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Oxygenates -- A Fuel Scientist's View

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In 1938, the American Petroleum Institute (API) published a summary of the technical characteristics of alcohol-gasoline blends, primarily ethanol blends. In this publication, it was concluded that

> *"alcohol-gasoline mixtures are not superior motor fuels for ordinary use. They are in most respects somewhat inferior to straight gasoline. Considered objectively, on the basis of their actual merit, they are certainly not worth a higher price than would be paid for gasoline of comparable octane rating, although their cost must be higher."*[1]

However, over fifty years later, the use of alcohol or alcohol derivatives in gasoline has been increasing steadily. Have the technical problems simply disappeared? No. Today, as in 1938, driveability degradation and lower fuel economy may still be problems with alcohol or alcohol-derived ether blends. And in the past several years, additional problems have been identified. So what is the attraction to use oxygenates in gasoline?

One factor is the Environmental Protection Agency's mandated phasedown of lead in leaded gasoline. Lead compounds have been used for over sixty years to improve the octane quality of gasoline. Octane quality, for those who are not familiar with the term, is a measure of a fuel's resistance to knock in an engine. Automobile engines have a certain octane requirement, and using a gasoline with an octane quality below this octane level will cause knocking, pinging, and possibly engine damage.

(Figure 1) Addition of a very small amount of lead additive gives a large increase in octane quality of gasoline, compared to other octane improving additives. However, beginning in the 1975 model year, vehicles were designed to run only on unleaded gasoline. (Figure 2) And in 1985 the EPA began to phase down the amount of lead allowed in leaded gasoline to the current 0.1 grams of lead per gallon (quarterly average).[2] This amounted to a 91 % reduction from early 1985 to 1986. All leaded motor gasoline will eventually be phased out under the Clean Air Act amendments that have been passed by Congress.

This loss of lead as an octane improver can be made up in different ways. (Figure 3) One is by refinery processing. This includes addition of octane-improving processes such as isomerization or alkylation, or increasing reformer severity. However, these options are expensive, require a lot of lead time, or result in lower yields. High octane hydrocarbons, such as toluene or xylene, can be used to increase octane, but these stocks are typically expensive, as they have alternate use in the chemicals market. A third alternative is the use of oxygenated high-octane blending agents such as alcohols or ethers.

(Figure 4) These are some of the oxygenates currently allowed in unleaded gasoline. Gasohol, or 10% ethanol, has been used for several years, especially in farm belt states. Oxinol-50 had been used commercially by ARCO in the East, but is not currently economically attractive. The DuPont and Texas Methanol waiver fuels, to my knowledge, have not yet seen significant commercial use. MTBE is an ether which is made from methanol and isobutylene. It can be used in unleaded gasoline at a maximum of 15 volume percent.[3] Of all the oxygenates mentioned, its use has grown the most in the past decade. Ethers like ETBE or TAME may also be used in gasoline, up to about 12.7 vol. %, under EPA's "substantially similar" definition, which allows up to 2 wt. % oxygen in the fuel.[4] (One organization has petitioned EPA to allow higher levels-- up to 2.7 wt. percent oxygen, the level contributed by about 15% MTBE-- in unleaded gasoline.[5])

ADVANTAGES

There are advantages for using oxygenates in gasoline. (Figure 5) Some oxygenates, like ethanol and MTBE, are available for purchase from large-scale producers, so they can be used immediately in the event of refinery problems. Unocal began using MTBE in 1986, for example, when we had an FCC unit problem at one of our refineries and needed additional octane. Economics may be favorable compared to other octane enhancers--methanol made from natural gas has historically been inexpensive on a per gallon basis compared to gasoline and ethanol has been made economically attractive through federal, and in some cases, state tax breaks.

There may also be environmental benefits. Some areas have carbon monoxide problems in the winter. Because of this problem, some states have required the use of oxygenates, such as ethanol or MTBE, in gasoline during winter months. Use of oxygenate blends in older vehicles, especially in high altitude areas, can reduce carbon monoxide emissions. I'll discuss why in more detail later.

Proponents of alcohol use also claim that the use of alcohols could reduce the country's dependence on foreign crude oil. Ethanol and methanol can be produced from domestic resources--ethanol from corn and other agricultural products and methanol from coal, of which there are abundant reserves in this country. However, the economics of producing alcohols from these resources are not attractive without some form of subsidy at this time, and concern about greenhouse gases makes production of methanol from coal less attractive.

