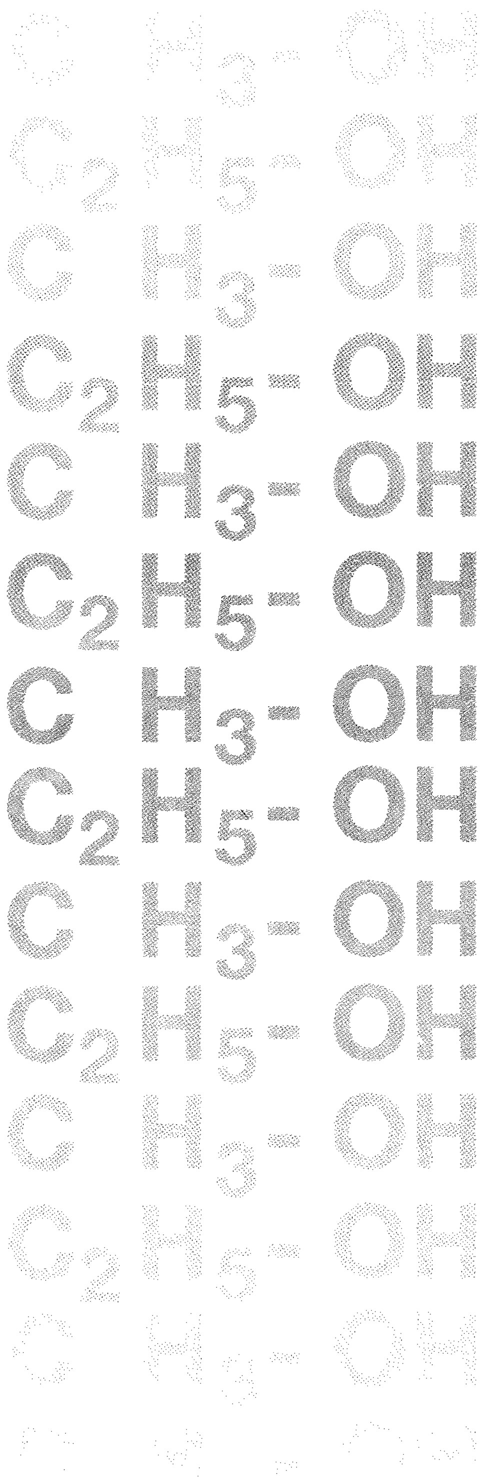

PROPERTIES OF ALCOHOL TRANSPORTATION FUELS

Alcohol Fuels Reference Work #1

Prepared for:
Biofuels Systems Division
Office of Alternative Fuels
U.S. Department of Energy

Prepared by:
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July 1991

PROPERTIES OF ALCOHOL TRANSPORTATION FUELS

Alcohol Fuels Reference Work #1

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Section 1

INTRODUCTION

Section 1
INTRODUCTION

During the mid and late 1980s, research on alcohol fuels undertaken in the United States, Japan, and Europe expanded greatly. This research has covered the entire alcohol production, distribution and utilization process, from the selection of high-yield cultivars as feedstocks for the production process to the performance of neat alcohol fuels and blends in production passenger vehicles. Much of the recent research on alcohol fuel utilization has been undertaken by or funded by the R&D departments of private firms, as they seek new fuel and vehicle combinations to meet projected environmental and efficiency requirements for the 1990s. The state-of-the-art has been evolving very rapidly, as public and private sector groups continue research and development efforts that will lead to expanded alcohol fuel production and usage. The results of this research have been published primarily in journals dedicated to the scientific and engineering community, and have not been broadly disseminated to the public policy community. In addition, new information has been developed incrementally, and no compilation of recent findings is currently available.

At the same time, a broad spectrum of public sector decision-makers have become interested in potential applications of alcohol fuels to solve specific problems. These range from city and state officials, seeking to comply with required reductions in vehicle emissions of carbon monoxide and nitrous oxides, to federal officials currently engaged in follow-up to the recently published National Energy Strategy and examining options to reduce future importation of crude oil and refined petroleum products.

