asserts that the alcohol fraction of evaporative emissions should not be counted.

American Methyl's evaporative emissions analysis is based on subtracting 7.5% of the evaporative emissions from methanol-gasoline blends tested in two cars by DuPont and then comparing the remaining emissions to DuPont's test results for the same two cars using straight gasoline of almost the same FEVI. Using this approach, American Methyl calculates that the evaporative emissions increase in non-alcohol emissions at equal FEVI is 21%. American Methyl says this increase in emissions would not be sufficient to cause a significant increase in the failure of vehicles to meet evaporative emission standards based on the results of certification tests conducted from 1975 to 1982.

It is questionable whether American Methyl's extrapolation of the test tube analysis of vapor alcohol fraction to vehicle evaporative emissions is reasonable. Charcoal cannisters used to control evaporative emissions do not adsorb all compounds with equal efficiency and the temperature of the fuel during vehicle evaporation may significantly affect the composition of the evaporating vapors. However, there are three more basic problems with American Methyl's analysis:

1. The subtraction of the alcohol fraction of evaporative emissions is inappropriate.

2. The increase in evaporative emissions which occurred on the two cars tested by DuPont is significantly lower than typical of other tests.

3. The extent to which an increase in evaporative emissions will cause vehicles to fail the standards is substantially underestimated if the in-use performance of motor vehicles is ignored.

These three deficiencies in American Methyl's analysis are discussed in greater detail below.

Methanol and Butanol Evaporative Emissions Contribute to Ozone Formation and Should Not Be Ignored

Evaporating alcohols clearly contribute to the total evaporative emissions from vehicles using methanol or methanol and butanol mixed with gasoline. However, these emissions should not be ignored just because the evaporative

emissions standard is referred to as a "hydrocarbon" standard. As noted in the Federal Register, the evaporative emissions standard, "...refers to a composite sample of the fuel evaporative emissions..." determined using a specific procedure. Alcohols are detected by the specified procedure and it is appropriate that they are measured since alcohols contribute to photochemical air pollution just like gasoline.

Based on rates of reactions with the hydroxyl radical (OH), the primary chain carrier in photochemical air pollution, both methanol and butanol have been compared to other organic compounds.[1]* Using a five class reactivity scale, methanol and butanol fall into the middle class, Class III. Compounds in this class are 100 to 1,000 times more reactive than methane. Other compounds in the same reactivity class such as hexane, pentane, butane, and toluene are evaporated from straight gasoline. All compounds in this class have a "half life" of 0.1 to 1.0 days. They contribute significantly to ozone formation, especially when multi-day episodes or long-range transport are involved.

Given the requirements of the test procedures and the contribution of methanol and butanol to smog formation, there is no justification for the exclusion of these compounds from the evaporative emissions that result from the use of additives such as Methyl-10.

Methanol-Gasoline Blends Cause Evaporative Emissions to Increase Substantially Even When Volatility is Controlled

The fact that evaporative emissions from methanol-gasoline blends cannot be controlled through the use of comparable volatility specifications is clearly indicated in the data from the Coordinating Research Council (CRC) testing of methanol-gasoline blends. Our analysis of the CRC data is based on the draft Phase II Report for a "Performance Evaluation of Alcohols-Gasoline Blends in the Late Model Automobiles" prepared by SCI. Four of the five blends evaluated contained methanol or methanol plus butanol in amounts that are consistent with the specifications for the use of Methyl-10. One of the blends (MG-5) contained 40% more oxygen than the 5% limit proposed for Methyl-10 blends.

The blends tested by CRC would be expected to reflect the evaporative emissions performance of gasoline containing Methyl-10. The absence of the corrosion inhibitor used in Methyl-10 would not be expected to influence the evaporative emission characteristics of the fuels tested by CRC.

*Superscripts denote references listed at end of text.

The properties of the CRC blends and the baseline gasoline used in the evaporative emission testing are shown in Table 1. As can be seen from the table, the volatility of the blends was controlled so that each of the blends had a lower RVP than the straight gasoline used in the testing program. Three of the four blends that are consistent with the suggested specifications for the use of Methyl-10 (MG-1, MG-2, and MG-3) also had lower FEVI than the straight gasoline. The other blend (MG-4) had only slightly higher FEVI than the gasoline.

Blend MG-3, 8.8% methanol and 2.7% butanol, was volatility adjusted through the use of 50% less butane and 25% less pentane than in the base gasoline. The other four blends were volatility adjusted by using 100% less butane than in the base gasoline. All of the alcohol-gasoline blends were below the maximum RVP specified by ASTM for either winter or summer gasolines in any area of the country.

Table 1

CRC Test Fuel Properties

	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
Methanol %	0.0	3.31	3.54	8.83	9.75	13.35
Isobutanol %	0.0	1.21	0.05	2.66	0.0	1.80
Total Alcohol %	0.0	4.52	3.59	11.49	9.75	15.15
RVP, psi	9.7	8.0	8.7	7.6	8.7	8.4
FEVI	12.8	10.9	11.5	11.6	13.2	13.8
% Oxygen Content (calculated)	0.0	1.9	2.9	5.0	4.9	7.1

The results of the evaporative emission testing conducted for CRC are shown in Table 2. Data are shown for all ten of the 1980 model cars that were tested. The first letter of the vehicle designation is either an "O" or a "C". The "O" designation indicates an open-loop emission control system. The "C" designation indicates closed-loop. The second digit of the vehicle designation indicates the number of cylinders

Table 2

CRC Evaporative Emission Test Results
(grams per test)

Car Number	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
O4-1	1.47	1.83	2.58	3.18	2.75	2.82
O4-2	1.70	1.88	2.22	2.12	2.15	2.34
C4-1	3.17	6.82	6.38	9.52	11.80	9.55
C4-2	2.34	4.26	4.77	5.17	4.62	8.15
C6-1	2.32	2.68	3.59	3.73	4.14	4.26
O6-1	3.29	4.13	6.04	4.18	5.63	4.81
O4-3	3.46	5.79	4.07	5.83	8.57	6.88
O4-4	3.51	4.02	4.18	4.63	4.25	7.56
C4-3	4.07	6.38	6.84	13.15	18.75	19.64
C4-4	3.79	4.81	4.83	5.24	6.62	5.62
10 Car Average	2.91	4.26	4.55	5.67	6.93	7.16
Change from Base Gasoline	0.0%	+46.4%	+56.4%	+94.8%	+138.1%	+146.0%

of the test car and the third digit indicates whether the car is the first, second, third, or fourth test vehicle with the same type of emission control system and number of cylinders.

As shown in Table 2, every single car experienced an increase in evaporative emissions on every one of the five blends. Average increases for all ten cars ranged from 46.4% to 146%. The highest increase in emissions for a blend consistent with the suggested specifications for the use of Methyl-10 was 138.1% for the blend that contained 9.75% methanol with no cosolvent.

Many In-Use Vehicles Will Fail to Meet Evaporative Emission Standards With the Use of Methyl-10

Analyses, such as that done by American Methyl, which only consider the effect of blends on the test results of certification cars present an unrealistic assessment of the increased failure of vehicles to meet emission standards. The emission standards do not just apply to the certification vehicles, they also apply to properly maintained cars in customer service for the vehicle's useful life. To avoid recalls of cars in customer service, manufacturers must achieve a reasonable margin of safety

with their certification cars because it is widely recognized that the 50,000 durability test required of certification cars does not subject the evaporative emission control system to as much stress as will occur in customer service.

Average mileage accumulation rates in customer service are approximately 30 miles per day and each day the evaporative emission control system must control several relatively long hot soaks. However, during the certification testing program it is not uncommon for a test car to accumulate 600 miles per day with only two or three short hot soaks. Per mile of vehicle travel, the evaporative emission control system may go through 20 to 30 times more storage and purging cycles in the real world.

Since the certification testing of evaporative emission control systems does not fully simulate real world deterioration, the in-use data provides a more accurate representation of whether a fuel which increases evaporative emissions will "cause or contribute" to a failure of the standards over the useful life of a vehicle.

To determine the probable effect on the ability of cars to meet the evaporative emission standards with the increase in emissions associated with Methyl-10, an analysis was conducted of the latest in-use surveillance test results published by ARB.[2] SHED test results were available for 20 1980 model California cars. These cars are required to meet the 2 gram per test evaporative emission standard which applies federally for 1981 and subsequent models.

Hot soak and diurnal emissions for each of the 20 cars from the in-use surveillance testing were increased by 171% and 28% respectively. These increases, based on the CRC data, are the same as we used in our earlier analysis of the Petrocoal waiver reconsideration. They represent a net evaporative emissions increase of about 120%, somewhat lower than the worst case results for blends consistent with the suggested specifications for Methyl-10 blends. It should also be noted that the FEVI of the worst case Methyl-10-type blend was almost the same as for the base gasoline. An evaporative emission increase of 120% therefore represents the effect of a high methanol content Methyl-10 blend with FEVI controlled to that of straight gasoline.

The decision to base the analysis on the CRC data was due to the fact that it is the largest data base available on the effect of volatility adjusted methanol-gasoline blends. Criticism of the CRC data based on the argument that the lack of a corrosion inhibitor in the fuel may have contributed to excess emissions from fuel system leaks does not appear to be supported by the data. Some of the tests on straight gasoline were made both before and after tests on the blends and the evaporative emissions from the

Table 3

Evaporative Emissions of Vehicles Certified Under 2 Gram Per Test SHED Standard

Car No.	ARB Surveillance Data Hot Soak	Diurnal	Total	Estimated Emissions With Methyl-10 Hot Soak	Diurnal	Total
096	0.85	0.30	1.15	2.30	0.38	2.68*
148	2.92	4.23	7.15*	7.92	5.41	13.33*
155	1.06	0.38	1.44	2.87	0.49	3.36*
163	0.83	0.34	1.17	2.25	0.43	2.68*
240	0.44	0.27	0.71	1.19	0.35	1.54
279	0.47	0.22	0.69	1.27	0.28	1.55
295	1.13	0.18	1.31	3.06	0.23	3.29*
298	11.72	0.37	12.09*	31.77	0.47	32.24*
299	0.85	0.29	1.14	2.30	0.37	2.67*
341	0.79	0.21	1.00	2.14	0.27	2.41*
343	0.61	0.19	0.80	1.65	0.24	1.89
344	0.92	1.79	2.71*	2.49	2.29	4.78*
345	1.05	0.81	1.86	2.85	1.04	3.89*
347	0.73	0.49	1.22	1.98	0.63	2.61*
349	0.53	0.65	1.18	1.44	0.83	2.27*
350	0.60	0.21	0.81	1.63	0.27	1.90
351	3.89	0.49	4.38*	10.55	0.63	11.18*
352	0.96	0.30	1.26	2.60	0.38	2.98*
378	1.33	0.14	1.47	3.61	0.18	3.79*
379	1.33	0.13	1.46	3.61	0.17	3.78*
Average	1.65	0.60	2.25	4.47	0.77	5.24
Failure Rate		20%			80%	
Grams/Mile**		0.24			0.61	

* Fails 2.0 gram standard

** Grams/Mile = $\frac{\text{(hot soak grams)(3.58 trips/day) + diurnal grams}}{\text{27.4 miles/day}}$

straight gasoline were not significantly different after the fuel system had been exposed to the corrosive effects of methanol. This result is not surprising due to the relatively short duration of the testing program. The results of the analysis are shown in Table 3.

As shown in the table, when tested on gasoline, the surveillance testing indicates that 20% of the cars certified to the 2 gram SHED standard fail to meet the standard. The average emissions from the cars is just over the standard at 2.25 grams per test. However, when we adjusted the emissions to account for the use of Methyl-10, the failure rate increases to 80% and the average emissions increase to 5.24 grams per test.

Also shown in Table 3 is the projected effect of Methyl-10 on the grams/mile of HC emissions equivalent to the SHED test emissions. On straight gasoline the evaporative emissions of the 1980 model cars average 0.24 grams/mile. On Methyl-10 they are estimated to be 2 1/2 times larger at 0.61 grams per mile.

It also should be noted that the effect of Methyl-10 may be underestimated due to the fact that the evaporative emission increases on which the analysis is based were derived from relatively low mileage testing. Although only limited data are available it has been reported[3] that a severe deterioration in the activated charcoal control systems for vehicle diurnal evaporative emissions is associated with the use of methanol/gasoline blends. This phenomenon may be the result of the hygroscopic nature of methanol or the behavior of the azeotropic methanol/gasoline mixtures.

Analyses Done by ARCO and DuPont Do Not Show That Fuels With Equal Volatility Have Equal Evaporative Emissions

In recent comments filed in reference to the reconsideration of the Petrocoal waiver, ARCO and DuPont submitted analyses[4,5] which are relevant to the question of whether some volatility constraints on the use of an additive like Methyl-10 would be sufficient to prevent increases in evaporative emissions. Our review of these analyses indicate that statistical techniques used were incapable of recognizing the effect of methanol addition.

ARCO Analysis - ARCO's analysis of available evaporative emission data on a variety of straight gasolines and alcohol gasoline blends repeatedly refers to the existence of "a positive correlation between evaporative emissions and FEVI" even when data from both straight gasoline and alcohol-gasoline blends are analyzed together. ARCO's analysis may lead the reader to the conclusion that it is only FEVI which effects evaporative emissions and that some type of control of FEVI will prevent evaporative emission increases from methanol blending.

ARCO's analytical technique involved the performance of linear regressions to determine the relationship between FEVI and evaporative emissions for a variety of different fuels tested in the same car or cars. Because ARCO repeatedly found "a positive correlation between evaporative emissions and FEVI" the erroneous conclusion was drawn that control of FEVI will prevent evaporative emission increases from methanol blending.

The available data do indicate that higher FEVI causes higher evaporative emissions. However, FEVI is only one of the factors affecting evaporative emissions. The available data also quite clearly indicate that the presence of methanol causes higher evaporative emissions at equal FEVI. By failing to use statistical techniques that would have shown this effect, ARCO failed to determine whether FEVI is the only significant factor affecting evaporative emissions.

ARCO's analysis is analogous to attempting to define the weight of an object by measuring only its size, and ignoring what it is made of. Because size and weight are correlated, such an analysis could lead one to erroneously conclude that the weight of an object can be accurately predicted by only knowing its size. This is illustrated by the following example.

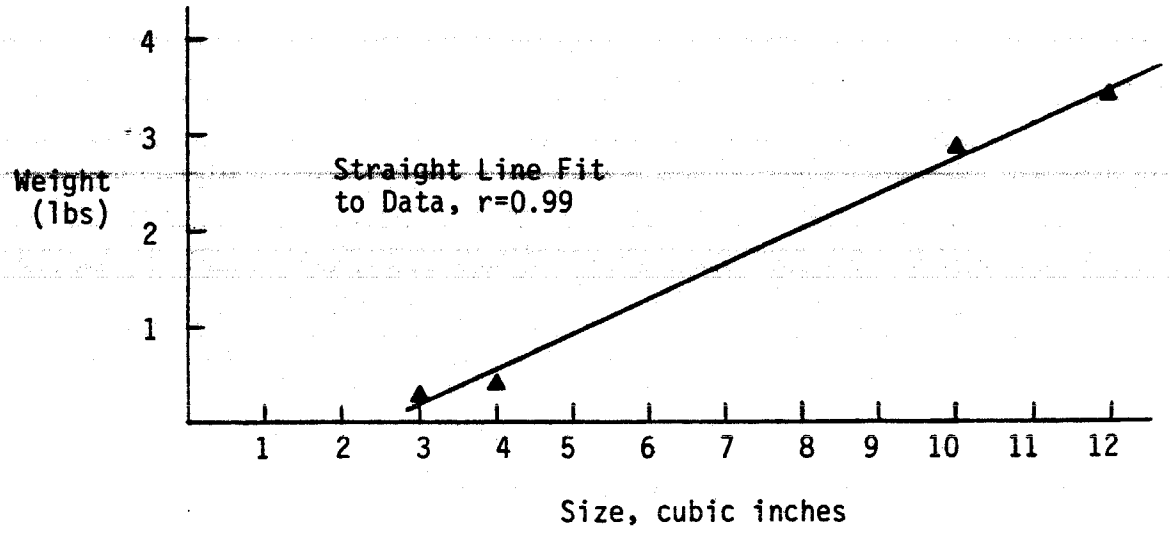
Consider two blocks of aluminum of 3 and 4 cubic inches in size, and two blocks of steel of 10 and 12 cubic inches. Since aluminum weighs 0.100 pounds per cubic inch, the aluminum blocks would weigh 0.3 and 0.4 pounds. Since steel weighs 0.284 pounds per cubic inch, the two steel blocks would weigh 2.84 and 3.41 pounds. Linear regression of these data would indicate that the weight of all four blocks can be predicted quite closely by just knowing their size. The correlation coefficient for the straight line fit to the data is an amazingly high 0.99. Clearly a "positive correlation between weight and size" has been demonstrated as shown in Figure 1.

Using the correlation established above to determine what size limit would keep blocks from weighing more than 1 pound, we would set such a size limit at 5.23 cubic inches. However, a 5.23 cubic inch steel block would weigh 1.49 pounds. Even though our correlation between size and weight was excellent it turns out that the results cannot be used to accurately predict weight of blocks based on their size.