The primary reason for a refiner to use oxygenates in gasoline is octane enhancement. (Figure 6) Shown here are typical octane blending values of some of the alcohols, MTBE, and normal butane and toluene for comparison. All, to varying degrees, will increase the octane quality of an 87 octane gasoline. For example, 10% ethanol in an 87 octane regular gasoline will bring the octane quality of the fuel up to about 90 octane, essentially a premium product. In general, the octane boost of most oxygenates is greater in low octane grades (e.g., in regular vs. premium). Thus when considering an oxygenate for octane enhancement, the user should consider overall refinery need when optimizing the use of the oxygenate (e.g., get the greatest "bang for the buck"). This is done with complex refinery linear programs which can optimize the use of stocks, given grade volume requirements, availability of stocks, and fuel specifications.

DISADVANTAGES

Why aren't all refiners using alcohols or ethers in gasoline? There are some drawbacks. (Figure 7) One characteristic of the lower alcohols, especially methanol, is they tend to increase the volatility of gasoline. Blends which contain methanol must meet volatility standards. To meet these standards after methanol is added to the fuel, lower quantities of volatile components such as butane can be used in the base gasoline. Because butane is inexpensive and has good octane quality, economics dictate using as much butane as possible. So for a given volatility, this means the economics of using a blendstock which raises volatility, like methanol, are less attractive. Ethanol blends, on the other hand, are not required under current EPA rules to meet the same volatility standards as gasoline. This has made it possible to blend ethanol with gasolines of normal volatility at a marketing terminal. Otherwise, low volatility base gasolines would be required for ethanol blends as well. Ethers do not increase the vapor pressure of typical gasolines, and thus have an advantage over the lower alcohols from which they are derived.

Another problem with using lower alcohols in gasoline is that alcohols are extremely soluble in water. Hydrocarbons are not. So when an alcohol/gasoline blend contacts even small amounts of water, the water can draw the alcohol from the gasoline into the water and form a separate layer at the bottom of a fuel tank. Not only does this lower the octane quality of the fuel above the water-alcohol layer, if a slug of this water-alcohol mixture enters a vehicle's engine, the vehicle will probably stall, and in some engines may cause damage. Because of its high potential for phase separation, all methanol blends must contain higher alcohol(s) (cosolvents) to increase the water tolerance. Daily monitoring of service station fuel tanks is necessary when marketing any alcohol blend to maintain product quality. Ethers, on the other hand, are not very soluble in water, and blends containing ethers have very little tendency to phase-separate. For this reason, ether blends can be pipelined, while alcohol blends can not under most pipeline regulations.

Alcohol blends, especially those containing methanol, also have a greater tendency than gasoline to damage materials found in fuel systems, both metallic and non-metallic. For this reason, most commercial methanol/cosolvent blends are likely to contain additives to prevent corrosion. Damage to elastomeric parts, such as hoses and seals, however, can still occur. Automobile manufacturers began using more alcohol-resistant parts several years ago, but older cars still on the road may have problems on alcohol blends, as can any equipment that was not designed to use alcohol blends. MTBE blends are typically compatible with fuel system materials at the levels normally used in gasoline (i.e., under 15 vol. %). High concentrations, however, will cause damage to fluoroelastomers, such as Viton, so appropriate material selection is necessary for handling neat MTBE when shipping it or handling it in the refinery.

Using an oxygenate/gasoline blend may also affect how well a car runs. Driveability problems, such as hard cold-starting, hesitation, and stalling may increase when using an oxygenate blend. Most automobile engines are set to run properly on gasoline; when an oxygenate is added to gasoline, it reduces the amount of oxygen required to burn the fuel, so the air-fuel mixture being burned by the engine is lean--there is more air than required for the amount of fuel introduced to the engine. This is not a big problem for most newer cars, but may be for older or particularly sensitive vehicles.

