

SYMPOSIUM ON OXYGENATES AS FUEL ADDITIVES
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FUTURE FUEL DIVERSIFICATION WITH OXYGENATES

William J. Piel
ARCO Chemical Company
3801 West Chester Pike
Newtown Square, Pa 19073

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INTRODUCTION

Fuel oxygenate blending in motor fuels first became commercialized in 1969 with the blending of t-butyl alcohol in gasoline. This first fuel alcohol was made by adding oxygen to isobutanes. Now most of this alcohol production is converted to isobutylene for methyl tertiary butyl ether (MTBE) production. MTBE blending was first commercialized in the U.S. in 1979 when the U.S. EPA granted a section 211F waiver request to blend it into unleaded gasoline. MTBE use grew during the 1980's as a high octane replacement for lead compounds in gasoline. Similarly, 10% ethanol blending was approved in 1978. With a government tax incentive for alcohols made from renewable sources, ethanol's use also grew as a non-petroleum gasoline extender in the mid-1980's.

Relative to mobile source emissions, the 1990 revision to the Clean Air Act (CAA) requires reductions of carbon monoxide (CO), volatile organic compounds (VOCs), and toxics from gasoline fueled vehicles. Reductions in nitrogen oxides (NOx) and greenhouse gases (such as carbon dioxide - CO₂) were not required. The strategy in the CAA to decrease ground level ozone is by reducing VOC mass emissions by 15% in 1995 and 25% in 2000. The other attributing compound to ozone, NOx emissions, are only capped at the 1990 levels in the CAA. Based on the predictive models developed by the U.S. EPA and by the California Air Resource Board (CARB), it appears that the fuel reformulation will be able to achieve the year 2000 performance requirements targeted in the CAA.

Fuel oxygenates played a key role in both the Oxygenated Fuels and Reformulated Fuels outlined in the CAA. The next wave of environmental interest is to possibly modify motor fuels and/or motor vehicles for reductions in NOx emissions and greenhouse gases such as CO₂. Fuel oxygenates can also play a significant role in such fuel modifications. To achieve the maximum emissions reduction potential, minor engine modifications may be required to take full advantage of the possible fuel property improvements.

FUEL OXYGENATES

Though MTBE and ethanol are the most commonly used oxygenates, there are many other potential fuel oxygenates that are being developed or investigated such as TAME (tertiary amyl methyl ether) and ETBE (ethyl tertiary butyl ethers)(Ref 1). The properties of these oxygenates and others are listed in Table 1. The most useful property of the oxygenates is their high octane. Outside of metal compounds, oxygenates are generally the only high octane alternative to aromatics in gasoline. The potential octane contribution of oxygenates are shown in Figure 1 as a function of the their oxygen contribution in gasoline.

While mixtures of alcohols are allowed up to 3.7 weight percent oxygen in gasoline under various EPA approved waivers, ethers are currently limited to 2.7 weight percent oxygen in gasoline. Under these limits, ethers can potentially add 3 to 4 octane numbers to the gasoline pool. If the oxygen limit for mixed ethers were raised to 3.7 percent, ethers could contribute 4 to 5 octane numbers, and up to 20+ volume percent to gasoline. Their potentially large octane and volume contribution can play a significant role in replacing most of the aromatics in gasoline, and modifying future gasoline formulations for reductions in NOx and CO₂ emissions as will be discussed later.

Besides their octane, a major advantage of ethers over aromatics is their relatively lower boiling temperatures. Since lead phasedown in gasoline, the increased use of aromatics in premium gasolines have lead to poor mid-range volatility and a degradation of cold engine driveability and performance(Ref 2). The automakers have been making an effort to limit this performance degradation by proposing a cap on a Driveability Index (DI) that is calculated from distillation temperatures of gasoline. Using their individual boiling temperatures, then DI differences between ethers and aromatics are illustrated in Figure 2. Though both provide octanes higher than a 100 (r+M)/2, the DI of most ethers are favorably lower while the high boiling temperatures of the aromatics contributed to higher DI for gasoline, particularly premium gasolines. The DI benefits of using ethers for octane is best illustrated by comparing the DI changes between the 1992 and 1993 winter DI averages for the oxygenated and non-oxygenated cities in the AAMA (American Automobile Manufacturers Association) gasoline surveys.