In the above example, one of the reasons the correlation coefficient was so high is that the aluminum blocks in our data set were at one end of the size spectrum and the steel blocks were at the other end. With the sample of blocks segregated in this manner the apparent ability to accurately predict weight knowing only the size of metal blocks is

Figure 1

Relationship Between The Size and Weight of Metal Blocks

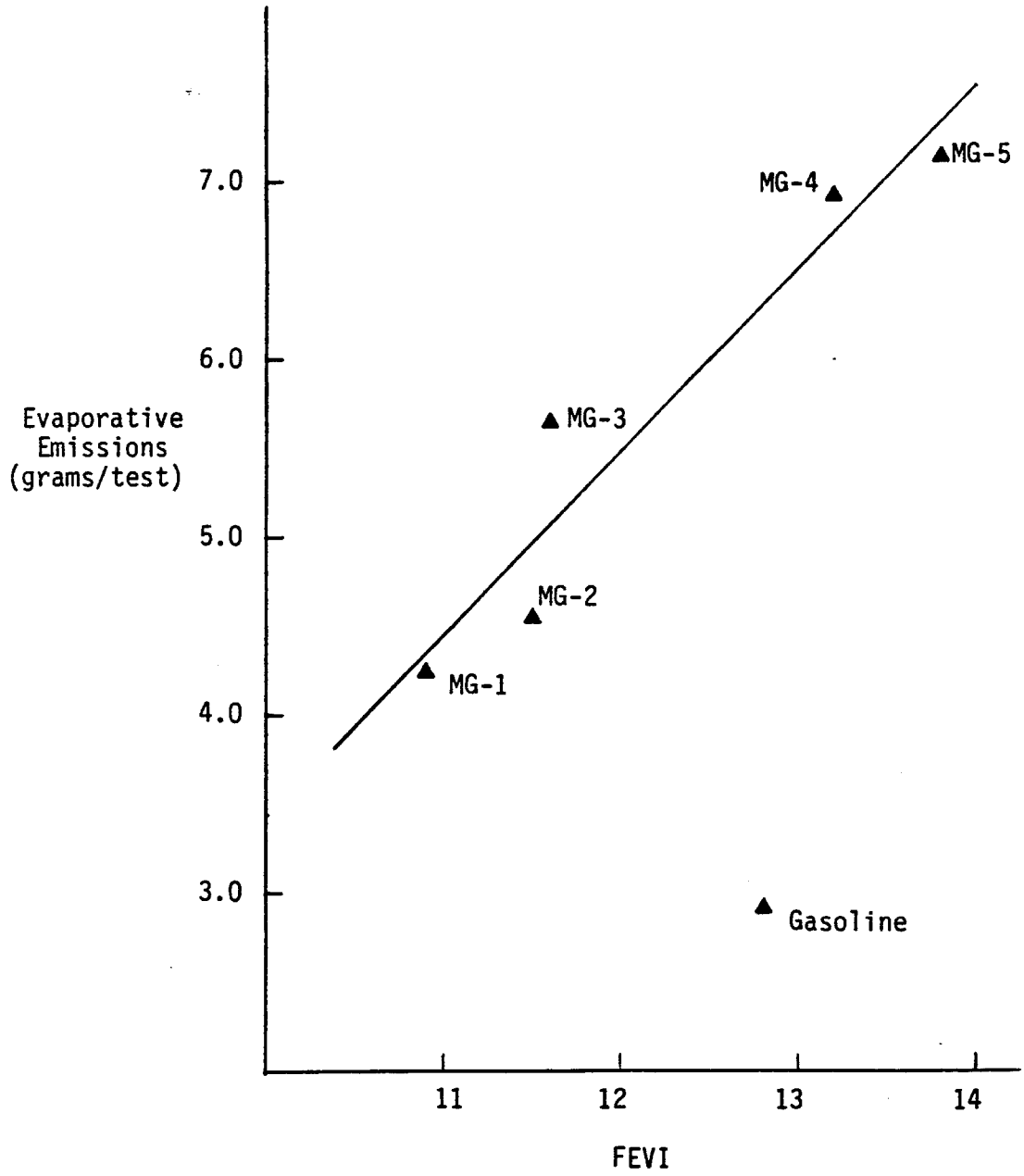


maximized. This same phenomenon occurred during ARCO's analysis of the relationship between evaporative emissions and FEVI. The data representing fuels with low FEVI and low evaporative emissions were usually straight gasoline. The data representing fuels with high FEVI and high evaporative emissions were usually alcohol-gasoline blends. Even though the correlation coefficients reported by ARCO may look reasonable, use of ARCO's approach would result in substantial underestimates of evaporative emissions from low FEVI methanol-gasoline blends just as the correlation we established between the weight and size of metal blocks resulted in underestimates of the weight of small steel blocks.

In the test program conducted by CRC, methanol-gasoline blends of both higher and lower FEVI than the baseline gasoline were evaluated. As shown in Figure 2, the evaporative emissions of the blends do appear to correlate quite well with FEVI. The correlation coefficient for the least squares fit to the data for the blends only is 0.96, indicating a high correlation between evaporative emissions and FEVI. Based on other studies it is clear that there is a relationship between evaporative emissions and FEVI for straight gasoline, but it is a different relationship. This is obvious from the data shown in Figure 2.

Figure 2

Relationship Between Evaporative Emissions and FEVI
Based on the CRC Data



For the FEVI of the baseline gasoline, the least squares line fit to the blend data predicts 6.33 grams per test of evaporative emissions. However, the actual evaporative emissions for the straight gasoline were only 2.91 grams. A

methanol gasoline blend of equal FEVI to the gasoline is predicted to yield 117.5% higher evaporative emissions.

It should also be noted that, under a contract with Coal Fuels Corporation, the CRC data have also been analyzed by Energy and Environmental Analysis, Inc. (EEA). EEA's report[6] contains several conclusions with which we do not agree. For example, EEA said that test cars which exceeded the evaporative emissions standard on the base gasoline should not be considered. This does not appear reasonable to us for two reasons. First, it is well established that all cars do not perform as well as the certification cars upon which compliance with the standard is originally based. Second, the base gasoline used in the CRC tests was not Indolene certification fuel and it may have had slightly higher evaporative emissions potential.

The EEA report also states, "Most of the data cited by MVMA show that, while methanol may increase emissions relative to a base fuel, vehicles fueled with methanol blends still meet the applicable evaporative emission standard. In those cases where vehicles exceed the standard when fueled with methanol, they frequently exceeded the standard fueled with the base gasoline." EEA seems to be arguing that significant evaporative emission increases should be acceptable provided the percentage of cars which fail the standard does not increase significantly. We do not believe waivers should be granted for fuels which clearly increase the amount by which cars fail the standard. Furthermore EEA's analysis ignores the real world deterioration of evaporative emission control systems. The fact that methanol-gasoline blends significantly increase the emissions of test cars which are under the standards means that more cars will fail the standard in customer service.

The important point of the EEA report with respect to the correlation between evaporative emissions and FEVI is that EEA's analysis demonstrates that there is an emission "offset" for methanol-gasoline blends compared to straight gasolines of equivalent FEVI. EEA found that methanol-gasoline blends cause higher evaporative emissions than straight gasoline at the same FEVI. This "emission offset" was also found in our own analysis of the data. ARCO did not use an analytical approach that was capable of identifying the offset.

DuPont Analysis - Dupont's analysis of the relationship between evaporative emissions and volatility is very similar to ARCO's and it suffers from the same basic deficiency. In addition to concluding that FEVI is a reasonable predictor of the evaporative emissions of both blends and straight gasoline, DuPont suggests that an alternative measure of fuel volatility which it calls an "Evaporative Index" would be even more appropriate.

We have independently analyzed the CRC data using DuPont's Evaporative Index and reached conclusions which are contrary to DuPont's. Using the distillation characteristics of the test fuels from the CRC report, we found a correlation coefficient of 0.871 for a straight line fit to the blend data for Evaporative Index and evaporative emissions. This was somewhat poorer correlation than we found between evaporative emissions and FEVI. We also found that the relationship between evaporative emissions and Evaporative Index for straight gasoline was substantially different than for methanol-gasoline blends. At the same Evaporative Index it appears that blends have about twice the evaporative emissions.

The reason for the difference between our analysis and DuPont's appears to be that DuPont used a different set of test results for calculating the Evaporative Index of the CRC test fuels. DuPont used the average of "round robin" test results from a variety of laboratories that were obtained sometime after the testing program had been completed. We relied on the data in the SCI report which was reported before the testing began. The test results used by DuPont showed that the base gasoline had a much lower Evaporative Index than the blends. We have no way of knowing which set of tests are more accurate. The data used by DuPont was obtained using more measurements; however, the fuel was also subject to more handling. Given the paucity of data which is available on the relationship between evaporative emissions and Evaporative Index, it would seem highly inappropriate to base a waiver for Methyl-10 on the condition that the volatility of Methyl-10/gasoline blends be limited to some as yet undefined level of Evaporative Index. Further analysis of the effect of Evaporative Index may demonstrate that its control is inadequate to prevent significant evaporative emissions increases due to methanol addition.

American Methyl's Analysis of Exhaust Emission Impacts is Not Meaningful

Data generated by American Methyl in support of its waiver request are not meaningful because of the non-representative testing methods employed. No conclusions regarding whether Methyl-10 will cause or contribute to the failure of vehicles to achieve compliance with emission standards can be made based on the data.

Exhaust emissions data developed by American Methyl are based on the concentration of pollutants measured during steady state operation of sixteen vehicles. American Methyl's analysis of the data indicates a misunderstanding of the manner in which vehicles contribute to air pollution and the importance of evaluating vehicle exhaust emission rates on a mass basis.

The steady state data reflect none of the cold start and transient emissions performance characteristics of the tested fuels. More importantly, the effect of Methyl-10 on the mass emission rate of vehicles was not calculated. On vehicles without feedback control of fuel metering, the enleanment effects of methanol would have caused reduced pollutant concentrations even with no change in mass emission rates. Based on the vehicle descriptions provided, it appears that ten of the vehicles tested did not have feedback control. It is difficult to tell much about the vehicles that were tested since the vehicle descriptions used throughout the application were inadequate. No descriptions of the emission control systems were provided even for models that were certified with more than one control system depending on the region of original sale (California, high altitude, and regular 49-states).

Methyl-10 Will Increase NOx Emissions

Based on its analysis of the effect of Petrocoal, a very similar additive to Methyl-10, EPA concluded that the exhaust emission effects of the additive would be insignificant for hydrocarbons, a reduction in carbon monoxide, and an increase in NOx. EPA reported, "...hydrocarbons (HC) do not increase, carbon monoxide (CO) emissions decrease, and oxides of nitrogen (NOx) likely increases, although the amount of the increase is modest." The waiver decision also says, "While it does cause NOx emissions to increase modestly, it is not likely to cause a significant failure of vehicles to meet NOx emission standards...."

The CRC data on the effect of methanol-gasoline blends is generally consistent with EPA's findings regarding Petrocoal; however, somewhat larger NOx emission increases were apparent. Exhaust emission test results from the CRC study are summarized in Table 4. For the blend which represents the worst case Methyl-10 usage, hydrocarbons were reduced by 16.1% or 0.05 grams per mile. This decrease was far less than the 0.37 gram per mile increase in evaporative emissions calculated above. CO emissions were reduced by 44%. However, NOx emissions were about 27% higher.

In our earlier comments on the reconsideration of the Petrocoal waiver,[7] we calculated the effect of a very similar (30%) increase in NOx emissions on the ability of cars to meet the NOx standards based on an analysis of ARB in-use surveillance data. The surveillance data used represented the emission performance of a sample of the fleet after all tampering has been corrected and obvious defects have been repaired. The results for open loop cars, typified by 1979 models, are shown in Table 5. The results for closed-loop cars, typified by 1980 model California cars, are shown in Table 6.

Table 4

CRC Exhaust Emission Test Results
(grams/mile)

	Base Gasoline			8.8% Methanol + 2.7% Butanol		
Car	HC	CO	NOx	HC	CO	NOx
O4-1	0.17	2.03	1.64	0.14	1.01	2.19
O4-2	0.26	3.40	1.21	0.29	2.69	1.89
C4-1	0.35	6.96	0.76	0.25	2.86	1.18
C4-2	0.38	4.28	0.57	0.28	2.65	0.60
C6-1	0.33	6.96	0.65	0.29	4.19	0.96
O6-1	0.33	5.55	1.67	0.36	4.43	1.67
O4-3	0.17	3.32	0.84	0.15	1.64	1.26
O4-4	0.21	2.04	1.43	0.12	0.50	1.48
C4-3	0.50	8.26	0.53	0.45	3.97	0.75
C4-4	0.35	2.91	0.70	0.26	1.67	0.72
Average	0.31	4.57	1.00	0.26	2.56	1.27
Percent Change From Base Gasoline				-16.1	-44.0	+27.0

Table 5

ARB In-Use Surveillance Data
for 1979 Model Passenger Cars
NOx Exhaust Emissions After Repair
(grams/mile)

Emissions on Gasoline				Estimated Emissions With Methyl-10			
NOx	Miles	NOx	Miles	NOx	Miles	NOx	Miles
0.81	8637	1.18	22063	1.03	8637	1.51	22063
0.62	17535	1.20	5406	0.79	17535	1.53	5406
1.61*	23739	1.56*	17806	2.05*	23739	1.99*	17806
0.79	18725	1.33	10827	1.01	18725	1.70*	10827
1.29	18010	1.47	21538	1.65*	18010	1.88*	21538
0.81	19818	1.08	23774	1.03	19808	1.38	23774
1.06	28032	1.71*	33169	1.35	28032	2.18*	33169
1.40	33430	1.32	27705	1.79*	33430	1.68*	27705
1.34	35375	1.57*	10399	1.71*	35375	2.00*	10399
1.64*	28561	1.51	20743	2.09*	28561	1.93*	20743
0.96	17463	1.03	24363	1.22	17463	1.31	24363
1.60*	19817	0.86	32794	2.04*	19817	1.10	32794
1.26	22030	1.52	23170	1.61*	22030	1.94*	23170
1.27	17140	1.45	36901	1.62*	17140	1.85*	36901
0.89	45965	1.33	25304	1.14	45965	1.70*	25304
0.81	34394	1.17	15635	1.03	34394	1.49	15635
1.40	32480	0.58	29841	1.79*	32480	0.74	29841
1.72*	23562	1.52	24917	2.19*	23562	1.94*	24917
1.53	25536	1.39	8859	1.95*	25536	1.77*	8859
1.78*	19990	1.27	35153	2.27*	19990	1.62*	35153
1.44	28370	1.62*	16552	1.84*	28370	2.07*	16552
1.04	38517	0.94	28295	1.33	38517	1.20	28295
1.05	28296	1.44	33005	1.34	28296	1.84*	33005
1.14	7733	1.16	27885	1.45	7733	1.48	27885
1.10	30910	1.11	18835	1.40	30910	1.42	18835
1.10	25354	0.73	42697	1.40	25354	0.93	42697
1.00	21267	2.09*	35974	1.28	21267	2.67*	35974
1.25	47339	4.96*	36164	1.60*	47339	6.33*	36164
2.10*	42289	0.70	9574	2.68*	42289	0.89	9574
0.60	29943	0.67	34696	0.77	29943	0.85	34696
1.18	21433	2.03*	29503	1.51	21433	2.59*	29503
0.99	40307			1.26	40307		

Failure Rate = 20.6%

Average Emissions = 1.30

Failure Rate = 52.4%

Average Emissions = 1.66

*Fails 1.5 gram/mile standard

Table 6
ARB In-Use Surveillance Data for 1980 Model Passenger Cars
NOx Exhaust Emissions After Repair, (grams/mile)

Emissions on Gasoline				Estimated Emissions With Methyl-10			
NOx	Miles	NOx	Miles	NOx	Miles	NOx	Miles
0.29	4977	0.23	5242	0.39	4977	0.31	5242
0.95	9534	1.66*	13522	1.28*	9534	2.23*	13522
0.40	14977	0.52	1216	0.54	14977	0.70	1216
0.86	14222	0.43	999	1.16*	14222	0.58	999
0.89	43016	0.92	12218	1.20*	43016	1.24*	12218
0.72	13358	1.14*	17137	0.97	13358	1.53*	17137
0.49	18761	0.31	16372	0.66	18761	0.42	16372
1.09*	10141	1.05*	18375	1.46*	10141	1.41*	18375
0.48	17790	0.32	12273	0.65	17790	0.43	12273
0.84	27279	1.12*	13179	1.13*	27279	1.51*	13179
0.85	29371	0.90	14065	1.14*	29371	1.21*	14065
1.25*	23104	0.90	5320	1.68*	23104	1.21*	5320
1.95*	14380	0.89	5022	2.62*	14380	1.20*	5022
0.46	10941	0.87	15175	0.62	10941	1.17*	15175
0.89	12651	0.94	22705	1.20*	12651	1.26*	22705
1.33*	13508	0.49	15164	1.79*	13508	0.66	15164
0.69	4402	0.60	8540	0.93	4402	0.81	8540
0.53	12395	0.74	12187	0.71	12395	0.99	12187
0.66	25925	0.68	19608	0.89	25925	0.91	19608
1.32*	28972	0.65	18275	1.77*	28972	0.87	18275
1.12*	12170	1.06*	10873	1.51*	12170	1.42*	10873
0.89	9639	0.92	5506	1.20*	9639	1.24*	5506
1.11*	17396	0.90	18799	1.49*	17396	1.21*	18799
0.78	11229	0.93	17246	1.05*	11229	1.25*	17246
0.81	14981	0.80	9716	1.09*	14981	1.08*	9716
1.47*	9233	0.94	11880	1.98*	9233	1.26*	11880
1.12*	21082	1.98*	6509	1.51*	21082	2.66*	6509
1.31*	5398	1.09*	37275	1.76*	5398	1.46*	37275
0.63	22584	0.94	15569	0.85	22584	1.26*	15569
0.88	8708	0.94	4990	1.18*	8708	1.26*	4990
0.97	3367	0.94	14161	1.30*	3367	1.26*	14161
0.90	6492	0.96	13509	1.21*	6492	1.29*	13509
0.89	13645	0.92	16227	1.20*	13645	1.24*	16227
1.01	10262	1.54*	8983	1.36*	10262	2.07*	8983
0.92	12445	0.93	12540	1.24*	12445	1.25*	12540
0.88	11704	0.80	7006	1.18*	11704	1.08*	7006
1.04	14186	0.70	12134	1.40*	14186	0.94	12134
0.91	8544	1.03	18694	1.22*	8544	1.38*	18694
0.89	10564	1.18*	18328	1.20*	10564	1.59*	18328
1.00	15287	1.05*	24677	1.34*	15287	1.41*	24677
0.88	25411	1.10*	31297	1.18*	25411	1.48*	31297
0.81	14309	0.58	21959	1.09*	14309	0.78	21959
1.06*	24344	0.64	20355	1.42*	24344	0.86	20355
0.70	21443	1.06*	11538	0.94	21443	1.42*	11538
0.84	26289	0.60	13751	1.13*	26289	0.81	13751
Failure Rate = 25.6%				Failure Rate = 72.2%			
Average Emissions = 0.90				Average Emissions = 1.20			

As shown in Tables 5 and 6, the increased NOx emissions associated with the use of Methyl-10-type fuels has a major impact on the ability of both open-loop and closed-loop cars to meet emission standards in customer service. The increase in NOx increases the failure rate of open-loop cars to 52.4% from 20.6%. Average emissions for open-loop cars increase from 1.30 grams per mile (below the 1.5 standard) to 1.66 grams per mile. Closed-loop cars are even more significantly affected. The failure rate increases from 25.6% to 72.2% when the effects of Methyl-10-type fuels are accounted for. Average emissions increase from 0.90 grams per mile (below the 1.0 gram standard) to 1.20 grams per mile, 20% over the standard.

Methyl-10 Will Degrade Driveability and Induce Tampering

The effects of methanol-gasoline blends on driveability are associated with the enleanment effect. The decrease in the chemically correct (stoichiometric) air/fuel ratio associated with methanol-gasoline blends is due primarily to the fact that methanol contains oxygen and gasoline does not. A blend of 10% methanol and 90% unleaded gasoline has a stoichiometric air/fuel ratio of 13.9:1, 5.4% richer than pure gasoline. Since a 10% methanol-gasoline blend is only 0.6% greater density than gasoline, the net effect is that an engine will run 4.8% leaner on a 10% methanol-gasoline blend. Closed-loop vehicles can compensate for this enleanment effect during warmed up operation except for near wide open throttle operation on some vehicles. However, during the critical cold start and warmup operation, the closed-loop system cannot compensate for the enleanment caused by the methanol.

Most researchers report a noticeable increase in problems with stalling and surging when methanol-gasoline blends are used.[8, 9, 10] Reports of poor driveability during cold-start operation may also be due to the fact that methanol has a higher heat of vaporization than gasoline. In spite of the fact that methanol-gasoline blends are more volatile than gasoline, they do not vaporize as well in the intake system because of the higher heat of vaporization required.

The adverse effects on driveability associated with Methyl-10-type blends was clearly demonstrated in the CRC testing. The results of the driveability tests are summarized in Table 7. As shown in the table, the use of a blend allowed under the proposed Methyl-10 waiver increased driveability demerits by 144%. Such a significant increase in driveability problems is likely to induce some motorists to have their vehicles modified or adjusted to restore acceptable driveability. The effects of such adjustments on exhaust emissions can be substantial.