There are a few additional problems to be aware of with oxygenate blends. One is potential fuel filter plugging with alcohol blends. Alcohols have a tendency to loosen dirt and gums from the walls of fuel systems which have been in gasoline service; upon changeover to alcohol blends, these contaminants can be swept into fuel filters and cause plugging. To prevent contamination from service station tanks, fuel filters are normally installed on service station dispensers before alcohol blends are introduced. Ethers do not generally cause this type of problem, as they are less polar than the alcohols.

Fuel economy is theoretically poorer with oxygenate blends, as the oxygenates contain less energy by volume than straight gasoline. Methanol, for example, contains about half the BTU's per gallon compared to gasoline. MTBE has about 80% of the BTU content of gasoline. The difference in fuel economy for blends that contain 15% oxygenate or less may be so small, however, that it would not be noticeable by most consumers. In the case of a vehicle which has a rich air-fuel ratio, fuel economy may actually improve.

Most gasoline manufacturers use additives in gasoline to keep vehicle fuel system parts, such as carburetors or fuel injectors, clean. However, methanol and ethanol were found to degrade the performance of a typical gasoline detergent additive in a study conducted several years ago by Union Oil for the Department of Energy.[6] More detergent thus may be needed to keep fuel systems clean and maintain the original performance characteristics of the engine when alcohol blends are used. We have not observed degradation of additive performance with MTBE blends.

MTBE blends are very similar to straight gasoline, and virtually trouble-free (with the possible exception of odor). With appropriate additives to prevent corrosion and fuel system deposits, and with good maintenance procedures, problems with alcohol blends can be minimized. But knowing the advantages and disadvantages of oxygenates as gasoline components from a refiner's view is not enough to predict their future use. Other factors will influence their future growth.

AIR QUALITY (CARBON MONOXIDE)

(Figure 8) One major factor which is currently influencing oxygenate use in gasoline is air quality. As I mentioned before, some states (Colorado, Arizona, Nevada) now require alcohols or MTBE in gasoline during the winter. Other states with carbon monoxide problems are considering similar measures. And proposed Clean Air Act amendments contain provisions for oxygen content mandates for gasoline. This would encourage the growth of oxygenates in motor fuel use.

The effect on emissions is a result of air/fuel mixture enleanment, which I mentioned earlier in reference to the effect on driveability. The use of an oxygenate in gasoline reduces the amount of oxygen required for complete combustion of the fuel. In a vehicle designed to run on gasoline at a slightly rich air/fuel ratio (A/F) (as many older cars were designed to do), the use of an oxygenate blend can reduce the emissions of carbon monoxide and exhaust hydrocarbons because of A/F enleanment. Depending on the A/F of the vehicle, however, NOx emissions may increase. Enleanment of A/F can be obtained by adding oxygenates to gasoline or by adjusting the fuel metering equipment on the engine. The effect of A/F on emissions is shown in Figure 9.[7]

The carbon monoxide reduction benefit of using an oxygenate/gasoline blend is greater in vehicles with older emission control technology (vehicles which do not have closed loop feedback). In a modern car with closed loop feedback, the oxygen sensor detects excess oxygen in the exhaust and signals the electronic control unit to increase the supply of fuel to the engine when an oxygenate blend is used. Thus emissions effects (and driveability effects) are minimized. The use of an oxygenate-containing fuel thus provides little CO or hydrocarbon reduction while the closed loop feedback system is in operation. However, the closed loop system is not in operation during engine warmup. During warmup, the vehicle operates in an open loop mode, similar to a vehicle without closed loop feedback. Reductions in CO or hydrocarbons may occur during this warmup period.

Although emissions reductions are higher at higher fuel oxygen contents, test data indicate that most of the emission reductions occur within the first two percent oxygen in the fuel, and tapers off as oxygen content is further increased. ARCO Chemical, the largest producer of MTBE, estimates that a fuel containing 2 wt.% oxygen (or approximately 11 volume percent MTBE) would provide 80% of the CO emission reduction provided by a higher oxygen content fuel (e.g., 10% ethanol in gasoline, which contains about 3.5 wt. % oxygen) and that fifteen percent MTBE would provide about 90% of the emission benefits of the higher oxygen content fuels.[8]

AIR QUALITY (OZONE)

A regulation which may also affect oxygenate use is currently being phased in by the Environmental Protection Agency. Because many areas of the country have problems meeting ozone standards, the EPA now regulates vapor pressure of gasoline in an attempt to control hydrocarbon emissions due to evaporative emissions.[9, 10] Reducing vapor pressure of fuel will tend to slow the growth of alcohols as gasoline blendstocks, particularly methanol because it has such a large effect on volatility. Vapor pressure reduction regulations could also cripple ethanol blending, which currently enjoys an exemption from volatility restrictions. The EPA allows a 1 psi higher vapor pressure for ethanol blends, but in areas that have severe ozone nonattainment problems, this allowance may be removed in the future. Volatility reductions would tend to increase the use of ethers, especially TAME and ETBE, which have very low vapor pressures.