<u>Gasoline Grade</u>	<u>DRIVEABILITY INDEX</u>		<u>DI</u>
	<u>1992</u>	<u>1993</u>	<u>CHANGE</u>
Regular - Oxygenated	1112	1061	-53
Non-oxygenated	1071	1092	+21
Premium - Oxygenated	1154	1087	-67
Non-oxygenated	1153	1147	- 6

Though the non-oxygenated cities showed very little change in DI, the oxygenated cities (with predominately MTBE) showed very favorable decreases greater than 50 DI. Therefore, the use of ethers appears to provide an effective means for improving the mid-range volatility of the gasolines which should also benefit the 1990 CAA Reformulated Gasoline program.

EXHAUST NOx EMISSIONS

The work completed by AUTO/OIL established sulfur in gasoline as a major influence on tailpipe NOx because of its effect on the activity or efficiency of the catalytic converters(Ref 3). However, the other fuel variables that effect NOx emissions were not quite as clear(Ref 4-5). Since NOx is a side reaction of combining oxygen and nitrogen during the combustion process, NOx in engine exhaust is expected to be a function of the peak temperatures during combustion. The dilemma is what fuel property changes have the most influence on the peak combustion temperatures. Earlier research by others had found the flame temperature and resulting NOx emissions of fuels to be most easily correlated with the hydrogen to carbon ratio (H/C) of the fuel (Ref 6-8) where high H/C has a lower flame temperature and therefore lower NOx thermal equilibriums.

This relationship can also be seen in some more recent work conducted with ARCO Chemical Europe in conjunction with BP Oil, and Volvo. ECE emission test were conducted with 11 different fuels of varying composition but relatively similar octanes in two 1991 non-cat cars with VOLVO engines (B-230 2.3 litres, 4 cylinders). The relative change in the NOx emissions compared to each fuel's hydrogen to fuel ratio in this study is shown in Figure 3. Also, three of the fuels contained oxygen, one from ethanol and two from MTBE. The data in Figure 3 suggest that the NOx emissions are strongly related to the fuels' hydrogen to carbon ratio independent of oxygen content in the fuel. This correlation to H/C ratio is consistent with the results reported in previously referenced studies.

However, in addition to the flame temperature of the fuel, the ultimate combustion temperature would also be expected to be a function of the octane of the fuel. Octane is a good indicator of the fuel's resistance to autoignite under the more severe operating conditions in the engine. Low octane fuel may autoignite early prior to optimum timing under severe engine conditions and thereby increase peak pressures and temperatures. Therefore, higher octane fuels would be expected to suppress autoignition and generate lower peak temperatures and lower NOx under severe engine operating conditions. The possible sensitivity of NOx to octane, particularly motor octane, of the fuel has been observed in some previous studies(Ref 9-10).

To test this theory that NOx production may be influenced by octane number independent of fuel composition, the octane of a reference fuel was artificially lowered by adding minute amounts of tertiary butyl hydro peroxide (TBHP), a very powerful pro-knock compound. FTP emission tests were conducted on two cars (1991 Dodge Spirit 2.5 liter/TBI and 1990 Ford Probe 2.2 liter/PFI) using the reference fuel (indolene) and the same fuel with two levels of peroxide. The average results for the two cars is as follows:

<u>TBHP</u> <u>(ppm)</u>	<u>Fuel Octane</u>		<u>% NOx</u> <u>Changes</u>
	<u>MON</u>	<u>(R+M)/2</u>	
0	88.7	93.0	Base
420	87.2	91.4	+ 15%
1100	86.5	90.5	+ 14%

These results support the theory that octane number, independent of fuel composition, can also effect NOx emissions in the engine exhaust. Evidence of this octane effect has also been seen in Ethyl Corporation's work with MMT (methylcyclopentadienyl manganese tricarbonyl), a metal based octane additive. In the emission work to support a MMT waiver request, fuels containing 0.03125 grams of MMT per gallon increased the fuel's octane by approximately 0.8 octane numbers, but more importantly decreased NOx emissions(Ref 11).

A review of the emission results for AUTO/OIL's older car fleet shows similar fuel effects on the NOx emissions. Figure 4A shows the average NOx emissions relative to the fuels' H/C ratio. The AUTO/OIL's fuel matrix essentially falls into two groups: low H/C fuels and high H/C fuels. The NOx emissions from the high H/C fuels are approximately 12% lower than that from the low H/C fuels. The data also shows no oxygen effects since the emissions for the oxygenated fuels appear to be evenly dispersed among the non-oxygenated fuels. As Figure 4A shows, there also is more variance in the low H/C fuel group than the high H/C group. Much of this variance seems to be explained by the motor octane which varies as much as 5 octanes for the low H/C fuels as shown in Figure 4B. Though motor octane seems to explain some of the variance in the high H/C fuels as well, it is not as clear since the range of motor octane is only 2.5 numbers for this group.