Table 7

CRC Driveability Test Results

Car	Driveability Demerits: Base Gasoline	Driveability Demerits: 8.8% Methanol + 2.7% Butanol
O4-1	75.0	204.0
O4-2	49.0	89.5
C4-1	86.0	180.0
C4-2	75.5	108.5
C6-1	44.5	111.5
O6-1	21.0	61.0
O4-3	39.5	92.5
O4-4	51.5	193.5
C4-3	17.5	97.0
C4-4	45.5	94.5
Average	50.5	123.2
Increase in Driveability Demerits With Methanol Addition		+144.0%

Limited test results have been identified which determined the effect on exhaust emissions of readjusting vehicles to offset the degradation in driveability caused by a switch to alcohol-gasoline blends.[11] Three different 1978 model passenger cars equipped with 1.6, 3.3, and 5.0 litre engines were adjusted to optimize driveability after their driveability had been adversely affected by a switch to a 15% methanol-gasoline blend.

Adjustments made to the vehicles included:

1. Spark timing advanced 4°
2. Idle speed increased 50 RPM

3. Idle mixture enriched for best idle quality

4. Part throttle mixture adjusted on two of the three cars to optimize driveability

After these modifications had been completed, two of the cars had driveability ratings that were almost identical to what they had on straight gasoline. The third car had improved driveability compared to the use of the alcohol-gasoline blend without adjustments; however the vehicle was still experiencing a 50% increase in driveability problems compared to gasoline. The driveability tests that were run indicate that the adjustments made to compensate for the use of the alcohol-gasoline blend were not greater than required to restore the original level of drive performance.

Table 8 shows the effect of the adjustments made to restore driveability on the exhaust emission changes caused by the methanol-gasoline blend. As would be expected the switch to the methanol-gasoline blend initially reduced CO emissions. The 39.3% reduction shown in the table is reasonably consistent with data for Methyl-10-type fuels. HC was reduced initially by 11.1%. When the vehicles were adjusted to restore their driveability the CO emissions were 138.3% higher than when they were running on gasoline in their baseline condition. HC was increased 59.3% from the baseline.

The reason that the CO emission levels in the adjusted configuration were higher than the gasoline baseline is probably associated with the inability to restore adequate acceleration enrichment with the adjustments that were made. Because it was not practical to increase the accelerator pump shot, the basic air/fuel ratio of the carburetors had to be adjusted rich enough to compensate for the driveability problems caused by this lack of adequate acceleration enrichment.

After the vehicles were modified to restore their driveability, they were switched back to gasoline to determine what the effects would be on emissions and driveability. Driveability was determined to be superior to the baseline condition because of the mixture enrichment. NOx emissions were 1.3% less than in the baseline configuration, however, the increases in hydrocarbon and CO emissions were enormous. HC had increased to 189% above the baseline and CO had increased by 360%.

These data indicate that additives like Methyl-10 have the potential to produce emissions in customer service far beyond the levels that are normally associated with such additives during laboratory evaluations.

Table 8

Effect of Methanol-Gasoline Blend Use
and Subsequent Adjustments to Restore Driveability
on Exhaust Emissions

	HC	CO	NOx
3 '78 model cars, no adjustments*	-11.1%	-39.3%	-4.6%
3 '78 model cars, adjusted to restore driveability*	+59.3%	+138.3%	+19.1%
3 '78 model cars, switched back to gasoline after adjustments to restore driveability on methanol blends	+189%	+360%	- 1.3%

* Emission changes as compared with straight gasoline

Source: Reference 11

Materials Compatibility With Methyl-10 Has Not Been Demonstrated

The materials compatibility data supplied by American Methyl do not substantiate a lack of materials compatibility problems. Because of the lack of high mileage and long calendar time data on a variety of motor vehicles, it appears that the conclusion reached by EPA during the evaluation of the similar Petrocoal additives prepared by American Methyl (then Anafuel) is still appropriate, "...there appears to be no available data, either in the published literature or supplied by Anafuel, which would conclusively demonstrate that Petrocoal would be safe (from an emissions control standpoint) to operate in currently available motor vehicles over long time periods." The EPA report goes on to say, "The elastomers tested by Anafuel were noted in the existing literature as being the most resistant to attack by methanol...."

The data submitted by American Methyl indicate significant corrosion of lead and zinc. Lead is one of the principal components in the "terneplate" fuel tank coatings which are commonly used. American Methyl concludes that the observed corrosion rates for these compounds are not sufficient to result in penetration of the fuel tank over the life of the

typical vehicle. This rational ignores the effect that terneplate corrosion can have on other fuel system components. Excessive wear of Viton fuel inlet needles has been associated with exposure of the needles to lead hydroxychloride particles.[12] These particles can be formed from the corrosive effects of methanol on fuel tank linings. Deterioration of fuel inlet needles can lead to carburetor flooding and greatly increased emissions.

The existence of materials compatibility problems with other methanol-gasoline blends produced by or under license from American Methyl have apparently already occurred in customer service. Newhall, one of the marketers of Petrocoal in California, reports[13] that numerous complaints about driveability problems were received when they began marketing Petrocoal at the 12% total alcohol level last year. Newhall reports that accelerator pump failures appear to be at least partially responsible for driveability problems. Some of the driveability problems experienced by Newhall's own employees were solved by the replacement of accelerator pumps. Fuel additives which cause accelerator pump failures or plugged fuel filters can increase emissions in two ways. First, the failure can lead to lean misfire which significantly increases hydrocarbon emissions. Second, the failure can lead to tampering (such as idle mixture enrichment) in an attempt to solve the driveability problem induced by the component failure.

Given the lack of evidence that Methyl-10 will be free from materials compatibility problems, we believe it would be inappropriate for EPA to grant the waiver request.

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COMMENTS REGARDING MVMA PETITION FOR
RECONSIDERATION OF PETROCOAL 211(f) WAIVER

COMMENTS REGARDING MVMA PETITION FOR RECONSIDERATION OF PETROCOAL 211(f) WAIVER

Submitted to: U.S. Environmental Protection Agency
Central Docket Section (LE-131)
Public Docket EN-81-8
Gallery 1, West Tower
401 M Street, S.W.
Washington, D.C. 20460

Submitted by: California Air Resources Board
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Summary

An analysis conducted by the California Air Resources Board (ARB) indicates that there are significant evaporative emission increases and other problems associated with the use of methanol/butanol-gasoline blends even when ASTM volatility specifications are met. The ARB concurs with the Motor Vehicle Manufacturers Association (MVMA) position regarding the adverse air quality effects associated with the use of "Petrocoal". We agree with MVMA that EPA should reconsider and revoke the waiver of Clean Air Act section 211(f)(1) for Petrocoal.

New data are available which indicate that some of the assumptions and conclusions made during the previous EPA consideration of Petrocoal are not valid. These data include the Coordinating Research Council testing of methanol-gasoline blends, in-use surveillance testing of cars designed to meet the SHED test-based evaporative emissions standard, and the consumer experience with the use of Petrocoal. Our analysis of these and other data indicates that there are four major emissions related problems associated with Petrocoal:

1. Petrocoal will more than double evaporative emissions even if ASTM volatility specifications are met. The percentage of cars failing to meet the 2 gram evaporative emission standard in customer service will increase substantially. 80% of the vehicles using Petrocoal are estimated to fail the evaporative standard. Only 20% are failing the standard using conventional gasoline.

2. Petrocoal will increase NOx emissions by approximately 30%. The percentage of properly maintained cars failing to meet the NOx emission standards in customer service will increase substantially with Petrocoal use. An estimated 52% of 1980 and earlier models will fail the NOx standards using Petrocoal compared to a 20.6% failure rate on conventional gasoline. 72.2% of 1981 and later models are estimated to fail the NOx standards with Petrocoal compared to 25.6% with gasoline.

3. Petrocoal will increase driveability problems by about 144%, creating a substantial incentive for "tampering" to restore driveability. Tampering sufficient to offset the effect of Petrocoal can increase HC emissions by about 60%, CO emissions by about 140%, and NOx emissions by about 20%. Tampered cars switched back to gasoline will exhibit even higher emissions.

4. Materials compatibility problems also occur with Petrocoal. The materials compatibility testing conducted by Anafuel was grossly inadequate and therefore did not indicate problems. However, failures of elastomeric components have already occurred due to Petrocoal use in Southern California.

Based on the latest available data, fuels like Petrocoal which contain significant amounts of methanol and four carbon alcohols will clearly cause and contribute to the failure of emission control systems to achieve compliance with the emission standards. Emission increases occur even if the maximum alcohol content of the fuel is restricted to less than 5%. Such fuels certainly do not meet the Clean Air Act requirements for waiver of section 211(f)(1).

Background

Section 211(f) of the Clean Air Act prohibits the introduction of new fuels and fuel additives unless it is demonstrated that "...such fuel or fuel additive... will not cause or contribute to a failure of any emission control device or system (over the useful life of any vehicle in which such device or system is used) to achieve compliance by the vehicle with the emission standards...." EPA's determination that a fuel known as "Petrocoal" meets the requirements for a waiver of the section 211(f) prohibition was based on data from testing conducted by System Controls Inc. for Anafuel Unlimited (the fuel producer), General Motors, and EPA.

According to Anafuel Unlimited, "Petrocoal is essentially a methanol-based synthetic fuel extender." (See Anafuel waiver application.) The fuel tested to obtain data for submission to EPA was described by Anafuel as, "...a fuel blend called "Petrocoal" which consists of 15% proprietary additive and 85% of the base fuel." Anafuel said, "The base fuel is a commercially available unleaded gasoline." In its application for waiver, Anafuel said, "We hereby request a waiver for introduction into unleaded gasoline of our proprietary fuel known as Petrocoal which consists, when blended with unleaded gasoline, of up to 12% methanol by volume and up to 6% of certain C-4 alcohols by volume in the presence of a proprietary inhibitor of not less than .023 g/gallon and not more than .033 g/gallon...."

From the above definitions it is not entirely clear whether "Petrocoal" is supposed to define an additive or a complete fuel. EPA finally decided to treat Petrocoal as a complete fuel.

Although Petrocoal requested approval for up to 18% total alcohol, EPA conditioned the waiver on the use of a maximum of 15% total alcohol and a maximum methanol to four carbon alcohol ratio of 6.5:1. The rational for the restriction to 15% was apparently that 15% represented the maximum alcohol content of any Petrocoal fuels tested. However, our review of the Docket indicates no evidence that any of the fuels tested actually contained 15% total alcohol. An analysis of fuel supplied to GM for testing indicates a total alcohol concentration of about 10% when Petrocoal additive is blended with pure hydrocarbons in a 15/85 ratio. A Department of Energy Analysis of the Petrocoal tested by EPA indicated 12.1% total alcohol.

The confusion associated with the definitions of Petrocoal initially supplied to EPA are undoubtedly responsible for the inconsistencies in the way the effect of Petrocoal on emissions was determined. Some of the tests that were run to determine emission impacts of Petrocoal were based on a comparison of a commercially available unleaded gasoline and the same gasoline with an additive supplied by Petrocoal while other tests were based on a comparison of commercial unleaded gasoline and blends of Petrocoal additive in unleaded blendstocks (not finished gasoline).

A summary of the tests used by EPA to compare commercially available unleaded gasoline to the fuels tested which contained Petrocoal additive are summarized in Table 1. As can be seen from the table, evaporative emissions with Petrocoal were consistently higher and CO emissions were consistently lower. HC and NOx emission results were mixed.

Table 1

Average Effect of Petrocoal on Emissions
Available at Time of Original Waiver Decision

	Change in Emissions w/ Petrocoal			
Data Source	HC	CO	NOx	Evap.
Anafuel/SCI	-14.6%	-38.2%	+11.2%	+158.6%
GM-1	-5.6%	-32.1%	-9.1%	+42.1%
GM-2	+20.9%	-5.0%	-10.2%	+31.0%
EPA-1	+2.2%	-20.0%	+18.3%	+239.6%
EPA-2	+0.9%	-26.1%	+8.3%	+83.7%

Note: GM-1 = comparison of Indolene with Indolene + Petrocoal additive

GM-2 = comparison of Indolene with blendstock + Petrocoal additive

EPA-1 = comparison of Indolene with fuel supplied by Anafuel

EPA-2 = comparison of Shell unleaded with fuel supplied by Anafuel

EPA's analysis of the available exhaust emission data resulted in a finding that, "...hydrocarbons (HC) do not increase, carbon monoxide (CO) emissions decrease, and oxides of nitrogen (NOx) likely increases, although the amount of the increase is modest." The waiver decision also says, "While it does cause NOx emissions to increase modestly, it is not likely to cause a significant failure of vehicles to meet NOx emission standards...."

Regarding evaporative emissions, the waiver decision states, "...controlling the volatility of Petrocoal within ASTM specifications should adequately control evaporative emissions and they should be no worse than those of commercially available fuels."

Regarding issues which are indirectly related to emissions, EPA concluded driveability and materials compatibility would not be a problem with Petrocoal. The waiver decision says, "The information developed by Anafuel, EPA and other commenters on driveability, in conjunction with market demands placed on a fuel manufacturer for an acceptable fuel, lead me to conclude that driveability is not a significant problem with Petrocoal." The only quantitative data in the record was based on driveability testing done by GM. GM found an average 200-400% increase in cold-start driveability demerits on two cars that were tested.

It was also noted in the record that two of the five vehicles tested by EPA had experienced driveability problems that were apparently corrected through maintenance. One of the repairs used to correct a driveability problem at EPA was the replacement of an accelerator pump cup that had swollen and began sticking. Notwithstanding this occurrence, the waiver decision also concludes that the Petrocoal, "does not present a materials compatibility problem affecting emissions...."

Because of concerns about the consistency of the fuels used in the testing on which the waiver grant was based, and because of concerns regarding the interpretation of the available data by EPA, the Motor Vehicle Manufacturers Association has petitioned EPA for reconsideration of the Petrocoal waiver decision. MVMA has also submitted the results of tests conducted by CRC on a variety of blends containing methanol which are more representative of the fuel allowed under the Petrocoal waiver than the fuels originally tested by EPA, GM, and Anafuel.

Because of concerns about the effect of Petrocoal-like fuels on air quality, the California Air Resources Board has independently analyzed the CRC data, the record on which the waiver grant was based, and other data.

Evaporative Emissions

A major shortcoming of the data base used for the Petrocoal waiver decision was the lack of comparisons between Petrocoal and conventional gasoline blended to the same volatility level. Although the original data indicated consistently higher evaporative emissions with Petrocoal, Anafuel asserted that the high emissions were due to the fact that the Petrocoal fuel had not been blended to the same volatility of the gasolines which were used for baseline evaporative emission testing.

The waiver decision stated that controlling Petrocoal to the ASTM volatility specifications would prevent evaporative emission increases. The waiver decision says this conclusion is based on EPA's belief that Front End Volatility Index (FEVI) and evaporative emissions are well correlated. There are two problems with the conclusion that constraining Petrocoal to meet ASTM specifications will prevent evaporative emission increases:

1. Petrocoal blends meeting ASTM specifications will have higher FEVI than gasoline meeting the same specifications.

2. Petrocoal will have higher evaporative emissions than gasoline of equivalent FEVI.

Regarding the first point, ASTM specifications control Reid Vapor Pressure (RVP), not FEVI, and the relationship between RVP and FEVI is not the same for methanol-gasoline blends as it is for gasoline. A methanol-gasoline blend controlled to the same RVP of gasoline will have a significantly higher FEVI. This occurs because of the "knee" in the distillation curve which is caused by the addition of methanol. This "knee" increases the percent of the blend which evaporates at 158°F even when butane and/or pentane is removed to the point where the RVP is equal to the base gasoline. Since FEVI = RVP + .13(% evaporated @ 158°F), FEVI will be higher with a methanol-gasoline blend than with straight gasoline even at constant RVP.

Regarding the second point, the relationship between evaporative emissions and FEVI with straight gasoline does not hold for blends like Petrocoal. The effect of methanol addition on the 100-200°F range of the distillation curve is so severe that hot soak emissions are much greater than for a gasoline of equal FEVI. FEVI is not an adequate measure of the evaporative emissions difference between fuels that are as different as conventional gasoline and Petrocoal. In addition, methanol has been shown to substantially degrade the effectiveness of the activated charcoal canisters. This effect does not show up under short term testing programs such as were used in the evaluation of Petrocoal.

CRC Evaporative Emissions Data - The fact that evaporative emissions from methanol-gasoline blends cannot be controlled through the use of comparable volatility specifications is clearly indicated in the data from the CRC testing of methanol-gasoline blends. Our analysis of the CRC data is based on the draft Phase II Report for a "Performance Evaluation of Alcohols-Gasoline Blends in the Late Model Automobiles" prepared by SCI. Of the five blends evaluated, two were especially representative of the methanol and four carbon alcohol combinations that are allowed under the Petrocoal waiver. The absence of the

"proprietary inhibitor" used in Petrocoal would not be expected to influence the evaporative emission characteristics.

The properties of these two blends and the baseline gasoline used in the evaporative emission testing are shown in Table 2. As can be seen from the table, the volatility of the blends was controlled so that FEVI was comparable for each of the fuels. In order to achieve comparable FEVI's, the RVP of the blends was lower than straight gasoline. Blend MG-5, 13.4% methanol and 1.8% butanol, was volatility adjusted by butane removal from the base gasoline. Blend MG-3, 8.8% methanol and 2.7% butanol, was volatility adjusted through the removal of 50% of the butane and 25% of the pentane in the base gasoline. The methanol to butanol ratio for the MG-3 blend is well within the 6.5 specification in the waiver. The methanol/butanol ratio of the MG-5 blend exceeds 6.5 by only 14%. Both of the blends are far below the maximum RVP specified by ASTM for either winter or summer gasolines in any area of the country.

Table 2

CRC Test Fuel Properties

	Straight Gasoline	Blend MG-3	Blend MG-5
Methanol, vol %	0.0	8.83	13.35
Isobutanol, vol %	0.0	2.66	1.80
Total Alcohol, vol %	0.0	11.49	15.15
Methanol/Butanol Ratio	-	3.32	7.42
RVP, psi	9.7	7.6	8.4
FEVI	12.8	11.6	13.8

It should be noted that the specifications for the tested blends shown in Table 2 may be somewhat different from the specifications that have been reported to EPA by MVMA. We understand that MVMA has obtained the results of supplemental tests of the fuels that were not available to ARB. However, the supplemental testing produced results that were very comparable to the results from the supplier of the fuels on which our analysis is based.

The results of the evaporative emission testing conducted for CRC are shown in Table 3. Data are shown for all ten of the 1980 model cars that were tested. The first letter of the vehicle designation is either an "O" or a "C". The "O" designation indicates an open-loop emission control system. The "C" designation indicates closed-loop. The second digit of the vehicle designation indicates the number of cylinders of the test car and the third digit indicates whether the cars is the first, second, third, or fourth test vehicle with the same type of emission control system and number of cylinders.