Another issue that may increase the use of oxygenates is being debated in Congress. Gasoline aromatics reductions are being considered for Clean Air Act amendments. Loss of octane associated with reducing aromatic content may be partially made up through the use of oxygenates. Demand for oxygenates would increase dramatically if the aromatics reduction proposals pass.

ECONOMICS

A factor which hurts alcohol blends is the low price of gasoline relative to alcohols. Even with recent increases in gasoline prices, oxygenates have a difficult time competing with refinery processing as a means of increasing octane quality. Ethanol, which as a fuel extender can compete only with the help of a 6 cents per gallon of blend federal tax incentive and some state tax incentives, would not survive on its own if these were eliminated. This is been done in the past few years in many states which have lost large amounts of highway revenues to ethanol blending.

PUBLIC ACCEPTANCE

One of the most important problems that alcohol blends must overcome in order to grow, however, lies not in their economics but in acceptance in the marketplace. Bad publicity about improper or illegal blends has made the public wary of fuels that contain alcohols. Owners manuals of some auto manufacturers still warn against using methanol blends, and say to switch back to gasoline if problems occur on ethanol blends. The Coast Guard and marine engine and boat manufacturers have in the past warned boaters about using alcohol blends, because of the potential for the alcohol to damage hoses and increase the potential for fires.[11, 12] And two-stroke engine manufacturers are concerned about phase separation--if the alcohol/water portion of a phase-separated blend gets into a two-stroke engine, the lack of lubrication may cause serious engine damage.[13]

MTBE blends, on the other hand, are generally well accepted by consumers, automobile manufacturers, and the petroleum industry. MTBE has many properties (e.g., volatility, material compatibility, phase separation properties, etc.) that make it more attractive to refiners and marketers compared to the lower alcohols. For these reasons, Unocal favors MTBE over ethanol or methanol/cosolvent blends as a component for gasoline. We expect few problems associated with the use of MTBE when the finished blend meets the ASTM Specification for Automotive Spark-Ignition Engine Fuel, D 4814.

NEAT METHANOL AS A MOTOR FUEL

Because of the problems associated with alcohols in gasoline, I believe the major growth of alcohol fuels may come not as blending components for gasoline, but from their use in vehicles specifically designed to run on straight alcohols (probably methanol). This would allow engine designers to take advantage of the octane quality and combustion characteristics of the alcohols. (Figure 10)

Methanol has very good octane quality, wider flammability limits than gasoline, and a high latent heat of vaporization. If a vehicle is designed to use methanol, the engine compression ratio can be increased and the air/fuel ratio made leaner compared to what is typically used for a gasoline engine. This along with the increased charge density achievable with methanol results in increased engine efficiency and power.

However, because methanol contains about half the energy per gallon that gasoline does, a methanol vehicle's driving range is significantly shorter than that of a comparable gasoline vehicle, even with improvements in efficiency. The lower energy density of methanol also affects the economics of using methanol as a motor fuel--even at a lower per gallon cost, the cost per mile on methanol is still higher than that on gasoline.

Engine lubrication and low temperature starting are currently problems in methanol vehicles, and there are some safety problems with neat methanol that are not problems with gasoline or diesel fuel. The cold-start and safety problems are largely taken care of by blending 15%

gasoline into methanol to provide sufficient volatility for starting the engine and to handle the safety problems associated with 100% methanol (M100).

One of the biggest barriers to wide spread use of methanol as a motor vehicle fuel is the "Chicken and Egg" problem. Automakers have been reluctant to introduce new vehicles for which no fuel is available. Fuel distributors are reluctant to introduce fuel for which there are no vehicles.