The review of these studies suggest that much of the fuel effects on NOx emissions from gasoline vehicles can be explained by three main factors: the H/C ratio and the motor octane of the fuel as it effects peak combustion temperatures, and the fuel's sulfur content for its effect on the catalyst activity in the catalytic convertor. One other fuel quality for investigation is the ability of the fuel to warm-up the engine quicker (with higher DI), and thereby increase total NOx over an emissions test cycle. However, this might offset by the catalytic convertor also warming up quicker.

CARBON DIOXIDES EMISSIONS

Carbon dioxide (CO₂) from fuel combustion is considered to be a major source of greenhouse gases, and the current administration is dedicated to capping the year 2000 greenhouse gases at the same level as 1990. Though the stationary power sources may have the flexibility to switch from high fossil carbon fuels such as coal or heavy oils to low fossil carbon fuels such as natural gas or biomass fuels as a way to reduce CO₂, transportation fuels are not quite as flexibility. However, the CO₂ emissions associated with gasoline energy content is still related to the H/C ratio of the fuel components as shown in Figure 5. Aromatics represent the highest carbon content fuels and therefore the gasoline components with the highest CO₂ per unit of energy. Ethers, like paraffins, are gasoline components with the lowest CO₂ per unit of energy. Therefore, using ethers in place of aromatics for octane in gasoline may be an effective way to reduce fossil carbon dioxide emissions from gasoline by 4 to 5 percent. This CO₂ relationship to fuel H/C is consistent with the analysis reported by the AUTO/OIL analysis (Ref 12).

Raising the octane of gasoline presents another opportunity to significantly reduce CO₂ emissions from transportation fuels by allowing the automakers to raise the compression ratios of the engines of their new car models. Increasing the compression ratio would reduce fuel consumption by increasing the thermal efficiency of the engine's operation. The optimum octane for gasoline was last debated in industry about two decades ago when unleaded gasoline was about to be widely distributed in the marketplace (Ref 13-21). The conclusion from most of these studies was that the optimum octane for unleaded gasoline was around 91 to 92 (R+M)/2 octane even though the industry went with 87 (R+M)/2 as the standard octane for gasoline. The economic basis used in these studies was generally limited to comparing the cost of fuel savings versus the cost of raising the octane of gasoline. The environmental benefit of reducing CO₂ emissions was not considered in these studies at the time. If it had been included, it would have further supported the higher octane fuel / higher compression engine combination.

Figure 6 shows typical relationships to engine compression ratio which is derived from one of these studies (Ref 15). In the range of interest, Figure 6 shows that increasing the compression ratio by two numbers would increase fuel efficiency by approximately 10 percent but would also increase engine's octane requirement by approximately 6 octane numbers. This study suggest that each octane is potentially worth 1.8 % increase in fuel efficiency or fuel economy. This ratio between efficiency and octane seems to be approximately the same in most of these studies.

Some of these studies also attempted to address the issue on whether there was any increase in other emissions such as NOx or hydrocarbons(Ref 18-21). Their results suggested that there was little change in these emissions after re-optimizing other engine operating parameters such as timing and air to fuel mixtures. However, these studies did not evaluate any possible emission reduction benefits associated with also raising the fuel's octane for the higher compression ratio operation.

What these prior studies did not review in their analysis is any possible loss in driveability performance associated with higher fuel octane, particularly if high boiling aromatics should be the main source of the octane increases. As mentioned earlier, this is now a major concern of the automakers. Therefore, the source of increased octane would likely have to be from ethers which can potentially add five octane numbers to the gasoline pool with out worsening the driveability index of the gasoline.

Another benefit of using ethers instead of aromatics for octane is their greater increase in combustion gas volumes. Higher H/C ratio fuels generate more moles or volumes of product gases per volume of combustion air that is consumed or drawn into the engine's cylinders. This higher volume of combustion gases increases combustion pressures even further for an added boost in engine efficiency and power. This comparison between ethers and aromatics is illustrated in Figure 7. In general, the ethers provide about 4 to 5 percent more gas volume than the aromatics during combustion.