Table 3

CRC Evaporative Emission Test Results
(grams per test)

	Base Gasoline			8.8% Methanol + 2.7% Butanol			13.4% Methanol + 1.8% Butanol		
Car	Diur.	HS	Total	Diur.	HS	Total	Diur.	HS	Total
O4-1	0.555	0.912	1.467	1.198	1.979	3.177	0.813	2.008	2.820
O4-2	0.794	0.901	1.695	0.834	1.288	2.122	0.700	1.640	2.340
C4-1	1.216	1.952	3.168	2.582	6.936	9.518	1.067	8.487	9.554
C4-2	0.709	1.632	2.341	1.049	4.117	5.166	1.313	6.832	8.145
C6-1	0.610	1.708	2.317	0.831	2.900	3.731	1.024	3.232	4.256
O6-1	1.276	2.011	3.287	1.315	2.861	4.176	1.542	3.270	4.812
O4-3	1.049	2.408	3.457	1.268	4.560	5.827	1.322	5.559	6.881
O4-4	0.938	2.568	3.506	1.079	3.554	4.632	1.241	6.316	7.557
C4-3	1.946	2.126	4.071	1.716	11.433	13.148	2.243	17.396	19.639
C4-4	1.163	2.623	3.785	1.434	3.811	5.245	1.660	3.960	5.619
Average	1.026	1.884	2.909	1.331	4.344	5.674	1.293	5.870	7.162
Percent Change From Base Gasoline				+29.7	+130.6	+95.1	+26.0	+211.6	+146.2

As shown in the table, every car experienced a significant increase in evaporative emissions on both of the Petrocoal-like blends. On the average, the diurnal emissions increased by 27.9% and the hot soak emissions increased by 171.1%. Total emissions increased by 120.7%.

It should also be noted that the CRC data indicate significant evaporative emissions increases for Petrocoal-like fuels with as little as 4.5% total alcohol content. A blend (MG-1) containing 3.3% methanol and 1.2% butanol caused an average 46.4% increase in evaporative emissions of the same ten test vehicles even though the Reid Vapor Pressure of the blend was adjusted to 8.0 psi, 17.5% lower than the 9.7 RVP baseline gasoline.

ARB Surveillance Data - To determine the probable effect on the ability of cars to meet the evaporative emission standards with the increase in emissions associated with Petrocoal-like blends, an analysis was conducted of the latest in-use surveillance test results published by ARB.[1]* SHED test results were available for 20 1980 model California cars. These cars are required to meet the 2 gram per test evaporative emission standard which applies federally for 1981 and subsequent models. Since the certification testing of evaporative emission control systems does not fully simulate real world deterioration, the in-use data provides a more accurate representation of whether a fuel which increases evaporative emissions will "cause or contribute" to a failure of the standards over the useful life of a vehicle.

Hot soak and diurnal emissions for each of the 20 cars from the in-use surveillance testing were increased by the average increase in evaporative emissions calculated from the CRC data on the Petrocoal-like fuels. The results of the analysis are shown in Table 4. When tested on gasoline, the surveillance testing indicates that 20% of the cars certified to the 2 gram SHED standard fail to meet the standard. The average emissions from the cars is just over the standard at 2.25 grams per test. However, when we adjusted the emissions to account for the use of Petrocoal the failure rate increases to 80% and the average emissions increase to 5.24 grams per test.

Also shown in Table 4 is the projected effect of Petrocoal on the grams/mile of HC emissions equivalent to the SHED test emissions. On straight gasoline the evaporative emissions of the 1980 model cars average 0.24 grams/mile. On Petrocoal they are estimated to be 2 1/2 times larger at 0.61 grams per mile.

* Superscripts denote references listed at end of text.

Table 4

Evaporative Emissions of Vehicles Certified Under
2 Gram Per Test SHED Standard

Car No.	ARB Surveillance Data Hot Soak	Diurnal	Total	Estimated Emissions With Petrocoal Hot Soak	Diurnal	Total
096	0.85	0.30	1.15	2.30	0.38	2.68*
148	2.92	4.23	7.15*	7.92	5.41	13.33*
155	1.06	0.38	1.44	2.87	0.49	3.36*
163	0.83	0.34	1.17	2.25	0.43	2.68*
240	0.44	0.27	0.71	1.19	0.35	1.54
279	0.47	0.22	0.69	1.27	0.28	1.55
295	1.13	0.18	1.31	3.06	0.23	3.29*
298	11.72	0.37	12.09*	31.77	0.47	32.24*
299	0.85	0.29	1.14	2.30	0.37	2.67*
341	0.79	0.21	1.00	2.14	0.27	2.41*
343	0.61	0.19	0.80	1.65	0.24	1.89
344	0.92	1.79	2.71*	2.49	2.29	4.78*
345	1.05	0.81	1.86	2.85	1.04	3.89*
347	0.73	0.49	1.22	1.98	0.63	2.61*
349	0.53	0.65	1.18	1.44	0.83	2.27*
350	0.60	0.21	0.81	1.63	0.27	1.90
351	3.89	0.49	4.38*	10.55	0.63	11.18*
352	0.96	0.30	1.26	2.60	0.38	2.98*
378	1.33	0.14	1.47	3.61	0.18	3.79*
379	1.33	0.13	1.46	3.61	0.17	3.78*
Average	1.65	0.60	2.25	4.47	0.77	5.24
Failure Rate		20%			80%	
Grams/Mile**		0.24			0.61	

* Fails 2.0 gram standard

** Grams/Mile = $\frac{\text{(hot soak grams)(3.58 trips/day) + diurnal grams}}{\text{27.4 miles/day}}$

Long Term Evaporative Emissions Effect - Stamper[2] reports that a severe deterioration in the activated charcoal control systems for vehicle diurnal evaporative emissions is associated with the use of methanol/gasoline blends. Stamper explains this phenomenon as the result of the hygroscopic nature of methanol or the behavior of the azeotropic methanol/gasoline mixtures.

Once methanol is adsorbed onto activated carbon, water vapor entering the canister with the purge air is probably attracted to and adsorbed onto the methanol site. Over time more of the available adsorption sites become occupied with methanol and water molecules which are unlikely to be stripped off at temperatures and pressures that are typical of automotive evaporative emission canisters. In addition, Stamper says the presence of methanol in the gasoline tends to put higher molecular weight HC into the vapor space than would be present with gasoline alone. When the higher molecular weight HC is adsorbed onto the activated carbon, the azeotrope is broken, and thus, these compounds are not as likely to be removed under typical purge conditions. These HC compounds tend to occupy an increasing number of adsorption sites as the number of purge/load cycles increase, reducing the adsorption capacity of the canister.

Data reported by Stamper indicates that a three fold increase in diurnal emissions is likely to occur due to extended operation on fuels which contain significant amounts of methanol. If this effect occurs with Petrocoal then the emission increases shown by the CRC data will significantly understate the increased evaporative emissions associated with the use of this fuel.

Exhaust Emissions

Exhaust emission test results from the CRC study are summarized in Table 5. Hydrocarbons were reduced by 16.1% or 0.05 grams per mile on both of the Petrocoal-like blends. This decrease was far less than the 0.37 gram per mile increase in evaporative emissions calculated above. CO emissions were reduced by about 44% on both blends. However, NOx emissions were about 30% higher. If the NOx emission changes for the open-loop and closed-loop cars are calculated separately then it can be seen that the open-loop cars had a 27.6% increase in NOx and the closed-loop cars had an 34.4% increase.

To determine the effect of the NOx emissions increase on the ability of cars to meet the NOx standards the percentage increases from the CRC cars were applied to ARB in-use surveillance data. The increase shown for the open-loop cars was applied to surveillance data for 1979 model cars, the vast majority of which used open-loop control systems. The increase shown for the closed-loop cars was applied to the 1980 California cars, which are typified by closed-loop systems. The surveillance data used represents the emission performance of a sample of the fleet after all tampering has been corrected and obvious defects have been repaired. The results are shown in Tables 6 and 7.

Table 5

CRC Exhaust Emission Test Results
(grams/mile)

	Base Gasoline			8.8% Methanol + 2.7% Butanol			13.4% Methanol + 1.8% Butanol		
Car	HC	CO	NOx	HC	CO	NOx	HC	CO	NOx
O4-1	0.17	2.03	1.64	0.14	1.01	2.19	0.17	1.80	1.98
O4-2	0.26	3.40	1.21	0.29	2.69	1.89	0.24	2.56	2.10
C4-1	0.35	6.96	0.76	0.25	2.86	1.18	0.35	3.36	0.90
C4-2	0.38	4.28	0.57	0.28	2.65	0.60	0.30	3.08	0.80
C6-1	0.33	6.96	0.65	0.29	4.19	0.96	0.27	4.47	0.93
O6-1	0.33	5.55	1.67	0.36	4.43	1.67	0.33	4.39	1.35
O4-3	0.17	3.32	0.84	0.15	1.64	1.26	0.24	1.84	1.56
O4-4	0.21	2.04	1.43	0.12	0.50	1.48	0.12	0.51	1.88
C4-3	0.50	8.26	0.53	0.45	3.97	0.75	0.38	2.30	0.73
C4-4	0.35	2.91	0.70	0.26	1.67	0.72	0.19	1.50	1.04
Average	0.31	4.57	1.00	0.26	2.56	1.27	0.26	2.58	1.33
	Percent Change From Base Gasoline			-16.1	-44.0	+27.0	-16.1	-43.5	+33.0

Table 6

ARB In-Use Surveillance Data
for 1979 Model Passenger Cars
NOx Exhaust Emissions After Repair
(grams/mile)

Emissions on Gasoline				Estimated Emissions With Petrocoal			
NOx	Miles	NOx	Miles	NOx	Miles	NOx	Miles
0.81	8637	1.18	22063	1.03	8637	1.51	22063
0.62	17535	1.20	5406	0.79	17535	1.53	5406
1.61*	23739	1.56*	17806	2.05*	23739	1.99*	17806
0.79	18725	1.33	10827	1.01	18725	1.70*	10827
1.29	18010	1.47	21538	1.65*	18010	1.88*	21538
0.81	19818	1.08	23774	1.03	19808	1.38	23774
1.06	28032	1.71*	33169	1.35	28032	2.18*	33169
1.40	33430	1.32	27705	1.79*	33430	1.68*	27705
1.34	35375	1.57*	10399	1.71*	35375	2.00*	10399
1.64*	28561	1.51	20743	2.09*	28561	1.93*	20743
0.96	17463	1.03	24363	1.22	17463	1.31	24363
1.60*	19817	0.86	32794	2.04*	19817	1.10	32794
1.26	22030	1.52	23170	1.61*	22030	1.94*	23170
1.27	17140	1.45	36901	1.62*	17140	1.85*	36901
0.89	45965	1.33	25304	1.14	45965	1.70*	25304
0.81	34394	1.17	15635	1.03	34394	1.49	15635
1.40	32480	0.58	29841	1.79*	32480	0.74	29841
1.72*	23562	1.52	24917	2.19*	23562	1.94*	24917
1.53	25536	1.39	8859	1.95*	25536	1.77*	8859
1.78*	19990	1.27	35153	2.27*	19990	1.62*	35153
1.44	28370	1.62*	16552	1.84*	28370	2.07*	16552
1.04	38517	0.94	28295	1.33	38517	1.20	28295
1.05	28296	1.44	33005	1.34	28296	1.84*	33005
1.14	7733	1.16	27885	1.45	7733	1.48	27885
1.10	30910	1.11	18835	1.40	30910	1.42	18835
1.10	25354	0.73	42697	1.40	25354	0.93	42697
1.00	21267	2.09*	35974	1.28	21267	2.67*	35974
1.25	47339	4.96*	36164	1.60*	47339	6.33*	36164
2.10*	42289	0.70	9574	2.68*	42289	0.89	9574
0.60	29943	0.67	34696	0.77	29943	0.85	34696
1.18	21433	2.03*	29503	1.51	21433	2.59*	29503
0.99	40307			1.26	40307		

Failure Rate = 20.6%

Average Emissions = 1.30

Failure Rate = 52.4%

Average Emissions = 1.66

*Fails 1.5 gram/mile standard

Table 7
ARB In-Use Surveillance Data for 1980 Model Passenger Cars
NOx Exhaust Emissions After Repair, (grams/mile)

Emissions on Gasoline				Estimated Emissions With Petrocoal			
NOx	Miles	NOx	Miles	NOx	Miles	NOx	Miles
0.29	4977	0.23	5242	0.39	4977	0.31	5242
0.95	9534	1.66*	13522	1.28*	9534	2.23*	13522
0.40	14977	0.52	1216	0.54	14977	0.70	1216
0.86	14222	0.43	999	1.16*	14222	0.58	999
0.89	43016	0.92	12218	1.20*	43016	1.24*	12218
0.72	13358	1.14*	17137	0.97	13358	1.53*	17137
0.49	18761	0.31	16372	0.66	18761	0.42	16372
1.09*	10141	1.05*	18375	1.46*	10141	1.41*	18375
0.48	17790	0.32	12273	0.65	17790	0.43	12273
0.84	27279	1.12*	13179	1.13*	27279	1.51*	13179
0.85	29371	0.90	14065	1.14*	29371	1.21*	14065
1.25*	23104	0.90	5320	1.68*	23104	1.21*	5320
1.95*	14380	0.89	5022	2.62*	14380	1.20*	5022
0.46	10941	0.87	15175	0.62	10941	1.17*	15175
0.89	12651	0.94	22705	1.20*	12651	1.26*	22705
1.33*	13508	0.49	15164	1.79*	13508	0.66	15164
0.69	4402	0.60	8540	0.93	4402	0.81	8540
0.53	12395	0.74	12187	0.71	12395	0.99	12187
0.66	25925	0.68	19608	0.89	25925	0.91	19608
1.32*	28972	0.65	18275	1.77*	28972	0.87	18275
1.12*	12170	1.06*	10873	1.51*	12170	1.42*	10873
0.89	9639	0.92	5506	1.20*	9639	1.24*	5506
1.11*	17396	0.90	18799	1.49*	17396	1.21*	18799
0.78	11229	0.93	17246	1.05*	11229	1.25*	17246
0.81	14981	0.80	9716	1.09*	14981	1.08*	9716
1.47*	9233	0.94	11880	1.98*	9233	1.26*	11880
1.12*	21082	1.98*	6509	1.51*	21082	2.66*	6509
1.31*	5398	1.09*	37275	1.76*	5398	1.46*	37275
0.63	22584	0.94	15569	0.85	22584	1.26*	15569
0.88	8708	0.94	4990	1.18*	8708	1.26*	4990
0.97	3367	0.94	14161	1.30*	3367	1.26*	14161
0.90	6492	0.96	13509	1.21*	6492	1.29*	13509
0.89	13645	0.92	16227	1.20*	13645	1.24*	16227
1.01	10262	1.54*	8983	1.36*	10262	2.07*	8983
0.92	12445	0.93	12540	1.24*	12445	1.25*	12540
0.88	11704	0.80	7006	1.18*	11704	1.08*	7006
1.04	14186	0.70	12134	1.40*	14186	0.94	12134
0.91	8544	1.03	18694	1.22*	8544	1.38*	18694
0.89	10564	1.18*	18328	1.20*	10564	1.59*	18328
1.00	15287	1.05*	24677	1.34*	15287	1.41*	24677
0.88	25411	1.10*	31297	1.18*	25411	1.48*	31297
0.81	14309	0.58	21959	1.09*	14309	0.78	21959
1.06*	24344	0.64	20355	1.42*	24344	0.86	20355
0.70	21443	1.06*	11538	0.94	21443	1.42*	11538
0.84	26289	0.60	13751	1.13*	26289	0.81	13751
Failure Rate = 25.6%				Failure Rate = 72.2%			
Average Emissions = 0.90				Average Emissions = 1.20			

As shown in Tables 6 and 7, the increased NOx emissions associated with the use of Petrocoal-like fuels has a major impact on the ability of both open-loop and closed loop cars to meet emission standards in customer service. The increase in NOx increases the failure rate of open-loop cars to 52.4% from 20.6%. Average emissions for open-loop cars increase from 1.30 grams per mile (below the 1.5 standard) to 1.66 grams per mile. Closed-loop cars are even more significantly affected. The failure rate increases from 25.6% to 72.2% when the effects of Petrocoal-like fuels are accounted for. Average emissions increase from 0.90 grams per mile (below the 1.0 gram standard) to 1.20 grams per mile, 20% over the standard.

Driveability and Materials Compatibility

The effects of methanol-gasoline blends on driveability are associated with the enleanment effect. The decrease in the chemically correct (stoichiometric) air/fuel ratio associated with methanol-gasoline blends is due primarily to the fact that methanol contains oxygen and gasoline does not. A blend of 10% methanol and 90% unleaded gasoline has a stoichiometric air/fuel ratio of 13.9:1, 5.4% richer than pure gasoline. Since a 10% methanol-gasoline blend is only 0.6% greater density than gasoline, the net effect is that an engine will run 4.8% leaner on a 10% methanol-gasoline blend. Closed-loop vehicles can compensate for this enleanment effect during warmed up operation except for near wide open throttle operation on some vehicles. However, during the critical cold start and warmup operation, the closed-loop system cannot compensate for the enleanment caused by the methanol.

Most researchers report a noticeable increase in problems with stalling and surging when methanol-gasoline blends are used. Reports of poor driveability during cold-start operation may also be due to the fact that methanol has a higher heat of vaporization than gasoline. In spite of the fact that methanol-gasoline blends are more volatile than gasoline, they do not vaporize as well in the intake system because of the higher heat of vaporization required.

The adverse effects on driveability associated with Petrocoal-like blends was clearly demonstrated in the CRC testing. The results of the driveability tests are summarized in Table 8. As shown in the table, the use of the blends increased driveability demerits by 144%. Such a significant increase in driveability problems is likely to induce some motorists to have their vehicles modified or adjusted to restore acceptable driveability. The effects of such adjustments on exhaust emissions can be substantial.

Table 8

CRC Driveability Test Results

Car	Driveability Demerits		
	Base Gasoline	8.8% Methanol + 2.7% Butanol	13.4% Methanol + 1.8% Butanol
O4-1	75.0	204.0	168.0
O4-2	49.0	89.5	84.5
C4-1	86.0	180.0	205.0
C4-2	75.5	108.5	103.0
C6-1	44.5	111.5	170.0
O6-1	21.0	61.0	135.0
O4-3	39.5	92.5	104.5
O4-4	51.5	193.5	87.5
C4-3	17.5	97.0	97.0
C4-4	45.5	94.5	76.5
Average	50.5	123.2	123.1
Increase in Driveability Demerits with Petrocoal		+144.0%	+143.8%

Limited test results have been identified which determined the effect on exhaust emissions of readjusting vehicles to offset the degradation in driveability caused by a switch to alcohol-gasoline blends.[3] Three different 1978 model passenger cars equipped with 1.6, 3.3, and 5.0 litre engines were adjusted to optimize driveability after their driveability had been adversely affected by a switch to a 15% methanol-gasoline blend.

Adjustments made to the vehicles included:

1. Spark timing advanced 4°
2. Idle speed increased 50 RPM
3. Idle mixture enriched for best idle quality
4. Part throttle mixture adjusted on two of the three cars to optimize driveability

After these modifications had been completed, two of the cars had driveability ratings that were almost identical to what they had on straight gasoline. The third car had improved driveability compared to the use of the alcohol-gasoline blend without adjustments, however the vehicle was still experiencing a 50% increase in driveability problems compared to gasoline. The driveability tests that were run indicate that the adjustments made to compensate for the use of the alcohol-gasoline blend were not greater than required to restore the original level of drive performance.

Table 9 shows the effect of the adjustments made to restore driveability on the exhaust emission changes caused by the methanol-gasoline blend. As would be expected the switch to the methanol-gasoline blend initially reduced CO emissions. The 39.3% reduction shown in the Table is reasonably consistent with data for Petrocoal-like fuels. HC was reduced initially by 11.1%. When the vehicles were adjusted to restore their driveability the CO emissions were 138.3% higher than when they were running on gasoline in their baseline condition. HC was increased 59.3% from the baseline.