Because of the rapid rate of change in the research knowledge, and the very specific needs of public policy decision-makers, a widening gap has emerged in knowledge of the state-of-the art in alcohol fuels. At the end of 1989, it was therefore determined by the Biofuels Systems Division of the U.S. Department of Energy to develop a series of Alcohol Fuel Reference Works. The publications are targeted specifically at public decision-makers to provide a comprehensive set of current information on all aspects of alcohol fuels, from feedstock growth performance and alcohol's chemical characteristics to infrastructure requirements for widespread sale of neat alcohol fuels.

The following report is the first in a series of Alcohol Fuel Reference Works. It presents a range of scientific and engineering information on the characteristics of alcohol fuels. Research findings and data from the period 1985-1990 are emphasized, although more generic information on characteristics has also been included from standard chemistry, engineering, and petrochemical reference texts published prior to 1985. This reference work is designed to serve as a desk companion for public policy decision-makers, and is organized by ten major topical areas. To facilitate usage, each section of the reference work has been designed to stand alone, with only infrequent cross-references to other sections. Key facts and definitions of terms are provided in a "quick reference" summary at the beginning of each major section. Extensive use of graphics has been made, whenever possible reproducing the full range of information presented in the original research reports.

The major foci of this report are the two primary fuel alcohols -- ethanol (ethyl alcohol) and methanol (methyl alcohol). Where particular research reports examined other alcohol fuels (propyl alcohol, isopropyl alcohol, decyl alcohol, etc.) or alcohol-based ethers (particularly methyl tertiary butyl ether or MTBE and ethyl tertiary butyl ether or ETBE), these results have also been included in the analysis. Due to increased interest in ETBE as a means for reformulating gasoline to meet the requirements of the 1990 revisions to the Clean Air Act, a separate section on ETBE has been included. In the case of engine-related research, there has been a great deal more recent published works on methanol and MTBE than has been published on ethanol and ETBE, and this is reflected in the information presented here. Throughout the series of reference works, however, every attempt has been made to present current research findings on both methanol and ethanol.

Section 2

BASIC CHEMISTRY OF ALCOHOL FUELS

Quick Reference Data

Chemical Formulae

- Ethanol (Ethyl Alcohol): CH_3CH_2OH (or C_2H_5OH)
- Methanol (Methyl Alcohol): CH_3OH
- Ethane: CH_3CH_3 (or C_2H_6)
- Methane: CH_4
- Gasoline: C_4 to C_{12}

Physical Properties	Ethanol	Methanol	Gasoline
- Molecular Weight (MW)	46.07	32.04	na
- Specific Gravity (60°F/60°F)	0.794	0.796	0.72-0.78
- Density (lb/gal @ 60°F)	6.61	6.63	6.0-6.5
- Boiling Point (°F)	78°C (172°F)	65°C (149°F)	27-225°C (80-437°F)
- Reid Vapor Pressure (RVP)			
-- Neat (psi)	2.3	4.6	na
-- Blended (psi)	12-27	93-98	8-15
- Pump Octane Number			
-- Neat	97	98	72-76
-- Blended	111	115	na
- Water solubility (volume % @ 70°F)	100%	100%	negligible
- Latent heat of vaporization			
-- Btu/gal @ 60°F	2,378	3,340	900
-- Btu/lb @ 60°F	396	506	150
- Heating Value (lower)			
-- Btu/lb	11,500	8,570	18,000-19,000
-- Btu/gal @ 60°F	76,000	56,800	109,000-119,000
- Energy Release (S ft^3 of stoichiometric volume)	94.7 Btu/ft^3	94.5 Btu/ft^3	95.2
- Stoichiometric air/fuel weight	9.00	6.45	14.7

Useful Terms and Definitions (also see Glossary)

- **Alcohol:** a hydrocarbon in which one atom of hydrogen has been substituted by a hydroxyl group (i.e., methane, a hydrocarbon, is CH_4 while methanol, an alcohol is CH_3OH; the "OH" being the hydroxyl group).