Therefore, using oxygenates to further increase gasoline octane can potentially help reduce fossil based CO₂ emissions in two ways: one by reducing the carbon to energy ratio of the fuel, and second to allow the automakers to increase the fuel economy of cars by raising the engine compression ratio. Also, if oxygenates become a significant proportion of gasoline, it opens up an avenue to use more renewable carbon in gasoline since the alcohols in oxygenates can be made from renewable resources (Ref 22). This can further reduce the fossil based CO₂ emissions from transportation fuels.

SUMMARY

A review of the available data suggest there is still potential to reduce NOx emissions and the fossil fuel based CO2 emissions from mobile sources. Based on the review presented here, both of these emission reductions can be accomplished by increasing the hydrogen / carbon ratio of gasoline and also raising its octane number, particularly the motor octane. This would have been difficult to accomplish if the high carbon content aromatics were the only source of high octanes for gasoline blending. However, with the development of oxygenates as an octane enhancer, particularly ethers, both of these changes in gasoline can be done simultaneously and are technically feasible. Based on the reviews of past studies, both these changes in the fuel are probably economically and environmentally justifiable. Therefore, fuel oxygenates are not only capable of adding oxygen to gasoline to improve combustion, but they are also tools for increasing fuel H/C ratios as well as adding more octane for potentially better engine efficiencies in the future.

ABBREVIATIONS

DI	- Driveability Index (1.5xT10 + 3.0xT50 + T90) degrees fahrenheit
ETBE	- Ethyl tertiary butyl ether
IPTBE	- Isopropyl butyl ether
MTBE	- Methyl tertiary butyl ether
NOx	- Nitrogen oxide compounds
MON	- Motor octane number
RON	- Research octane number
(R+M)/2	Average of RON and MON
H/C	- Hydrogen to carbon atomic ratio
CO2	- Carbon dioxide

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TABLE 1**TYPICAL PROPERTIES OF FUEL ALCOHOLS IN GASOLINE :**

	Methanol & Co- Solvent	(1) Ethanol	Iso- Propanol	tert- Butanol	Iso- Butanol	tert- Amyl Alcohol
OCTANES:						
Blending (R&M)/2	108+	115	106	100	102	97
VAPOR PRESSURE:						
Neat RVP (100F)	4.6	2.3	1.8	1.7	0.6	0.7
Blending RVP (2)	31+	18	14	9	5	6
BOILING PT. (F)	148	173	180	181	226	216
DENSITY (LB/GAL)	6.63	6.61	6.57	6.59	6.71	6.79
ENERGY DENSITY:						
MBTU/Gal (LHV)	56.8	76.0	87.4	94.1	95.1	100.1
HEAT OF VAPOR.:						
MBTU/Gal @ NBP	3.14	2.39	1.90	1.55	1.67	1.58
OXYGEN CONTENT (WT.%)	50	34.8	26.7	21.6	21.6	18.2
SOLUBILITY IN WATER: (WT.%)	I	I	I	I	10.0	11.5

TYPICAL PROPERTIES OF FUEL ETHERS IN GASOLINE :

	<u>MTBE</u>	<u>ETBE</u>	<u>DIPE</u>	<u>TAME</u>	<u>IPTBE</u>	<u>TAE6</u>
OCTANES:						
Blending (R&M)/2	110	112	105	105	113	100
VAPOR PRESSURE:						
Neat RVP (100F)	7.8	4.0	4.9	2.5	2.5	1.2
Blending RVP	8	4	5	2.5	2.5	1
BOILING PT. (F)	131	161	155	187	188	214
DENSITY (LB/GAL)	6.19	6.20	6.1	6.41	6.30	6.39
ENERGY DENSITY:						
MBTU/Gal (LHV)	93.5	96.9	100	100.6	NA	NA
HEAT OF VAPOR.:						
MBTU/Gal @ NBP	0.86	0.83	0.9	0.90	NA	NA
OXYGEN CONTENT (WT.%)	18.2	15.7	15.7	15.7	13.8	13.8
SOLUBILITY IN WATER: (WT.%)	4.3	2.6	2.0	2.0	NA	NA

I - Infinite Solubility
 NA - Not Available

- (1) Typical for methanol waivered blends with cosolvents
 (2) Blending RVP for 2.7% oxygen or higher in gasoline