The reason that the CO emission levels in the adjusted configuration were higher than the gasoline baseline is probably associated with the inability to restore adequate acceleration enrichment with the adjustments that were made. Because it was not practical to increase the accelerator pump shot, the basic air/fuel ratio of the carburetors had to be adjusted rich enough to compensate for the driveability problems caused by this lack of adequate acceleration enrichment.

Table 9

Effect of Alcohol-Gasoline Blend Use
and Subsequent Adjustments to Restore Driveability
on Exhaust Emissions

	HC	CO	NOx
3 '78 model cars, no adjustments	-11.1%	-39.3%	-4.6%
3 '78 model cars, adjusted to restore driveability	+59.3%	+138.3%	+19.1%

Note: Emission changes as compared with straight gasoline

Source: Reference 3

After the vehicles were modified to restore their driveability, they were switched back to gasoline to determine what the effects would be on emissions and driveability. Driveability was determined to be superior to the baseline condition because of the mixture enrichment. NOx emissions were 1.3% less than in the baseline configuration, however, the increases in hydrocarbon and CO emissions were enormous. HC had increased to 189% above the baseline and CO had increased by 360%.

The CRC driveability data are not inconsistent with the data in the record at the time the Petrocoal waiver was granted. The GM data indicated significant increases in driveability demerits. EPA did not evaluate the driveability of the Petrocoal equipped vehicles on anything other than a subjective basis. However, two of the vehicles tested by EPA experienced significant driveability problems. One of the problems was probably associated with the materials compatibility problems associated with Petrocoal (a swollen and sticking accelerator pump). However, the Ford Escort apparently experienced vapor lock induced stalls on several occasions.

EPA reported that the problem with the Escort stopped when the fuel filter of the vehicle was replaced. It should be noted, however, that the Docket contains a hand written memo from the driver of the cars saying that inspection of the fuel filter indicates it was not plugged and all indications were that the problem was caused by vapor lock. It is likely that a change in the weather, rather than a change in the fuel pump solved the problem.

EPA apparently chose to disregard the driveability problem associated with the failed accelerator pump; however, it is unlikely that the sticking accelerator pump would have been correctly diagnosed had the failure occured in customer service. The likely repair procedure would have been enrichment of the carburetor to mask the problem. This pump failure is one of the indications available that the secret inhibitor used in Petrocoal is not adequate to solve the materials compatibility problems associated with methanol.

The materials compatibility data supplied by Anafuel do not substantiate the lack of problems. As noted in the EPA report on materials compatibility submitted to the Docket, "...there appears to be no available data, either in the published literature or supplied by Anafuel, which would conclusively demonstrate that Petrocoal would be safe (from

an emissions control standpoint) to operate in currently available motor vehicles over long time periods." The report goes on to say, "The elastomers tested by Anafuel were noted in the existing literature as being the most resistant to attack by methanol...."

The existance of driveability and materials compatibility problems with Petrocoal has recently been documented from customer experience. For example, Newhall, one of the marketers of Petrocoal in California, reports[4] that numerous complaints about driveability problems were received when they began marketing Petrocoal at the 12% total alcohol level last year. In addition, Newhall reports that accelerator pump failures appear to be associated with the use of the fuel. Some of the driveability problems experienced by Newhall's own employees were solved by the replacement of accelerator pumps. Newhall has since decided to stop marketing the product.

Because of the significant increases in emissions that are associated with the tampering that will be done to vehicles to restore the driveability problems associated with the enleanment effects of Petrocoal and the materials compatability problems, it is inappropriate for EPA to assume that there will be no particular problem in this regard.

References

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2. K.R. Stamper, "Evaporative Emissions from Vehicles Operating on Methanol/Gasoline Blends," SAE paper no. 801360, October, 1980.

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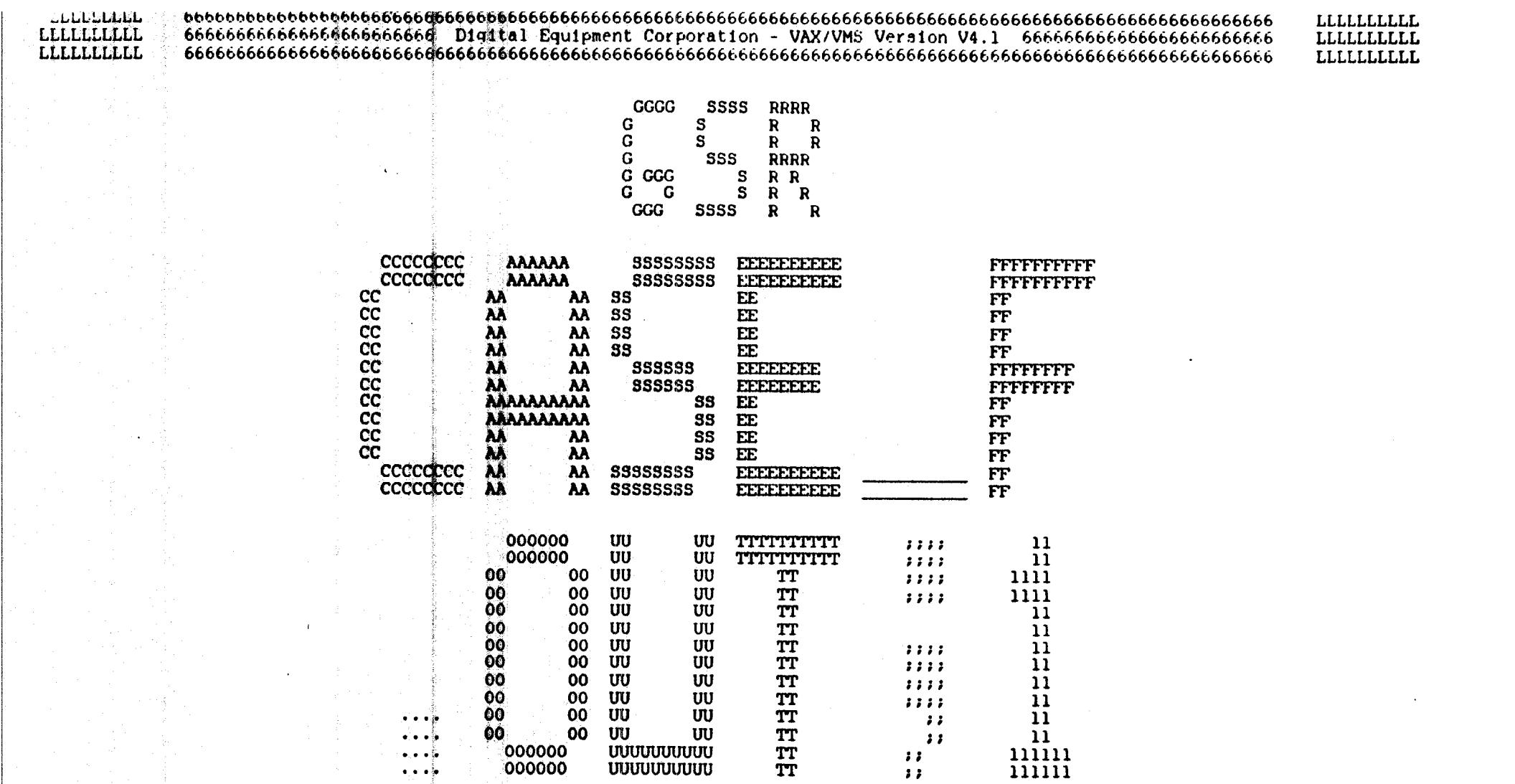
4. Personal communication with Henry Seal, Newhall.



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** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: BIE  AL PROGRAM
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** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: ANNUAL   PROGRAM
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** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: A   L   PROGRAM
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1980    EF EQUATION : FTP   HC=  0.27 +   0.10 * MILES/10000        0.27082     0.09926
1981    EF EQUATION : FTP   HC=  0.27 +   0.10 * MILES/10000        0.27236     0.09719
1982    EF EQUATION : FTP   HC=  0.26 +   0.09 * MILES/10000        0.25756     0.08540
1983    EF EQUATION : FTP   HC=  0.28 +   0.10 * MILES/10000        0.28398     0.09783
1984    EF EQUATION : FTP   HC=  0.29 +   0.10 * MILES/10000        0.28646     0.10291
198586  EF EQUATION : FTP   HC=  0.28 +   0.10 * MILES/10000        0.27899     0.10331
198789  EF EQUATION : FTP   HC=  0.28 +   0.11 * MILES/10000        0.28034     0.10634
1990+   EF EQUATION : FTP   HC=  0.28 +   0.11 * MILES/10000        0.27951     0.10748

1980    EF EQUATION : FTP   CO=  3.24 +   1.84 * MILES/10000        3.24085     1.84085
1981    EF EQUATION : FTP   CO=  3.20 +   1.76 * MILES/10000        3.19700     1.76078
1982    EF EQUATION : FTP   CO=  2.85 +   1.52 * MILES/10000        2.84824     1.51597
1983    EF EQUATION : FTP   CO=  3.19 +   1.79 * MILES/10000        3.18675     1.79164
1984    EF EQUATION : FTP   CO=  3.31 +   1.98 * MILES/10000        3.31419     1.97706
198586  EF EQUATION : FTP   CO=  3.14 +   2.01 * MILES/10000        3.14331     2.00604
198789  EF EQUATION : FTP   CO=  3.12 +   2.09 * MILES/10000        3.11665     2.08652
1990+   EF EQUATION : FTP   CO=  3.05 +   2.12 * MILES/10000        3.05163     2.11582
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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: ANNUAL   PROGRAM
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.000.000.000.045.161.176.185.193.199.202.205.207.209.210.211.212.213.216.231
.000.000.000.070.248.270.282.295.303.309.314.317.321.323.324.326.327.332.342
.000.000.039.139.163.179.188.197.203.207.211.213.215.217.218.219.220.223.238
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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: A  AL   PROGRAM
**

1980    EF EQUATION : FTP   HC=  0.27 +   0.10 * MILES/10000        0.27082     0.09926
1981    EF EQUATION : FTP   HC=  0.27 +   0.10 * MILES/10000        0.27236     0.09719
1982    EF EQUATION : FTP   HC=  0.26 +   0.09 * MILES/10000        0.25756     0.08540
1983    EF EQUATION : FTP   HC=  0.28 +   0.10 * MILES/10000        0.28398     0.09783
1984    EF EQUATION : FTP   HC=  0.29 +   0.10 * MILES/10000        0.28646     0.10291
198586  EF EQUATION : FTP   HC=  0.28 +   0.10 * MILES/10000        0.27899     0.10331
198789  EF EQUATION : FTP   HC=  0.28 +   0.11 * MILES/10000        0.28034     0.10634
1990+   EF EQUATION : FTP   HC=  0.28 +   0.11 * MILES/10000        0.27951     0.10748

1980    EF EQUATION : FTP   CO=  3.24 +   1.84 * MILES/10000        3.24085     1.84085
1981    EF EQUATION : FTP   CO=  3.20 +   1.76 * MILES/10000        3.19700     1.76078
1982    EF EQUATION : FTP   CO=  2.85 +   1.52 * MILES/10000        2.84824     1.51597
1983    EF EQUATION : FTP   CO=  3.19 +   1.79 * MILES/10000        3.18675     1.79164
1984    EF EQUATION : FTP   CO=  3.31 +   1.98 * MILES/10000        3.31419     1.97706
198586  EF EQUATION : FTP   CO=  3.14 +   2.01 * MILES/10000        3.14331     2.00604
198789  EF EQUATION : FTP   CO=  3.12 +   2.09 * MILES/10000        3.11665     2.08652
1990+   EF EQUATION : FTP   CO=  3.05 +   2.12 * MILES/10000        3.05163     2.11582
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                                    GGGG   SSSS  RRRR
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                                   G       SSS   RRRR
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                                   G   G      S  R  R
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CC           AA    AA            SS  EE                    EE
CC           AA    AA            SS  EE                    EE
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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: BIENNIAL PROGRAM
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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: ANNUAL   PROGRAM
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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: A   AL   PROGRAM
**

1980    EF EQUATION : FTP   HC=  0.27 +   0.13 * MILES/10000        0.27288     0.12728
1981    EF EQUATION : FTP   HC=  0.28 +   0.12 * MILES/10000        0.27608     0.12320
1982    EF EQUATION : FTP   HC=  0.26 +   0.11 * MILES/10000        0.25541     0.10918
1983    EF EQUATION : FTP   HC=  0.28 +   0.13 * MILES/10000        0.27897     0.12563
1984    EF EQUATION : FTP   HC=  0.28 +   0.13 * MILES/10000        0.27749     0.13440
198586  EF EQUATION : FTP   HC=  0.27 +   0.13 * MILES/10000        0.26723     0.13077
198789  EF EQUATION : FTP   HC=  0.27 +   0.13 * MILES/10000        0.26621     0.13231
1990+   EF EQUATION : FTP   HC=  0.26 +   0.13 * MILES/10000        0.26388     0.13128

1980    EF EQUATION : FTP   CO=  3.16 +   2.65 * MILES/10000        3.15693     2.64861
1981    EF EQUATION : FTP   CO=  3.14 +   2.53 * MILES/10000        3.13543     2.52513
1982    EF EQUATION : FTP   CO=  2.78 +   2.25 * MILES/10000        2.78231     2.24898
1983    EF EQUATION : FTP   CO=  3.07 +   2.64 * MILES/10000        3.06800     2.63831
1984    EF EQUATION : FTP   CO=  3.13 +   2.91 * MILES/10000        3.13197     2.90773
198586  EF EQUATION : FTP   CO=  2.88 +   2.86 * MILES/10000        2.88494     2.85509
198789  EF EQUATION : FTP   CO=  2.80 +   2.91 * MILES/10000        2.79991     2.91254
1990+   EF EQUATION : FTP   CO=  2.69 +   2.90 * MILES/10000        2.69228     2.90084
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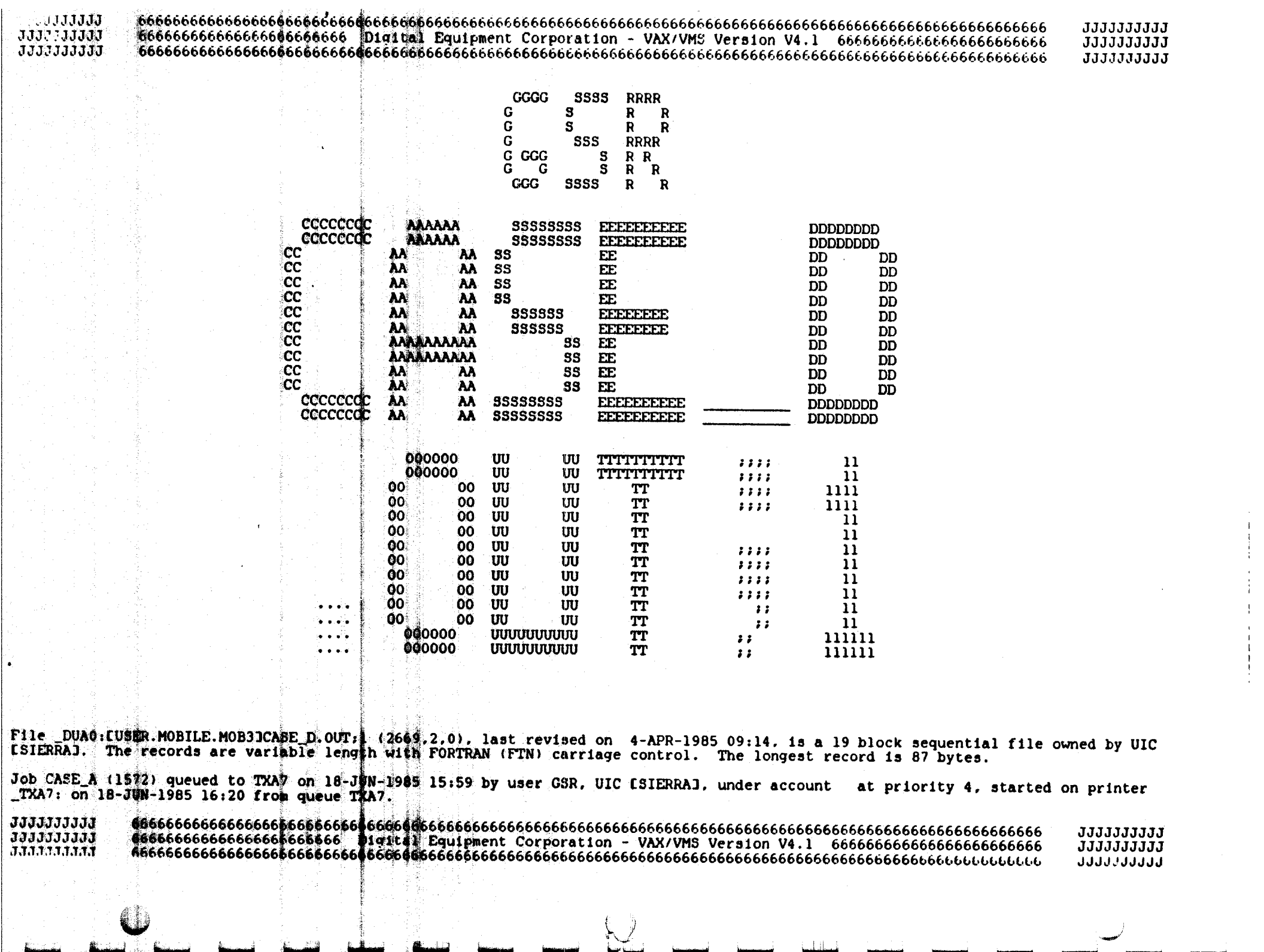

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**
** 1980 & LATER LOW-ALTITUDE CALIFORNIA CARS: B    IAL PROGRAM
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ENVIRONMENTAL IMPACTS OF METHANOL/GASOLINE BLENDS

Environmental Impacts of Methanol/Gasoline Blends

February 16, 1984

Abstract

A review of available data on the emission impacts of methanol/gasoline blends identifies six ways in which blend usage may result in increases in vehicle evaporative or exhaust emissions. The size of each emission increase ranges from indeterminate to an equivalent of nearly 0.5 grams per mile hydrocarbon emissions. The review identifies the need for additional research and testing into the effects of blend usage on vehicle emissions, and suggests that even stringent volatility controls on blends may be inadequate to avoid hydrocarbon emission increases. In addition, an increase in NOx emissions from methanol/blend usage is apparent.

Introduction

Despite 20 years of progress in controlling motor vehicle emissions, in many areas vehicles remain a significant source of air pollution due to growth in vehicle travel and the failure of vehicles to meet the emission standards in customer service. Vehicle inspection and maintenance (I/M) programs, tamper resistant design features on new vehicles, and other programs to improve in-use compliance will enable substantial further progress to be made in the control of motor vehicle emissions during the 1980's. However, the expanded use of methanol gasoline blends may offset much of this needed progress.

The California Air Resources Board (ARB) has long recognized the importance of motor vehicle fuel controls as an element of an effective emission control program. ARB regulations currently limit the lead content, sulfur content, MMT content, Bromine Number, and Reid Vapor Pressure (RVP) of gasoline sold in the State of California. U.S. Environmental Protection Agency (EPA) regulations also control the content of motor vehicle gasoline, but not in the important area of volatility. Since vehicle evaporative emissions are related to fuel volatility, and the use of methanol in gasoline can substantially increase a fuel's volatility, the potential for use of methanol/gasoline blends to result in an increase in emissions is a concern.