The California Energy Commission (CEC) has contracted with a couple of dozen service stations around California to provide M85 (85% methanol with 15% gasoline to help cold starting and improve safety characteristics). But because of the shorter range of methanol cars and the limited availability of fuel, the danger of running out of fuel is great.

To reduce this problem, automakers are developing vehicles which can run on any combination of methanol and gasoline-- so-called Flexible- or Variable-fueled vehicles. (Figure 11) These vehicles incorporate a sensor to determine what combination of methanol and gasoline is present in the fuel tank, so that fuel rate and ignition timing can be automatically adjusted.[14]

This type of vehicle cannot be optimized for methanol, and thus is considered a transition vehicle--a way to introduce methanol vehicles before a methanol distribution system is fully developed. In the meantime, some petroleum companies are offering M85 at selected stations in California under California Energy Commission contract. This is viewed by methanol proponents as a major breakthrough in the Chicken and Egg problem.

(Figure 12) Despite some of the problems which still exist, interest in vehicles designed to run on methanol is very high right now, because exhaust emissions from methanol vehicles have been estimated to contribute less to ozone formation than exhaust from gasoline-powered vehicles. Methanol can also be used in diesel applications and can significantly reduce NOx and particulate emissions in that application. Exhaust and evaporative emissions of vehicles running on the 85% methanol/15% gasoline blend (commonly called M85) described earlier are generally more reactive, however, than those for vehicles running on 100% methanol (M100). Efforts to improve M100's cold-starting and safety characteristics without the use of high volumes of hydrocarbons are still in progress.

Although methanol is less reactive toward forming ozone than typical gasoline exhaust components, aldehydes are much more reactive. Aldehyde emissions (especially formaldehyde) are higher from methanol-fueled engines than from gasoline-fueled engines. Depending on the level of aldehydes in methanol vehicle exhaust, there could be little or no air quality benefit of using methanol as a motor vehicle fuel. Regulatory agencies are still quantifying aldehyde emission levels from the methanol vehicles on the road, and the California Air Resources Board (CARB) has established vehicle emission limits for formaldehyde. Automakers are working on ways to meet these standards with methanol, but have not yet developed technology that is durable. Additional studies are also being done to try to better quantify the effects of methanol use on air quality.

Additional environmental concerns include the toxicity of both the fuel and exhaust emissions from vehicles fueled on methanol. Exhaust emissions of methanol-fueled vehicles consist mostly of methanol and formaldehyde. Both are toxic substances, and there is some concern about exposure to these compounds if methanol vehicles were in widespread use. Groundwater contamination is also a concern, as methanol is completely soluble in water and thus could not easily be separated out if a large quantity of methanol were to leak or be spilled.

As with any other fuel, methanol has its advantages and disadvantages. There are a number of uncertainties and problems which must yet be solved before this fuel and the vehicles to use it are introduced to consumers.

SUMMARY

(Figure 13) To review, the drive to provide higher octane fuels or to reduce carbon monoxide emissions will encourage the use of oxygenates as gasoline blending agents. The technical problems I have mentioned have caused minimal problems in practice, because most blenders have adhered to meticulous maintenance procedures. The main challenges to oxygenates as gasoline components thus will be their cost, governmental factors, such as more restrictive volatility regulations or the reduction of ethanol blend tax incentives, and negative public perception.

(Figure 14) The use of neat methanol may be a better way to use alcohols, though there are still unresolved problems. Additional research in cold-starting, lubrication, and aldehyde emissions is needed before vehicles designed to use methanol could be produced for consumers.

As the API said in 1938, alcohol-gasoline blends are not superior to gasoline of comparable octane quality. However, today we are concerned not only about vehicle performance, but with environmental and political factors as well. As the push to improve air quality intensifies, I believe the use of ethers in gasoline will continue to increase, because of their advantages over the lower alcohols from which they were derived. If the current problems can be overcome, methanol as a neat fuel may grow as well.