FIGURE 1

Potential Octane Contribution of Oxygenates in Gasoline

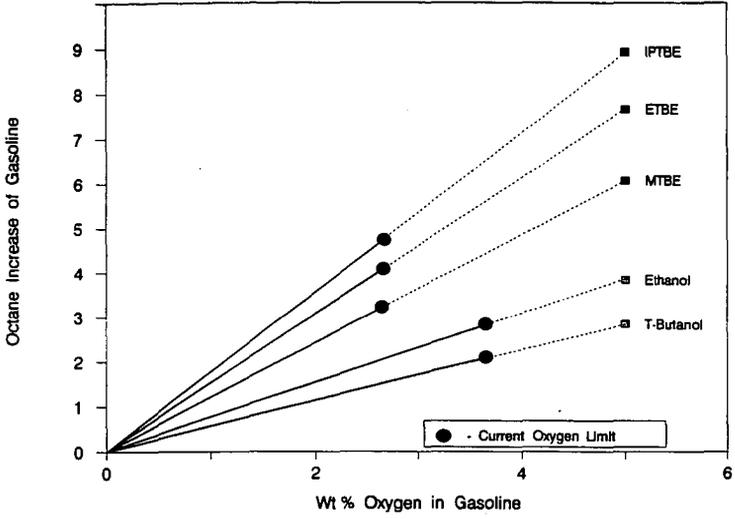


FIGURE 2

Driveability Index (DI) vs. Octane for High Octane Blending Components

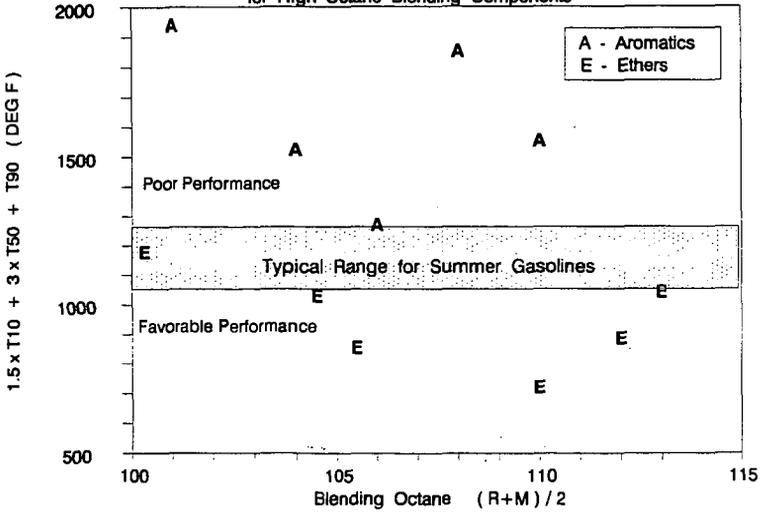


FIGURE 3

NOx Emissions Strongly Related To Fuel H/C Ratio