- **Exothermic:** chemical change accompanied by a liberation of heat.

- **High Molecular Weight/Long Chain Alcohols:** with respect to transportation liquid fuels, these are alcohols that have more than 4 carbon atoms (i.e., C_5 and above) in their molecular structure and their main use may be as additives and cosolvents in methanol to prevent phase separation and as corrosion preventives. They include n-decanol, n-hexanol, and n-octanol.

- **Hydrocarbon:** a compound composed of carbon and hydrogen atoms.

- **Hydroxyl:** the chemical group or ion OH that consists of one atom of hydrogen and one of oxygen, is neutral or positively charged and is characteristic especially in alcohols, oxygen acids, glycols, phenols, and hemiacetals.

- **Latent Heat Vaporization:** The amount of heat required to vaporize a unit quantity of a fuel generally measured at 1 atmosphere of pressure and at the boiling point of the liquid.

- **Low Molecular Weight/Short Chain Alcohols:** with respect to transportation liquid fuels, these are alcohols that have from 1 to 4 carbon atoms (i.e., C_1 - C_4) in their molecular structure and include methanol, ethanol, propanol and butanol.

- **Mole** (symbol "mol"): the quantity of a chemical substance that has a weight in mass units numerically equal to the molecular weight. In chemistry, moles are used as the standard unit of measure and for the comparison of compounds. The mass units must be specified, i.e., atoms, electrons, kilograms, etc.

- **Octane Number** (Rating): a measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the greater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

- **Stoichiometric:** characterized by, or being a proportion of, substances or energy exactly right for a specific chemical reaction with no excess of any reactant or product, i.e., chemically correct.

Key Issues and Implications

Issues and Implications

Issue # 1: The Presence of Oxygen in Alcohols

Alcohols, unlike petroleum-based products, contain a significant amount of oxygen as a basic component in their molecular structure.

Implications of Use of Alcohols and other Oxygenates:

- As a blending agent with gasoline, alcohol fuels (including the ethers derived from alcohol--ETBE and MTBE) offer an important option for reducing urban carbon monoxide (CO) pollution from existing vehicles, because their oxygen component helps assure that more complete combustion occurs (they allow leaner fuel/air ratios).

- Carbon monoxide emissions in older cars (pre-1981) can be reduced by 30%; newer cars (1981 and newer), which have a built-in oxygen sensor, can still have CO emissions reduced by as much as 10%.

Detailed Information: Refer to pages 2-1 through 2-4.

Issue #2: *Alcohols as Sources of Octane*

Alcohols have a higher octane rating than gasoline.

Implications of Alcohol's Higher Octane Rating:

- Alcohols can be used as blending agents to improve the octane rating of gasoline, increasing power output and reducing engine knock. This has been a particular benefit to smaller and independent gasoline distributors with no refining capability.
- Alcohols serve as domestically based alternatives for upgrading gasoline products made from many lower grade U.S. crude oils without having to turn to lighter imported crudes.
- Alcohols and alcohol-derived ethers can substitute for harmful aromatic octane enhancers (e.g., benzene) in the reformulation of gasoline.

Detailed Information: Refer to pages 2-5 through 2-6.

Issue #3: *Lower Energy Density of Alcohol Fuels*

Alcohol fuels have a lower energy density (lower Btu/gallon) than gasoline.

Implications of Lower Energy Density:

- Overall, flexible fuel vehicles (FFV) and neat alcohol vehicles will require larger fuel tanks or more frequent refills than straight gasoline or low-level blend vehicles. However, the higher combustion efficiencies offered by alcohol fuels will partially offset the reduced miles per gallon associated with the lower energy density of alcohol fuels.
- The fuel distribution infrastructure will require either increased storage capacity or greater rates of throughput.

Detailed Information: Refer to pages 2-6 through 2-9.