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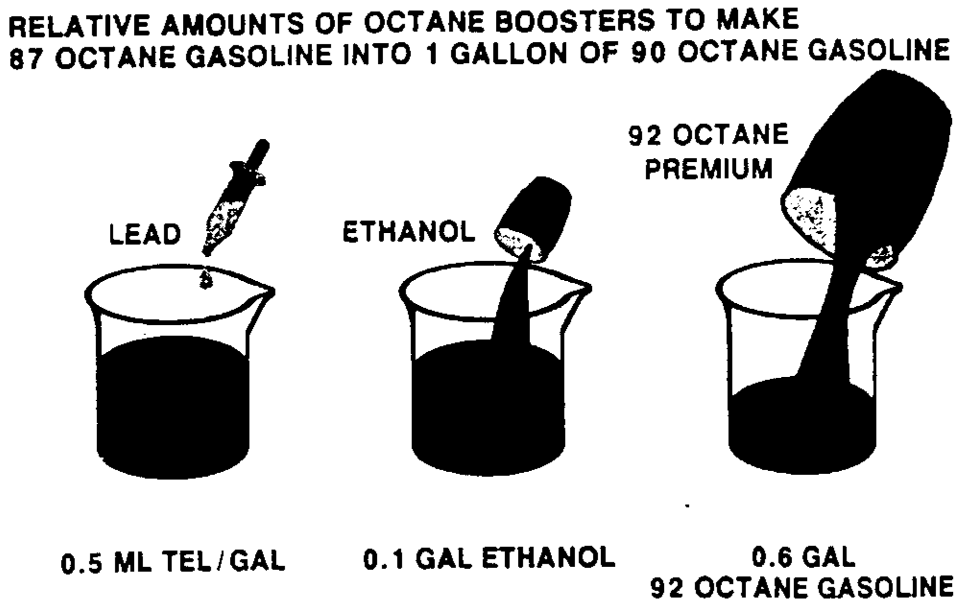