This paper has been prepared on the premise that in areas of the country with levels of ozone that exceed the national ambient air quality standards, the use of methanol/gasoline blends must not result in an increase in smog-forming pollutants. In this paper, we identify six areas of concern where the use of methanol/gasoline blends may conflict with that premise. The areas of concern are:

- Increase in evaporative emissions due to blend volatility.
- Increase in evaporative emissions due to intermittent blend usage.
- Increase in evaporative emissions due to evaporative control system degradation.
- Increase in smog formation due to higher photochemical reactivity of the evaporative emissions of blends.
- Increase in exhaust emissions of NOx.
- Increase in exhaust emissions of HC and CO due to driveability-induced readjustments and tampering.

Additional research may prove several of these areas not to be of concern. Restrictions, by regulation or by the blend marketers, in the formulation and use of blends may also address some of the concerns. However, it is uncertain if research and control will be adequate to assure there are no emission increases resulting from blend usage, and thus whether methanol/gasoline blends should be used at all in nonattainment areas remains an unanswered question.

Increase in Evaporative Emissions Due to Volatility

The effect of alcohol addition on the volatility of gasoline is illustrated in Figure 1. As shown in the figure, Reid Vapor Pressure, a measure of volatility at 100°F,

increases rapidly with only minor alcohol addition. Beyond the addition of 2% alcohol, RVP increases at a much lower rate.

Of the three most commonly used alcohols, methanol causes the greatest volatility increase. RVP will typically increase by about 3 psi with the addition of methanol in the range of 2-10 volume percent.

Methanol addition has an even greater effect on another measure of gasoline volatility, Front End Volatility Index (FEVI). FEVI is defined as RVP plus 13% of the fuel distilled at 158°F. Methanol addition significantly

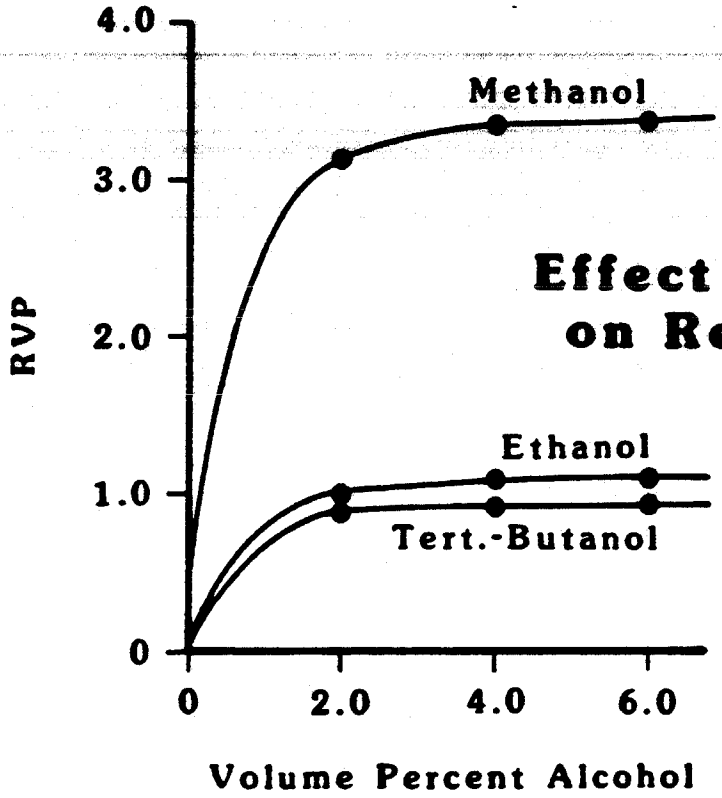


Figure 1

Effect of Alcohol Addition on Reid Vapor Pressure

increases the percent of fuel that is evaporated at temperatures in the range of 158°F, a temperature which gasoline in a carburetor float bowl typically reaches during a "hot soak" after the shut down of a warmed up engine.

Numerous studies have documented the fact that evaporative emissions increase as fuel volatility, measured by either RVP or FEVI, increases. However, the available data indicate that these volatility parameters are not sufficient to explain all of the variation in the evaporative emissions potential of various fuels.

The fact that evaporative emissions from methanol/gasoline blends cannot be controlled through the use of comparable volatility specifications is indicated in the data from the

Coordinating Research Council (CRC) sponsored testing of methanol/gasoline blends.[1]* Five blends which contained methanol or methanol plus butanol in amounts ranging from 3.5 to 15% total alcohol were included in the CRC study. Each of these five blends, in addition to a straight gasoline, were evaluated using ten 1980 model passenger cars. Five of the cars were equipped with "open-loop", oxidation catalyst control systems and five were equipped with "closed-loop" control systems incorporating 3-way catalysts.

Table 1 shows the properties of the six fuels used in the CRC testing program. As can be seen from the table, the volatility of the blends was controlled so that each of the blends had a lower RVP than the straight gasoline used in the testing program. Three of the five blends (MG-1, MG-2, and MG-3) also had lower FEVI than the straight gasoline. Blend (MG-4) had only slightly higher FEVI than the gasoline.

Blend MG-3, 8.8% methanol and 2.7% butanol, was volatility adjusted through the use of 50% less butane and 25% less pentane than in the base gasoline. The other four blends were volatility adjusted by using 100% less butane than in the base gasoline. All of the alcohol/gasoline blends were below the maximum RVP specified by ASTM for either winter or summer gasolines in any area of the country. The testing of these fuels provides a basis for examining the hypothesis that controlling RVP or FEVI of a methanol/gasoline blend to the same value as straight gasoline will result in no increase in evaporative emissions from vehicles using the blend.

Table 1

CRC Test Fuel Properties

	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
Methanol %	0.0	3.31	3.54	8.83	9.75	13.35
Isobutanol %	0.0	1.21	0.05	2.66	0.0	1.80
Total Alcohol %	0.0	4.52	3.59	11.49	9.75	15.15
RVP, psi	9.7	8.0	8.7	7.6	8.7	8.4
FEVI	12.8	10.9	11.5	11.6	13.2	13.8
% Oxygen Content (calculated)	0.0	1.9	1.8	5.0	4.9	7.1

*Superscripts denote references listed at end of text.

The results of the evaporative emission testing conducted for CRC are shown in Table 2. Data are shown for all ten of the 1980 model cars that were tested. The first letter of the vehicle designation is either an "O" or a "C". The "O" designation indicates an open-loop emission control system. The "C" designation indicates closed-loop. The second digit of the vehicle designation indicates the number of cylinders of the test car and the third digit indicates whether the car is the first, second, third, or fourth test vehicle with the same type of emission control system and number of cylinders.

As shown in Table 2, every single car experienced an increase in evaporative emissions on every one of the five blends despite the fact that each fuel had lower RVP than the straight gasoline, and three of the fuels had lower FEVI. Average evaporative emission increases for all ten cars ranged from 46.4% to 146%.

Table 2

CRC Evaporative Emission Test Results
(grams per test)

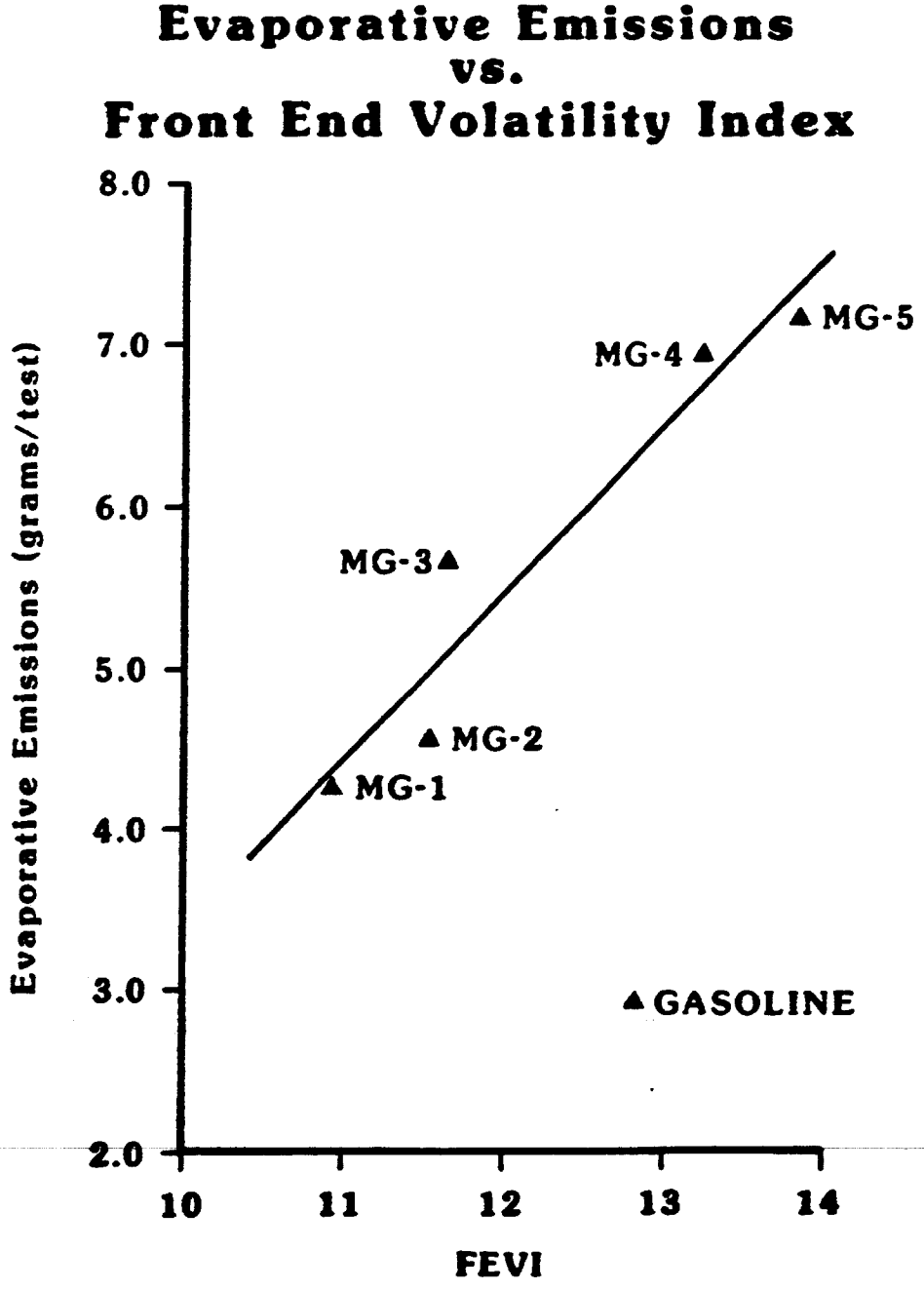
Car Number	Straight Gasoline	Blend MG-1	Blend MG-2	Blend MG-3	Blend MG-4	Blend MG-5
O4-1	1.47	1.83	2.58	3.18	2.75	2.82
O4-2	1.70	1.88	2.22	2.12	2.15	2.34
C4-1	3.17	6.82	6.38	9.52	11.80	9.55
C4-2	2.34	4.26	4.77	5.17	4.62	8.15
C6-1	2.32	2.68	3.59	3.73	4.14	4.26
O6-1	3.29	4.13	6.04	4.18	5.63	4.81
O4-3	3.46	5.79	4.07	5.83	8.57	6.88
O4-4	3.51	4.02	4.18	4.63	4.25	7.56
C4-3	4.07	6.38	6.84	13.15	18.75	19.64
C4-4	3.79	4.81	4.83	5.24	6.62	5.62
10 Car Average	2.91	4.26	4.55	5.67	6.93	7.16
Change from Base Gasoline	0.0%	+46.4%	+56.4%	+94.8%	+138.1%	+146.0%

Figure 2 graphically illustrates the evaporative emission test results of the CRC testing program. As shown in the figure, the evaporative emissions of the blends (ten car averages) do appear to correlate quite well with FEVI. The correlation coefficient for the least squares fit to the data for the blends only is 0.96, indicating a high correlation between evaporative emissions and FEVI. Other studies have shown there is also a relationship between evaporative emissions and FEVI for straight gasoline, but it appears to be a different relationship. This can also be seen in Figure 2.

For the FEVI of the baseline gasoline, the least squares line fit to the blend data predicts 6.33 grams per test of evaporative emissions. However, the actual evaporative emissions for the straight gasoline were only 2.91 grams. A methanol/gasoline blend of equal FEVI to the gasoline is predicted to yield 117.5% higher evaporative emissions.

A more detailed analysis of the CRC data indicates that this evaporative emission increase at equal FEVI is divided between an approximately 170% increase in hot soak emissions and 30% increase in diurnal emissions. In-use surveillance data on California cars certified to the 2 gram per test SHED evaporative emissions standard indicates that on gasoline their evaporative emissions average about 1.65 grams per test hot soak and 0.60 grams per test diurnal. Assuming 3.58 hot soaks and 27.4 miles of driving per day, the

Figure 2



average evaporative emissions of these cars on straight gasoline is 0.24 grams per mile. The typical increase in evaporative emissions at equal FEVI observed in the CRC testing program would result in these emissions increasing to 0.61 grams per mile, an increase of 0.37 grams per mile.

Based on the in-use surveillance data we have available on cars designed to meet a 2 gram per test standard,[2] the use of methanol/gasoline blends would increase the percentage of vehicles which fail to meet the 2 gram standard in customer service from 20% to 80%. This expected increase in the in-use evaporative emissions and evaporative emission standard failure rate is summarized in Table 3.

Table 3

Evaporative Emissions of Vehicles Certified Under 2 Gram Per Test SHED Standard

ARB Surveillance Data			Estimated Emissions Methanol/Gasoline Blends		
Hot Soak	Diurnal	Total	Hot Soak	Diurnal	Total
1.65	0.60	2.25	4.47	0.77	5.24
Failure Rate	20%			80%	
Grams/Mile*	0.24			0.61	

* Grams/Mile = $\frac{\text{(hot soak grams)(3.58 trips/day) + diurnal grams}}{\text{27.4 miles/day}}$

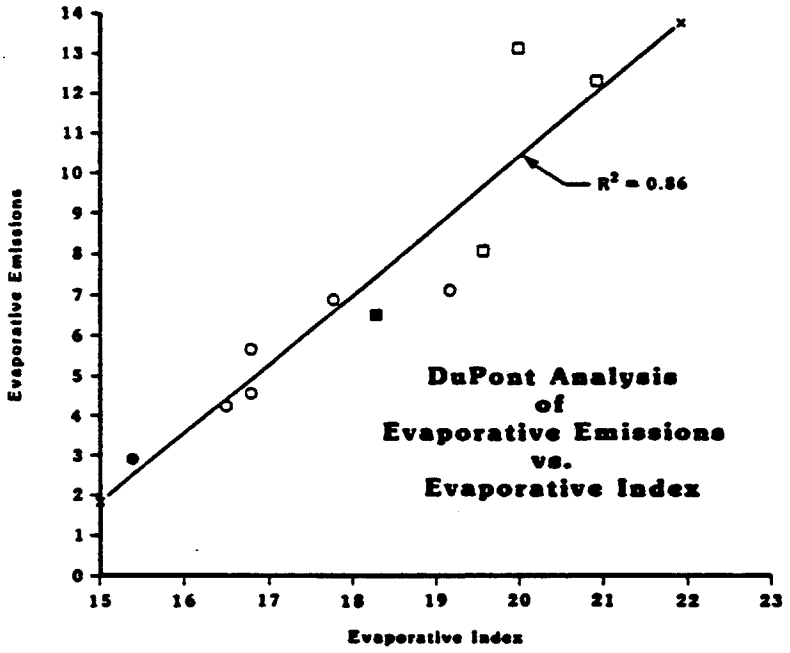
Others have analyzed the CRC data and other data on the effects of methanol/gasoline blends and concluded that the data show a correlation between FEVI and evaporative emissions for all of the fuels, blends as well as straight gasoline. It may be possible to demonstrate such a correlation statistically, but it is obvious that the correlation is improved when the methanol/gasoline blends are analyzed independently. FEVI is only one factor related to the effect of methanol addition on evaporative emissions. The control of FEVI alone does not appear to be sufficient to prevent an increase in evaporative emissions from vehicles using methanol/gasoline blends.

Other Volatility Measures - DuPont has analyzed the CRC data and concluded that an alternative measure of fuel volatility which it calls an "Evaporative Index" would be even more appropriate.[3] DuPont defines Evaporative Index as follows:

E.I. = 1.1(RVP) + 0.21(% evap.@ 200°F) - 0.32(% evap.@ 100°F)

We have independently analyzed the CRC data using DuPont's Evaporative Index and reached conclusions which are contrary to DuPont's. Figure 3 illustrates DuPont's analysis of CRC

Figure 3



data on alcohol/gasoline blends. In addition to the methanol blend testing, DuPont included test results from an earlier CRC testing program involving the use of ethanol/gasoline blends. As shown in the figure, it appears as though there is a good correlation between evaporative emissions and the Evaporative Index for all of the fuels, alcohol/gasoline blends and straight gasolines. In the figure, the straight gasolines are shown as a solid circle or square. The blends are shown as open circles and squares.

However, there are several problems with the DuPont analysis, in our opinion. First, DuPont did not use the fuel specifications reported by CRC for calculating the Evaporative Index of the CRC test fuels. DuPont used the average of "round robin" test results from a variety of laboratories that were obtained sometime after the testing program had been completed. The fuel specifications used by DuPont showed that the base gasoline used during the methanol blend testing had a much lower Evaporative Index

than the blends. However, the fuel specifications for the baseline gasoline appear unreasonable.

The specifications used by DuPont indicate that the baseline gasoline had 9.9% evaporated at 100°F, increasing to only 10.7% evaporated at 120°F. The percent fuel evaporated at 100°F appears to be greater than other fuels used in the study, and for the base gasoline results in a much steeper rise in temperature per volume evaporated than typical of commercial gasolines. Based on the distillation curves shown in the CRC report, the data used by DuPont represent a significant overestimate of the percent evaporated at 100°F. The Evaporative Index term is very sensitive to errors in the measurement of the front end of the distillation curve. The difference between the CRC distillation curves and those used by DuPont cause a large difference in the calculated value of the Evaporative Index.

Our recalculation of Evaporative Index vs. Evaporative Emissions, using the fuel specifications reported by CRC, is shown in Figure 4. By comparing Figure 4 to Figure 3, it can be seen that the difference between our calculated values of Evaporative Index and DuPont's are minor, except for the baseline gasoline used in the methanol blend testing. Illustrated on the figure is the change in Evaporative Index for this one fuel. With the use of the CRC fuel specifications, the correlation between Evaporative Index and evaporative emissions is significantly degraded.

The second problem we have with DuPont's Evaporative Index analysis is that it combines the results of two independent testing programs without normalizing the test results. Variations in vehicles and fuel blending components can result in significant changes in the average evaporative emissions that will be measured for a population of vehicles, independent of FEVI. This fact has not been accounted for in DuPont's analysis of the CRC test data from two different programs. The methanol/gasoline blend testing program used a ten vehicle subset of the fourteen vehicles used in the ethanol blend testing program. In addition, the baseline gasolines were blended from different components.