Issue #4: *Solubility in Water*

Low molecular weight alcohols (like ethanol and methanol) are 100% soluble in water. Because of the strong affinity between these alcohol molecules and water, phase separation can occur when small amount of water contaminate gasoline/alcohol blends.

Implications of Water Solubility and Phase Separation:

- Transport of alcohol blends through gasoline pipelines is a concern because water may be present at certain points in the pipeline. Major pipeline operators have been unwilling to transport these blends, thus necessitating splash blending in trucks, reducing the marketability of the blends.

Potential Solutions:

- Convert the alcohol to its ether form (MTBE or ETBE) which completely eliminates the problem, since these ethers are not soluble in water.
- Use additives such as "heavy" alcohols to help prevent phase separation.

Detailed Information: Refer to pages 2-12 through 2-13.

Issue #5: *Alcohols Have a Much Higher Latent Heat of Vaporization than Gasoline.*

Implications of High Latent Heat of Vaporization:

- Alcohol increases the power and efficiency of existing vehicles (offsetting the disadvantages associated with the lower energy density of alcohol).
- Contributes to cold start problems for neat alcohol or high-level alcohol/gasoline blends at cold ambient temperature, thus requiring the use of additives or a cold start subsystem in vehicles using these fuels.

Potential Solutions:

- Vehicle engines can be redesigned to take advantage of this characteristic.
- Additives such as gasoline or higher alcohols can be used to minimize cold start problems.

Detailed Information: Refer to pages 2-13 through 2-14.

Section 2
BASIC CHEMISTRY OF ALCOHOL FUELS

- Chemical Structure
- Physical Properties of Alcohols

Introduction

Alcohols -- especially methanol and ethanol -- are considered the leading candidates for long-term replacement of petroleum-based motor fuels (gasoline and diesel) in the future because of their ability to reduce urban air pollution and offset U.S. dependence on imported oil. But due to their different chemical structures, alcohols differ substantially from gasoline and diesel fuel in a number of important fuel parameters. This section examines the chemistry of alcohol fuels, including their physical properties, and explores these characteristics in relation to gasoline.

Chemical Structure

Gasoline, diesel fuels and other petroleum-based fuels are complex mixtures of hydrocarbons. The term "hydrocarbon" refers to compounds which are composed of carbon and hydrogen atoms. In contrast, an alcohol molecule consists of a hydrocarbon in which one atom of hydrogen has been substituted by a hydroxyl group. Thus, an alcohol molecule is normally represented in chemistry texts by the formula R-OH, where R is the remaining hydrocarbon group and OH represents the hydroxyl group. [1,2] R may be a benzene ring or isopropyl, propenyl, or butyl group, as shown in Table 2-1. The first four alcohols listed in Table 2-1 are collectively known as alkyl alcohols and are the chief alcohols of interest as motor fuels. In these alcohols, the symbol R indicates

TABLE 2-1. CHEMICAL STRUCTURE OF ALCOHOLS AND HYDROCARBONS

HYDROCARBON		R	ALCOHOL	
NAME	FORMULA		FORMULA	NAME
Methane	CH_4	CH_3 Methyl	CH_3-OH	Methanol (Methyl Alcohol)
Ethane	$CH_3\ CH_3$ (C_2H_6)	CH_3CH_2 Ethyl	CH_3CH_2-OH	Ethanol (Ethyl Alcohol)
Propane	$CH_3CH_2CH_3$ (C_3H_8)	$CH_3CH_2CH_2$ Propyl	$CH_3CH_2CH_2$-OH	Propanol (Propyl Alcohol)
Butane	$CH_3(CH_2)_2CH_3$ (C_4H_{10})	$CH_3(CH_2)_2CH_2$ Butyl	$CH_3(CH_2)_2CH_2$-OH	Butanol (Butyl Alcohol)
Propane	$CH_3CH_2CH_3$ (C_3H_8)	$(CH_3)_2CH$ Isopropyl	$(CH_3)_2CH$-OH	2-Propanol (Isopropyl Alcohol)
Isobutane	$(CH_3)_3CH$ (C_4H_{10})	$(CH_3)_3C$ tert-Butyl	$(CH_3)_3C$-OH	2-Methyle-2-Propanol (tert-Butyl Alcohol)
Propene	$CH_2=CH-CH_3$ (C_3H_6)	$CH_2=CH-CH_2$ Propenyl	$CH_2=CH-CH_2$-OH	2-Propenol
Propyne	$HC{\equiv}C-CH_3$ (C_3H_4)	$HC{\equiv}C-CH_2$ Propynyl	$HC{\equiv}C-CH_2$-OH	2-Propynol
Benzene	C_6H_6	C_6H_5 Benzyl	C_6H_5-OH	Phenol