Figure 1

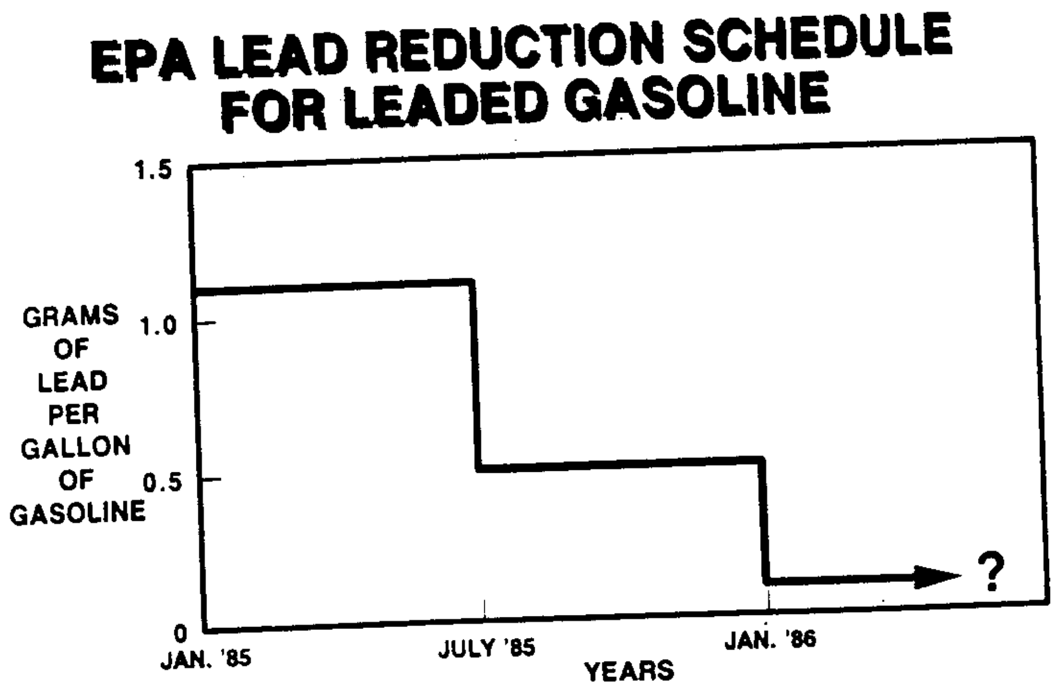


Figure 2

REFINER'S SOURCES OF OCTANE

- PROCESSING
- HYDROCARBONS
- OXYGENATES

Figure 3

TYPICAL OXYGENATED OCTANE ENHANCERS

	COMPOSITION	AMOUNT ALLOWED IN UNLEADED GASOLINE, VOL. %
ALCOHOLS		
GASOHOL	ETHANOL	10
OXINOL-50	50% METHANOL/ 50% TERTIARY BUTYL ALCOHOL	~9.4
ARCONOL	TERTIARY BUTYL ALCOHOL	~15.7
DUPONT WAIVER	METHANOL & COSOLVENT (BUTANOLS OR LOWER ALCOHOLS)	VARIES WITH COSOLVENT
TEXAS METHANOL	METHANOL & COSOLVENT (OCTANOLS OR LOWER ALCOHOLS)	VARIES WITH COSOLVENT
ETHERS		
MTBE	METHYL TERTIARY BUTYL ETHER	15
TAME	TERT-AMYL METHYL ETHER	~12.7
ETBE	ETHYL TERT-BUTYL ETHER	~12.7

Figure 4

ADVANTAGES OF USING OXYGENATES IN GASOLINE

- IMMEDIATE USE (PURCHASED OXYGENATES)
- ECONOMICS
- ENVIRONMENTAL BENEFITS (CO)
- REDUCED DEPENDENCE ON FOREIGN CRUDE
- OCTANE QUALITY

Figure 5

TYPICAL OCTANE BLENDING VALUES OF BLENDING AGENTS IN GASOLINE

	TYPICAL BLENDING VALUE, (R + M)/2
ETHANOL	117
OXINOL-50	107
ARCONOL	97
MTBE	110
N-BUTANE	92
TOLUENE	105

Figure 6

DISADVANTAGES OF USING OXYGENATES IN GASOLINE

- VOLATILITY (ALCOHOLS)
- PHASE SEPARATION (ALCOHOLS)
- MATERIAL COMPATIBILITY (PRIMARILY ALCOHOLS)
- DRIVEABILITY
- FUEL FILTER PLUGGING (ALCOHOLS)
- FUEL ECONOMY
- DETERGENT ADDITIVE PERFORMANCE (ALCOHOLS)

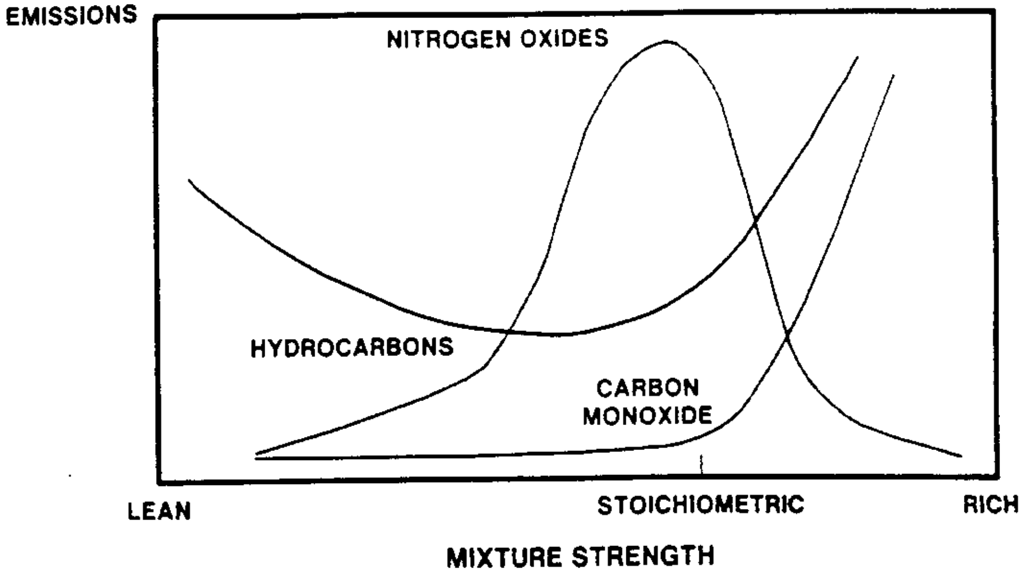
Figure 7

FACTORS WHICH WILL AFFECT OXYGENATE USAGE

- CARBON MONOXIDE STRATEGY
- GASOLINE VOLATILITY REDUCTIONS
- PROPOSED AROMATICS REDUCTIONS
- GASOLINE PRICE
- TAX BREAKS
- PUBLIC ACCEPTANCE