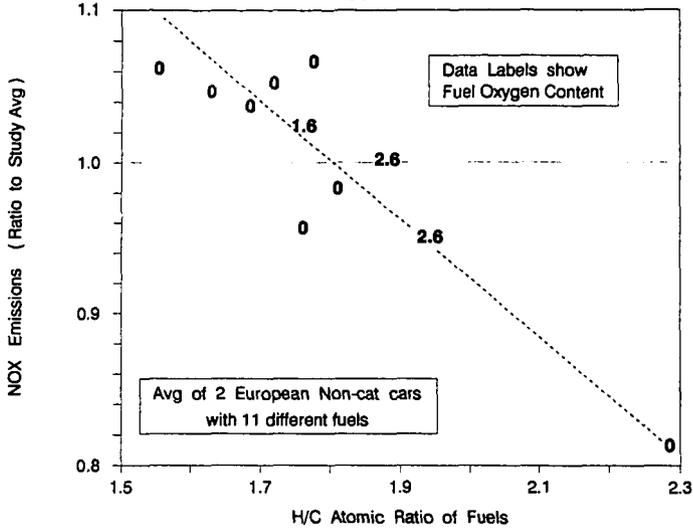


FIGURE 4A

NOx Emissions vs H/C Ratio of Fuel

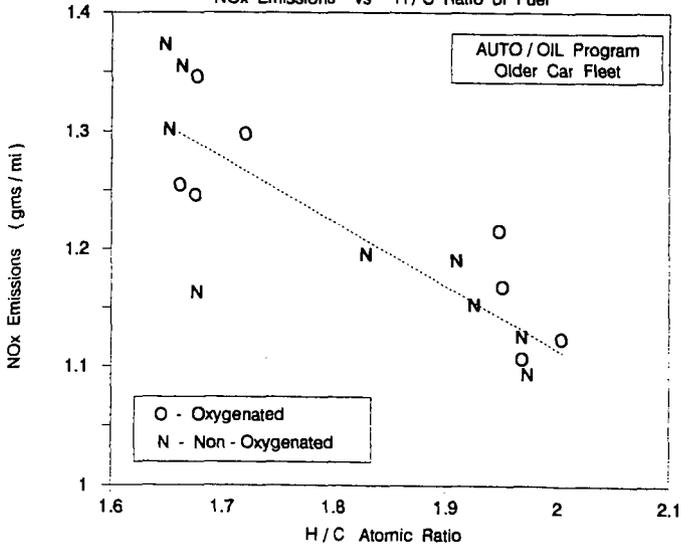


FIGURE 4B

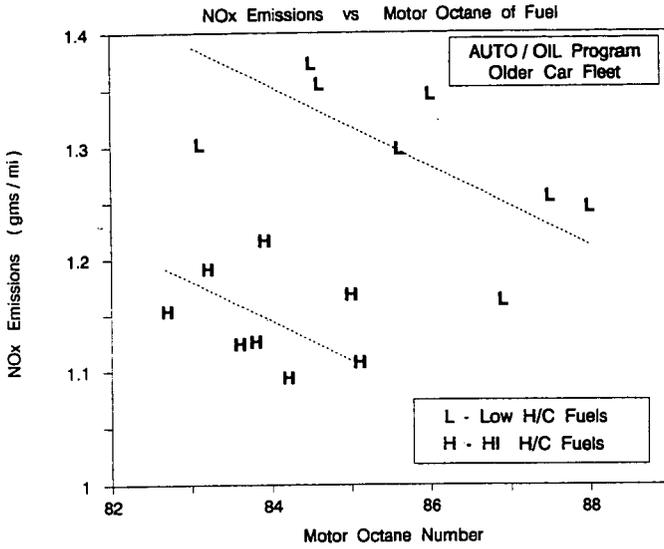


FIGURE 5

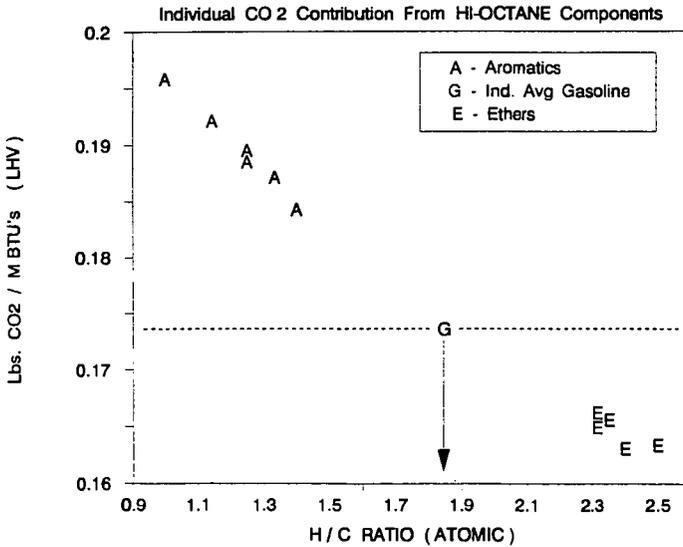


FIGURE 6

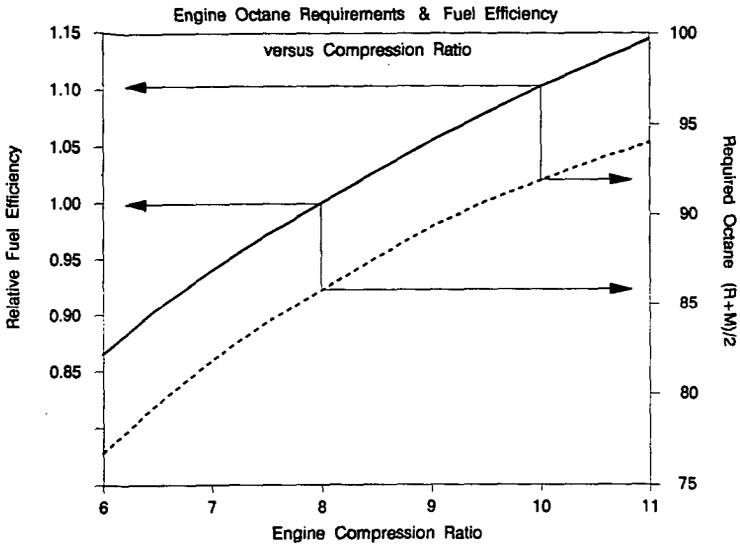


FIGURE 7