Figure 5 shows which data points are derived from the "Phase I" ethanol blend program and the "Phase II" methanol blend program. Figure 6 illustrates the effect of "normalizing" the two data sets so that the average evaporative emissions of both testing programs are identical on the baseline gasolines (which, coincidentally, had the same value of Evaporative Index in both testing programs). When the data are normalized in this fashion there is no apparent relationship between Evaporative Index and evaporative emissions. While we do not conclude there is no relationship between evaporative index and evaporative

emissions, this analysis brings into question the inclusion of both ethanol and methanol blends into analyses aimed at identifying a fuel volatility parameter which accurately predicts evaporative emissions.

Figure 4

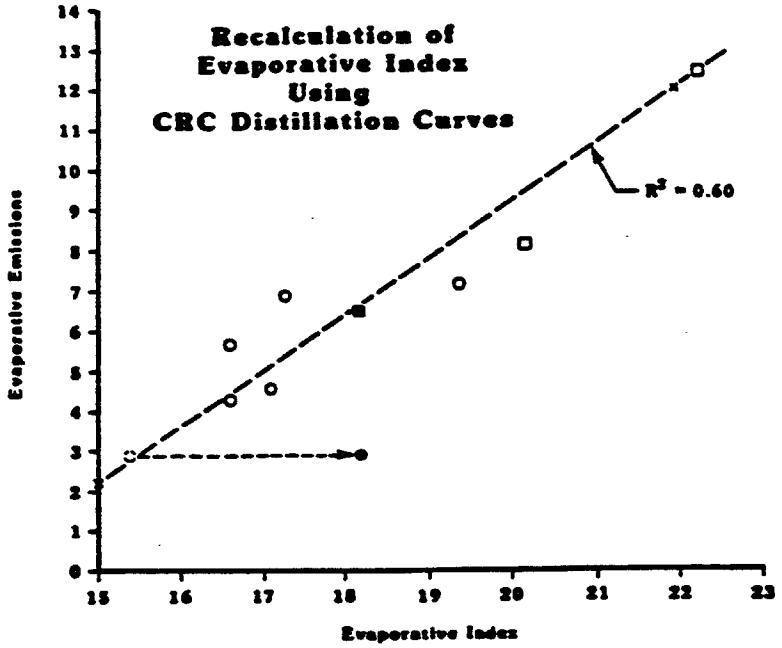


Figure 5

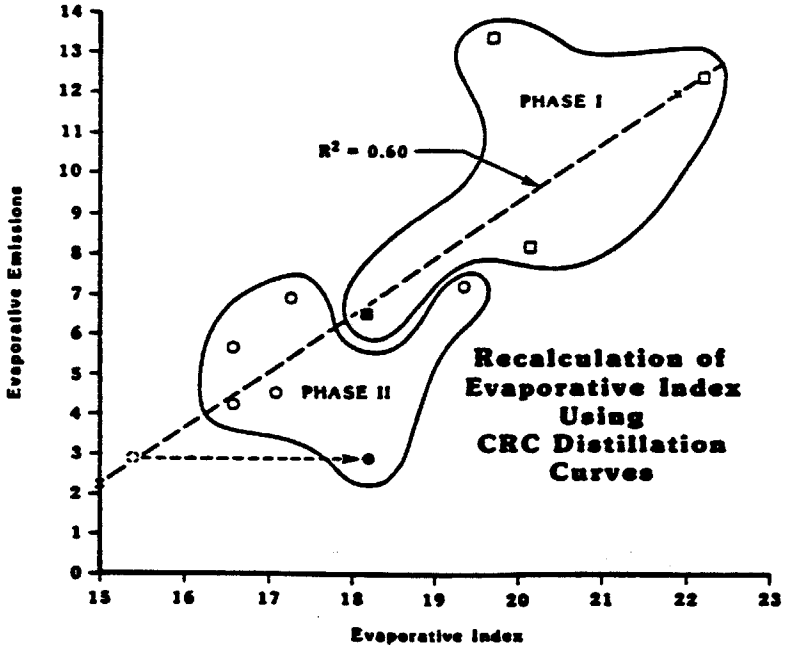
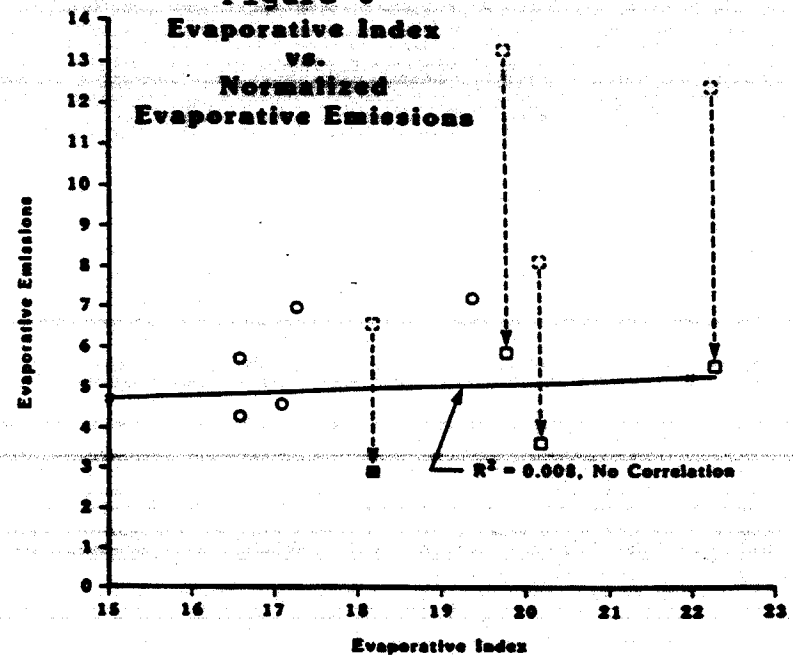


Figure 6



Oxinol Blends - A more limited data base was analyzed to evaluate the relationship between fuel volatility characteristics and evaporative emissions for gasoline blended with a 50/50 mixture of methanol and tertiary butyl alcohol ("Oxinol"). Data reported by ARCO[4] for Oxinol Blends of 3.5% oxygen content compared to straight gasolines are shown in Figures 7 and 8. At 3.5% oxygen, these blends contain slightly less than 10% total alcohol.

Figure 7

Relative Evaporative Emissions
vs.
RVP
For OXINOL and Gasoline

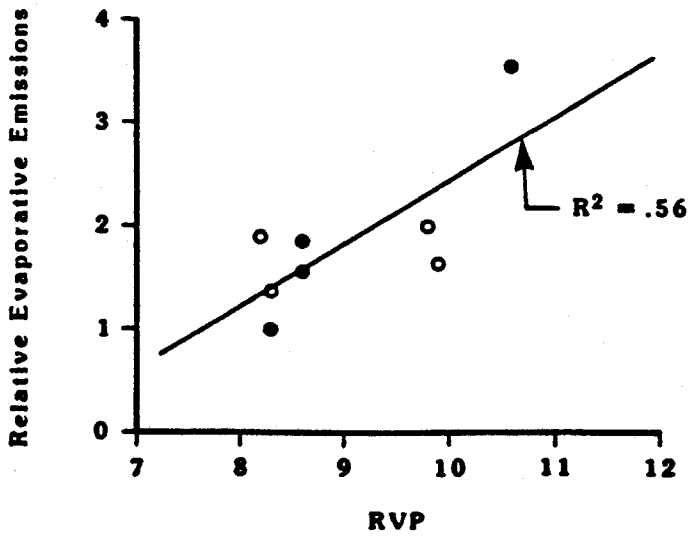
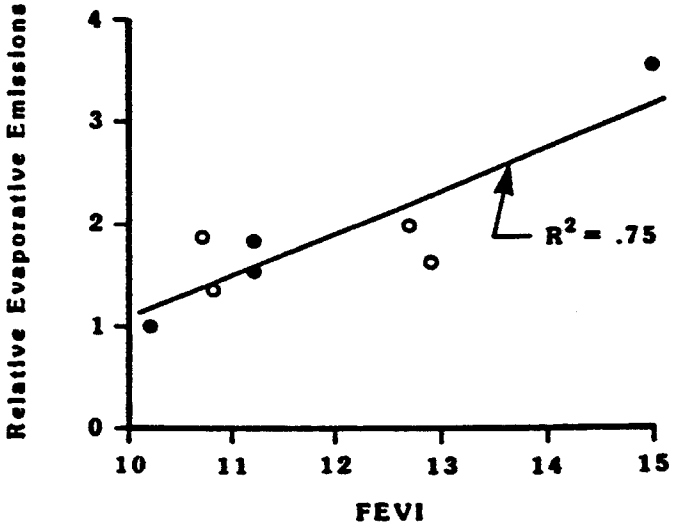


Figure 8

Relative Evaporative Emissions vs. FEVI For OXINOL and Gasoline



Data for straight gasolines are shown as solid circles and data for Oxinol blends are shown as hollow circles. As shown in the two figures, there is no clear difference between the evaporative emissions of the Oxinol blends and straight gasolines of equal RVP or FEVI. The test results are based on only four cars. The analysis of these data conflicts with the results of the CRC study. This discrepancy needs to be resolved by additional testing.

Although more data on the relationship between methanol blending, fuel volatility characteristics, and short term evaporative emissions is desirable, several points are already clear:

1. The addition of methanol to gasoline without a reduction in the amount of butane and other light hydrocarbons used in the gasoline will result in significant increases in fuel volatility.

2. Higher fuel volatility will significantly increase evaporative emissions.

3. Based on the CRC data, methanol/gasoline blends with RVP or FEVI equal to straight gasoline will have significantly higher evaporative emissions.

Effects of Intermittent Use of Blends

The above discussion suggests that some fairly restrictive type of volatility control will be required on methanol/gasoline blends to prevent increases in evaporative

emissions. However, even if the volatility of blends was controlled to a level necessary to prevent evaporative emissions from increasing after a switch from straight gasoline to a methanol/gasoline blend, "real world" evaporative emissions would increase due to intermittent usage of a methanol blend. The reason for phenomenon is related to the volatility characteristics illustrated earlier in Figure 1.

As shown in Figure 1, the boost in fuel volatility per volume percent addition of methanol is not a constant. Lower concentrations of methanol have a disproportionately greater effect on volatility than higher concentrations.

This effect is true for combinations of alcohols as well. Figure 9 illustrates data reported by ARCO[5] regarding the "Blending RVP" value of Oxinol as a function of its concentration in gasoline. This is another way of looking at the effect of alcohol addition on volatility. As shown in the figure, if a blend contains 10% Oxinol, the Oxinol will increase the RVP of the gasoline as though the Oxinol itself had an RVP of about 33. Therefore a mixture of 10% Oxinol and 90% gasoline with an RVP of 9.0 psi would result in a blend with an RVP of 11.4, a 27% increase. However, only half as much Oxinol would have a blending RVP value of about 52. A mixture of 5% Oxinol and 95% gasoline with an RVP of 9.0 psi would result in a blend with an RVP of 11.15, a 24% increase. Almost as great an increase in RVP occurs with the addition of half as much alcohol.

Because of this phenomenon, a mixture of a 9.0 RVP straight gasoline and a 9.0 RVP methanol/gasoline blend will have volatility in excess of 9.0 RVP. Such mixing will frequently occur when motorists sometimes purchase methanol gasoline blends and sometimes purchase straight gasoline.

Figure 9

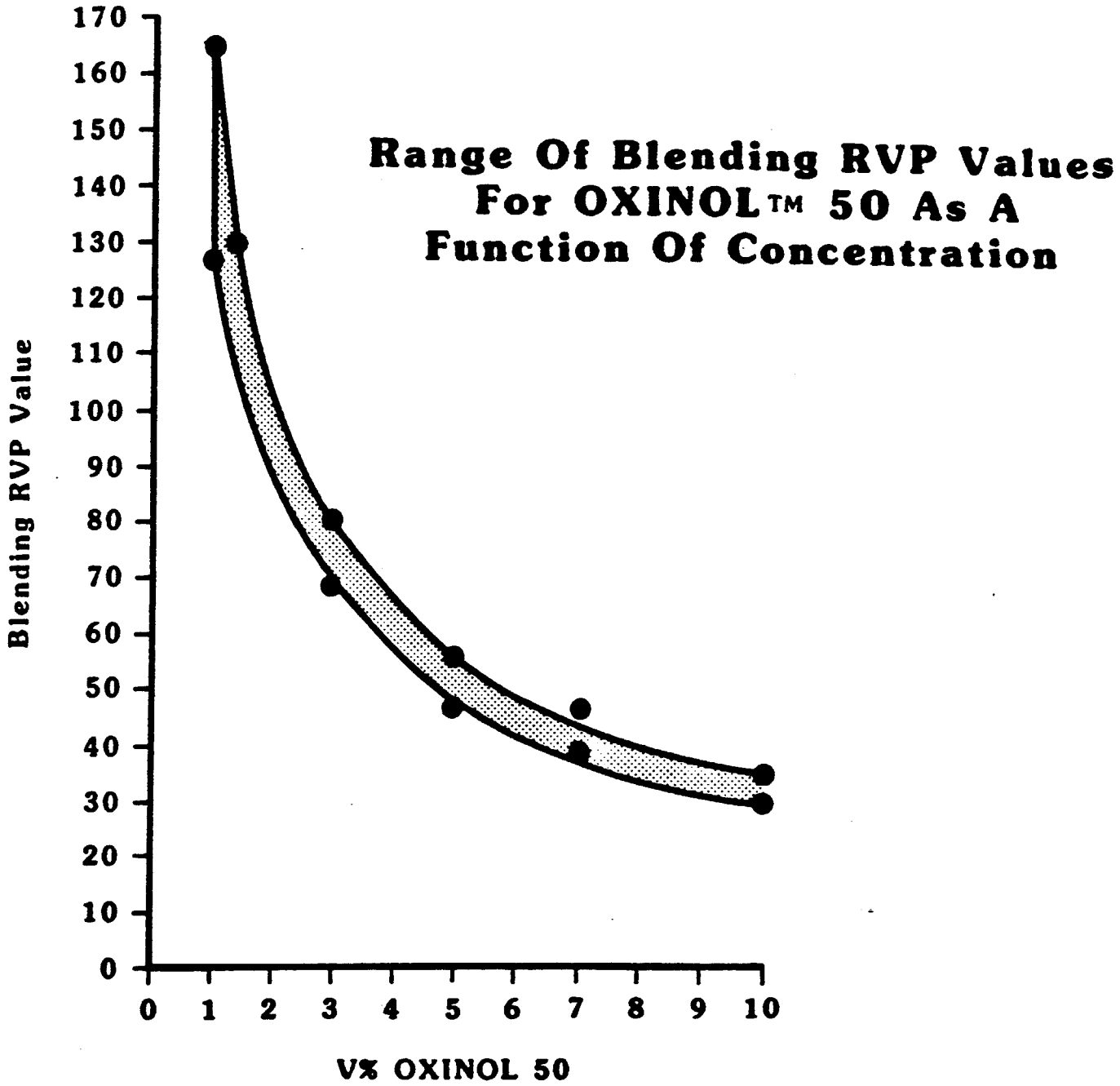

Range Of Blending RVP Values For OXINOL™ 50 As A Function Of Concentration
Blending RVP Value
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10
V% OXINOL 50

Figure 10 illustrates the effect of one possible intermittent use scenario. The calculations shown in this figure are based on the relationship between evaporative emissions and RVP shown in Figure 7 and the blending RVP values for Oxinol shown in Figure 9. It is assumed that a vehicle starts with a full tank of an Oxinol/gasoline blend that has been volatility adjusted to 9.0 psi RVP. Each time the level of the tank reaches one third capacity, it is refilled. Every third refueling is with an Oxinol/gasoline blend and the other refuelings are with straight gasoline of 9.0 psi RVP.

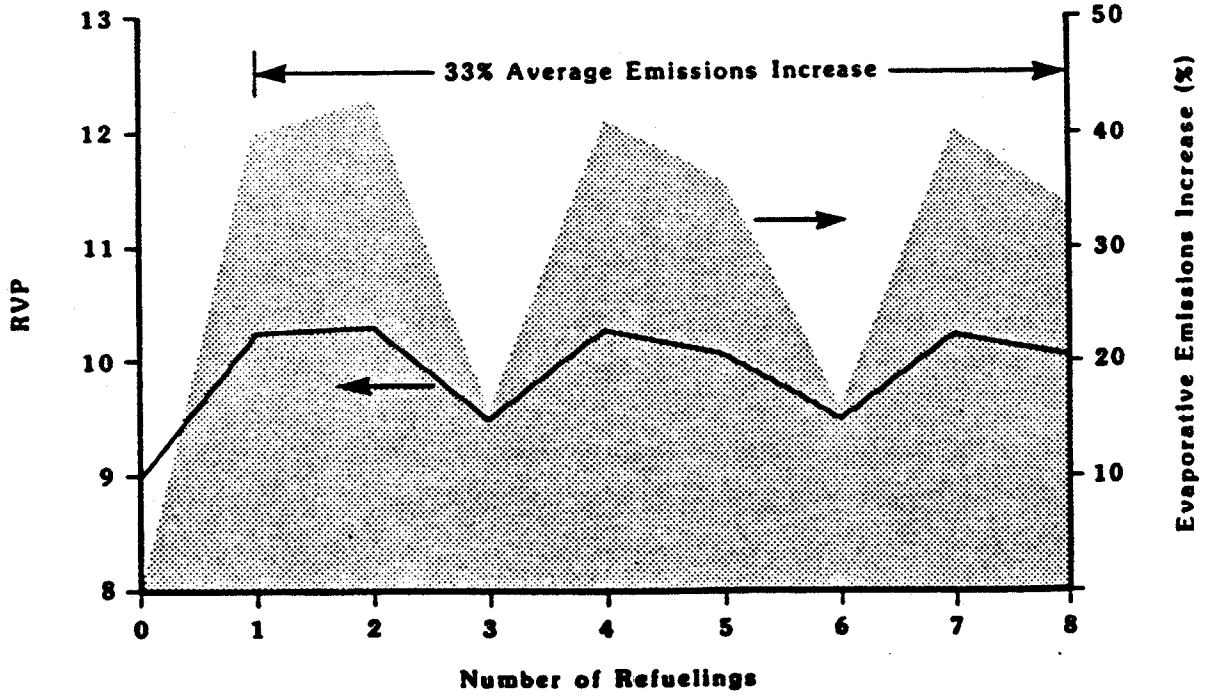
The initial tank of fuel contains 10% Oxinol with a Blending RVP value of 33. To achieve the overall blend RVP of 9.0, it must be mixed with a base gasoline which has been volatility adjusted to 6.33 RVP.

Upon the first refueling with straight gasoline, the concentration of Oxinol in the gasoline tank is reduced from 10% to 3.33%. The Blending RVP of the Oxinol rises to 70, as shown in Figure 9. The RVP of the mixture in the gasoline tank is calculated by averaging 3.33% of 70 Blending RVP Oxinol, with 30% of the 6.33 RVP gasoline the Oxinol was originally mixed with, and 66.7% of 9.0 RVP gasoline. The net result is 10.23 RVP for the entire tank, a 13.7% increase in RVP. This increase in RVP causes evaporative emissions to rise by 40%.

Figure 10

Effect of Intermittent Use of Volatility-Controlled OXINOL

(OXINOL Used Every Third Tank)



With the second refueling, RVP of the tank rises slightly to 10.30 RVP due to a further increase in the Blending RVP of the Oxinol as it is further diluted, combined with a reduction in the concentration of 6.33 RVP gasoline in the tank. Evaporative emissions are 43% above the baseline value.