Figure 8

EMISSION LEVELS DEPEND ON MIXTURE STRENGTH



SOURCE: BRINKMAN, N.D., ET AL. AS PRESENTED BEFORE THE SOCIETY OF AUTOMOTIVE ENGINEERS

Figure 9

USE OF METHANOL AS A MOTOR VEHICLE FUEL

ADVANTAGES

- HIGH OCTANE QUALITY
- WIDE FLAMMABILITY LIMITS
- HIGH LATENT HEAT OF VAPORIZATION

DISADVANTAGES

- LOWER VOLUMETRIC ENERGY DENSITY
- ENGINE LUBRICATION PROBLEMS
- LOW TEMPERATURE STARTING
- SAFETY CONSIDERATIONS
- FUEL AVAILABILITY

Figure 10

FORD FLEXIBLE FUEL VEHICLE

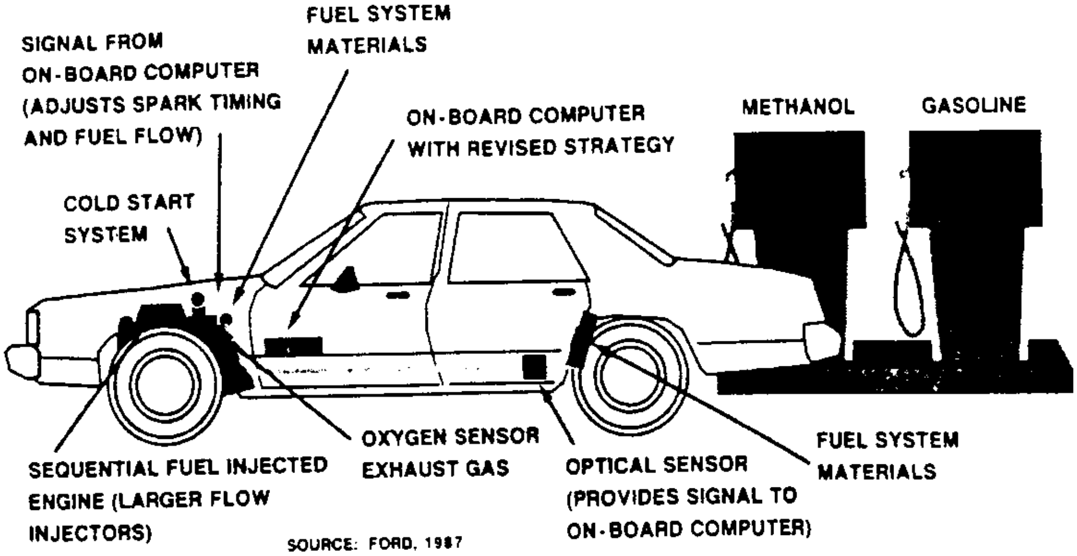


Figure 11

USE OF METHANOL AS A MOTOR VEHICLE FUEL

POTENTIAL ENVIRONMENTAL BENEFITS

- EXHAUST EMISSIONS--OZONE PRECURSORS, NOx, PARTICULATES

POTENTIAL ENVIRONMENTAL DRAWBACKS

- EXHAUST EMISSIONS--ALDEHYDES
- TOXICITY OF METHANOL AND FORMALDEHYDE
- GROUNDWATER

Figure 12

SUMMARY
OXYGENATE / GASOLINE BLENDS

- NEED FOR OCTANE QUALITY WILL PROBABLY ENCOURAGE GROWTH OF OXYGENATES AS GASOLINE BLENDING AGENTS
- TECHNICAL PROBLEMS WITH MTBE ARE MINIMAL
- TECHNICAL PROBLEMS WITH ALCOHOLS HAVE BEEN MINIMIZED BY METICULOUS MAINTENANCE
- GOVERNMENTAL FACTORS AND PUBLIC PERCEPTION WILL INFLUENCE FUTURE USE

Figure 13

NEAT ALCOHOLS AS MOTOR VEHICLE FUEL

- UNRESOLVED PROBLEMS
  - COLD-STARTING
  - LUBRICATION
  - ALDEHYDE EMISSIONS

Figure 14