When refueled with an Oxinol/gasoline blend at the third fill-up, the RVP of the tank drops to 9.49 due to the reduction in the Blending RVP of the Oxinol and the addition of more 6.33 RVP gasoline blending stock and the Oxinol. The RVP does not return to 9.0 because the presence of the tank bottoms keeps the overall Oxinol concentration below 10% and the Blending RVP of the Oxinol is still higher than its original value of 33. Evaporative emissions are 16% higher than the baseline value.

As the intermittent use of Oxinol/gasoline blends continues, the RVP of the tank follows the pattern illustrated in Figure 10. The average RVP of the tank after eight refueling cycles is 10.01, 11.2% higher than the RVP of the fuel the vehicle was using. Evaporative emissions increase by an average of 33%.

The above example illustrates a very serious problem with the use of methanol/gasoline blends which has not been adequately addressed. Intermittent use of the blends will obviously occur. The result will be that vehicle fuel tanks will contain higher volatility fuel than is being purchased by motorists. Not only will evaporative emissions be increased, vapor lock problems associated with higher volatility fuels may be encountered. To account for this situation, methanol blends may need to be formulated with a lower volatility than commercially available straight gasoline.

Effects of Blends on Evaporative Emission Control System Durability

Only limited data are available on the long term effect of methanol/gasoline blends on evaporative emissions. The effect of long term use is important because of the possible deterioration of evaporative emission control system performance that methanol exposure may cause.

Once methanol is adsorbed onto activated carbon, water vapor entering the canister with the purge air may be attracted to and adsorbed onto the methanol site. Over time more of the available adsorption sites may become occupied with methanol and water molecules which are unlikely to be stripped off and purged at temperatures and pressures that are typical of automotive evaporative emission canisters. In addition, according to some researchers,[6] the presence of methanol in the gasoline tends to put higher molecular weight HC into the vapor space than would be present with gasoline alone. When the higher molecular weight HC is adsorbed onto the

activated carbon, it is not as likely to be removed under typical purge conditions. As higher molecular weight HC compounds occupy an increasing number of adsorption sites, the adsorption capacity of the canister can be substantially reduced.

Data reported by the Department of Energy[6] indicates that the effectiveness of charcoal canisters was substantially degraded after 50,000 miles of operation on a blend of 10% methanol and 90% gasoline. Data reported for two 1977 model automobiles which used charcoal canisters for the control of diurnal evaporative emissions, is shown in Table 4.

Table 4

Diurnal Evaporative Emissions
(total organics, grams per test)

	Car A	Car B	Average
Fresh Canister	2.93	5.11	4.02
Aged Canister	11.47	12.45	11.96
Change in Emissions			+197.5%

As shown in Table 4, the effect of 50,000 miles of driving caused the average diurnal emissions of these two vehicle to increase by a factor of three. (Hot soak emissions control was not degraded because these vehicles were not subject to as stringent an evaporative emissions standard as late model cars, and hot soak losses were not vented to the canister.) Since late model cars use charcoal canisters for the control of both diurnal and hot soak emissions, this may be the level of increase that would eventually occur with late model cars using methanol/gasoline blends, even if the blends are volatility controlled to the extent necessary to eliminate evaporative emission increases in the short term.

Other high mileage test data have been reported which do not indicate the adverse effect on charcoal canister effectiveness which is shown in Table 4. However, other high mileage data are based on the use of accelerated mileage accumulation schedules. Such data are of virtually no use in evaluating the effects of methanol/gasoline blends on the long term effectiveness of the charcoal canisters and hoses which are critical to the performance of an evaporative emissions control system. In order to evaluate the "real world" effect that methanol may have on charcoal

canisters, it is necessary to use a testing procedure that will subject the canister to the same number of load/purge cycles that it will undergo in customer service.

An evaporative emissions control canister in the average passenger car would undergo well over 10,000 load/purge cycles throughout its lifetime (about 3 hot soaks per day of operation and 1 diurnal per day). However, during an accelerated 50,000 test, the canister may undergo only several hundred load/purge cycles.

More data are needed to better define the effect of methanol/gasoline blends on evaporative control system effectiveness in extended customer service. However, the currently available data indicate that there is a potentially serious problem.

Evaporative Emissions Reactivity

Data reported by the Department of Energy[6] indicate that the hydrocarbon composition of evaporative emissions with methanol/gasoline blends is different from that of straight gasoline. DOE reports an increase in the concentration of C_5 - C_7 hydrocarbons and notes that the compounds in this range have high photochemical reactivity. DOE concludes that the change in composition of the evaporative emissions could potentially increase the reactivity of the evaporative emissions.

More detailed investigation of the possible adverse effects of the change in evaporative emissions composition associated with methanol/gasoline blend use is needed.

Short Term Exhaust Emission Effects

Exhaust emission test results for one of the fuels used in the CRC study on methanol/gasoline blends are summarized in Table 5. The values contained in the table represent the average emissions of all ten vehicles included in the testing program. The trends evident in this table were also apparent in the test results of the other fuels. For the blend of 8.8% methanol with 2.7% butanol, hydrocarbons were reduced by 16.1% or 0.05 grams per mile. CO emissions were reduced by 44%. NOx emissions were about 27% higher.

Table 5

CRC Exhaust Emission Test Results
(grams/mile)

	Base Gasoline			8.8% Methanol + 2.7% Butanol		
Car	HC	CO	NOx	HC	CO	NOx
04-1	0.17	2.03	1.64	0.14	1.01	2.19
04-2	0.26	3.40	1.21	0.29	2.69	1.89
C4-1	0.35	6.96	0.76	0.25	2.86	1.18
C4-2	0.38	4.28	0.57	0.28	2.65	0.60
C6-1	0.33	6.96	0.65	0.29	4.19	0.96
06-1	0.33	5.55	1.67	0.36	4.43	1.67
04-3	0.17	3.32	0.84	0.15	1.64	1.26
04-4	0.21	2.04	1.43	0.12	0.50	1.48
C4-3	0.50	8.26	0.53	0.45	3.97	0.75
C4-4	0.35	2.91	0.70	0.26	1.67	0.72
Average	0.31	4.57	1.00	0.26	2.56	1.27
Percent Change From Base Gasoline				-16.1	-44.0	+27.0

The CO emission reduction associated with the blend is consistent with data which has been reported under many other testing programs. The oxygen content of the alcohol causes an enleanment of the air/fuel ratio which tends to reduce CO emissions.* The enleanment effect is probably also responsible for the slight reduction in hydrocarbon emissions.

For open-loop control system equipped vehicles, the effect of enleanment on NOx emissions would be expected to be a function of the calibration of each individual vehicle. NOx emissions are usually at a maximum at air/fuel ratios that are slightly leaner than stoichiometric. Enleanment would cause some vehicles to move closer to this point and others to mover farther away.

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*One of the factors related to the effect of methanol/gasoline blends on exhaust emissions is that the addition of alcohol tends to make a vehicle run with a leaner air/fuel ratio. There is sufficient oxygen to completely burn straight gasoline with 14.7 pounds of air for each pound of fuel. However, methanol requires only 6.45 pounds of air per pound of fuel because methanol contains 49.9 weight percent oxygen. Since the stoichiometric air/fuel ratio for methanol is richer than for pure gasoline, the stoichiometric air/fuel ratio of a blend of methanol and gasoline will also be richer. For example, when methanol and gasoline are mixed in a ratio of 1:9 (10% methanol), the stoichiometric air/fuel ratio is 13.9:1, 5.4% richer than pure gasoline.

Carburetors and fuel injection systems do not automatically compensate for the richer stoichiometric air/fuel ratio caused by the addition of alcohol to gasoline. Fuel metering systems generally meter a fixed volume of fuel per unit of engine air flow. However, because of the similarity in the density of gasoline and methanol, a 10% methanol/gasoline blend has only 0.6% greater density than gasoline, not a sufficient density increase to offset the 5.4% change in stoichiometric air fuel ratio caused by the addition of 10% methanol. The net effect is that an engine will run 4.8% leaner on a 10% methanol/gasoline blend. Use of a methanol/gasoline blend instead of gasoline therefore has an effect which is similar to readjusting the air/fuel ratio of an engine to a somewhat leaner setting.

For closed-loop controlled vehicles, one might expect the effect of alcohol addition to cause insignificant changes in NOx emissions. NOx emissions are fairly low while the vehicle is warming up in the open-loop mode, and once the vehicle is in the closed-loop mode it would be expected that the feedback controlled fuel metering system would overcome the enleanment effect of methanol addition. However, the CRC data indicate a significant NOx emission increase. Department of Energy tests also indicate a 47.9% increase in NOx emissions was associated with the use of a 10% methanol/gasoline blend in three 1978 model vehicles equipped with 3-way catalysts.[8] (The vehicles also demonstrated a 4.7% reduction in HC emissions and a 28.3% reduction in CO emissions.)

The increased NOx emissions associated with the use of methanol/gasoline blends in 3-way catalyst vehicles seems to indicate that the feedback control systems of these vehicles are not keeping the air/fuel ratio at stoichiometric conditions as well. Tests conducted by General Motors[9] have shown that 3-way catalyst NOx conversion efficiency is degraded with the addition of alcohol to gasoline even though the average air fuel ratio remains at stoichiometric. Oxygen sensor response characteristics may be altered in some way which degrades catalytic activity. It is also conceivable that the presence of methanol in the gasoline is causing a change in exhaust gas composition which affects the activity of the catalyst. Whatever the reason, the available data indicate that the addition of methanol to gasoline increases NOx emissions.

It should also be noted that the reduction in hydrocarbon exhaust emissions measured with the methanol/gasoline blend are insufficient to offset the increase in evaporative emissions. Evaporative emission increases are estimated at 0.37 grams per mile even for vehicles certified under the 2 grams per test SHED standard. This outweighs the .05 gram per mile reduction in exhaust hydrocarbons by more than a factor of seven.

Long Term Exhaust Emissions Effects

A serious concern regarding the long term effects of the use of methanol/gasoline blends involves the potential increase in exhaust emissions associated with tampering. Tampering may occur as a result of attempts to correct driveability problems associated with the enleanment effect caused by the use of oxygen containing fuels. Figure 11 illustrates the driveability problems that were observed during the CRC methanol blend testing program. As shown in the figure, driveability demerits were significantly increased as the oxygen content of the fuel was increased by the addition of methanol.

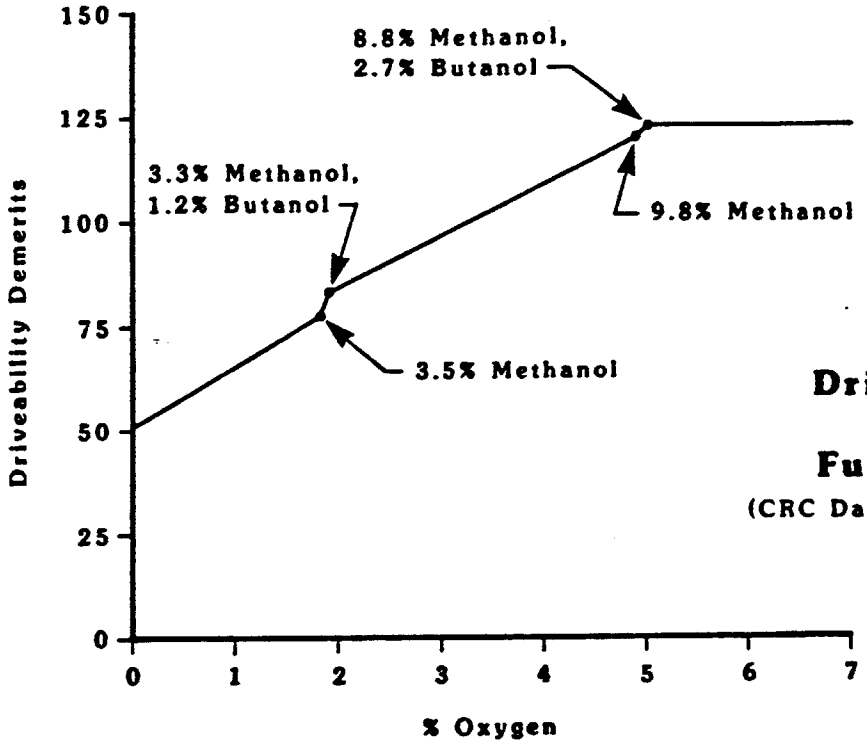


Figure 11
Driveability Demerits vs. Fuel Oxygen Content
(CRC Data for Methanol/Gasoline Blends)

Limited test results have shown the effect on exhaust emissions of readjusting vehicles to offset the degradation in driveability caused by a switch to alcohol-gasoline blends.[10] Three different 1978 model passenger cars equipped with 1.6, 3.3, and 5.0 litre engines were adjusted to optimize driveability after their driveability had been adversely affected by a switch to a 15% methanol-gasoline blend.

Adjustments made to the vehicles included:

1. Spark timing advanced 4°
2. Idle speed increased 50 RPM
3. Idle mixture enrichened for best idle quality
4. Part throttle idle mixture adjusted on two of the three cars to optimize driveability

After these modifications had been completed, two of the cars had driveability ratings that were almost identical to what they had on straight gasoline. The third car had improved driveability compared to the use of the alcohol/gasoline blend without adjustments; however the vehicle was still experiencing a 50% increase in driveability problems compared to gasoline. The driveability tests that were run indicate that the adjustments made to compensate for the use of the alcohol/gasoline blend were not greater than required to restore the original level of driveability performance.

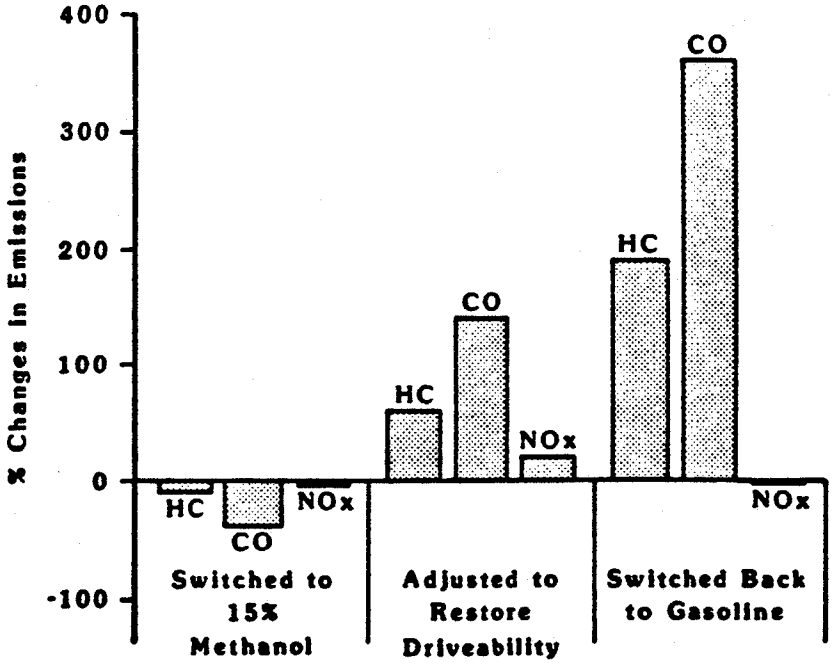
Figure 12 shows the effect of the adjustments made to restore driveability on the exhaust emission changes caused by the switch to the alcohol/gasoline blend. As would be expected the switch to the alcohol/gasoline blend initially reduced CO emissions. The 39.3% reduction shown in the figure is reasonably consistent with the information shown earlier for blends with somewhat lower methanol content. When the vehicles were adjusted to restore their driveability on the alcohol blend, the CO emissions were 138.3% higher than when they were running on gasoline in their baseline condition. HC emissions were also 59.3% higher following the readjustment.

The reason that the CO emission levels in the adjusted configuration were higher than the gasoline baseline is probably associated with the inability to restore adequate acceleration enrichment with the adjustments that were made. Because it was not practical to increase the accelerator pump shot, the basic air/fuel ratio of the carburetors had to be adjusted rich enough to compensate for the driveability problems caused by this lack of adequate acceleration enrichment.

After the vehicles were modified to restore their driveability on the methanol/gasoline blend, they were switched back to gasoline to determine what the effects would be on emissions and driveability. Driveability was determined to be superior to the baseline condition because of the mixture enrichment.

Figure 12

Effect of Tampering on Exhaust Emissions



NOx emissions were 1.3% less than in the baseline configuration; however, the increases in hydrocarbon and CO emissions were enormous. HC had increased to 189% above the baseline and CO had increased by 360%.

These results make it clear that the initial carbon monoxide emission reductions that can be demonstrated for a switch to methanol/gasoline blends may be of academic interest only. The increase in CO emissions that occurs if vehicles are readjusted to restore driveability can be much larger than the initial reduction, and thus driveability must be considered an environmental factor when evaluating the effect of methanol/gasoline blend usage on emissions.

Impact on Emissions

The emission increases identified for each area of concern are based on different vehicles and studies, and may not be cumulative, therefore it is not possible to estimate an overall emission increase associated with methanol/gasoline blend usage. However, a relative sense of the magnitude of the impact may be gained from an examination of the individual impacts.

Table 6

Area of Concern: HC	Possible Impact, gpm
Evap. increase: volatility	0.37
Evap. increase: intermittent use	0.08
Evap. increase: cannister degrades	0.47
Evap. increase: reactivity	?
Exhaust decrease	-0.05
Exhaust increase: tampered	up to .77

In comparison, the average in-use HC exhaust emission rate for a 1984 California model is 0.29 gpm when it is new, and 1.14 gpm at its half life. The average emission level of the California fleet is about 1.7 gpm, and California's biennial I/M program will reduce this by 0.4 gpm HC. Thus, it appears possible that the use of methanol blends could significantly increase overall fleet HC emissions, and has the potential to negate the benefits of the state's new vehicle inspection program.

Conclusions

1. Based on an analysis of the Coordinating Research Council (CRC) testing, use of methanol/gasoline blends will result in a significant increase in evaporative emissions even if fuel volatility, measured by RVP, FEVI, or EI, is controlled to the same volatility as straight gasoline.

2. Based on data presented by ARCO, FEVI may provide a volatility control for evaporative emission increases associated with use of certain blends of 50% methanol/50% tertiary butanol in gasoline. More test data are needed to resolve this apparent inconsistency with the results of the CRC study.

3. The fuel mixture resulting from the intermittent use of blends and straight gasoline will cause evaporative emission increases. This will occur even if the blend is volatility controlled such that use of the blend alone does not increase emissions compared to use of the straight gasoline alone.

4. Use of methanol/gasoline blends may cause long term deterioration of the vehicle evaporative control system. More study using real life evaporative collection/purge conditions is needed to quantify this possible effect.

5. Evaporative emissions resulting from use of methanol/gasoline blends may be more conducive to smog formation. More research into this possible effect is needed.

6. Use of methanol/gasoline blends will increase NOx exhaust emissions. Decreases in HC and CO exhaust emissions may occur, however, the decrease in HC exhaust emissions is much smaller than the increase in evaporative emissions.

7. The lower HC and CO exhaust emissions associated with methanol/gasoline blend usage may become large emission increases if owners readjust and tamper with their vehicles in order to correct poorer driveability that occurs with use of some blends.

8. Additional research is needed to better quantify the air quality impact of use of methanol/gasoline blends. Based on the available data, use of blends will most likely cause an increase in emissions of HC and NOx, and thus an increase in photochemical smog.

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