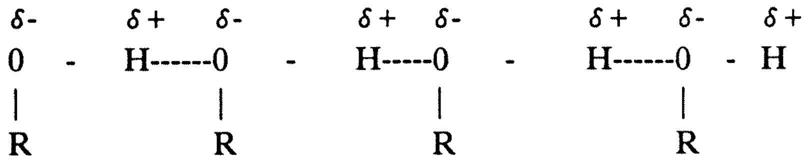
one of the alkyl groups ranging in order of complexity from CH_3 (methyl) to $CH_3(CH_2)_2CH_2$ (butyl).

Policy Issue #1

The presence of the oxygen molecule in the hydroxyl group gives alcohols and alcohol-derived ethers important combustion advantages when burned in an internal combustion engine. These "oxygenated" fuels can operate efficiently under "lean-burn" conditions (see pages 3-9 through 3-10), which results in lower production of the pollutant carbon monoxide (CO). The CO reductions are most dramatic in older vehicles, which are also the greatest sources of urban air pollution.

Physical Properties of Alcohols

The physical properties of a number of important alcohols are shown in Table 2-2 and Figure 2-1. [3] Physical properties of low-molecular-weight alcohols are markedly different from hydrocarbons with the same molecular weight (see Table 2-3 [4]). These differences are due to the presence of the hydroxyl group, which gives alcohols a polar structure. As a result, there is a strong tendency of alcohol molecules to associate with each other through "hydrogen bonds." In alcohols, hydrogen bonds arise from attraction between the hydrogen atom of one hydroxyl group and the oxygen atom of another hydroxyl group:



$$\begin{array}{ccccccccccccccc} \delta- & & \delta+ & & \delta- & & \delta+ & & \delta- & & \delta+ & & \delta- & & \delta+ \\ 0 & - & H & \text{------} & 0 & - & H & \text{-----} & 0 & - & H & \text{------} & 0 & - & H \\ | & & & & | & & & & | & & & & | & & \\ R & & & & R & & & & R & & & & R & & \end{array}$$

Hydrogen bond

TABLE 2-2. PHYSICAL PROPERTIES OF ALCOHOLS

CHEMICAL FORMULA	NAME	MELTING POINT (°C) (1 atm)	BOILING POINT (°C) (1 atm)	DENSITY $d^{20/4}$(g/mL)	WATER SOLUBILITY (g/100 mL H_2O) (20°C)
Monohydroxy Alcohols					
CH_3OH	Methyl alcohol	-97	64.7	0.792	∞*
CH_3CH_2OH	Ethyl alcohol	-117	78.3	0.789	∞
$CH_3CH_2CH_2OH$	Propyl alcohol	-126	97.2	0.804	∞
$CH_3CH(OH)CH_3$	Isopropyl alcohol	-88	82.3	0.786	∞
$CH_3CH_2CH_2CH_2OH$	Butyl alcohol	-90	117.7	0.810	7.9
$CH_3CH(CH_3)CH_2OH$	Isobutyl alcohol	-108	108.0	0.802	10.0
$CH_3CH_2CH(OH)CH_3$	*sec*-Butyl alcohol	-114	99.5	0.808	12.5
$(CH_3)_3COH$	*tert*-Butyl alcohol	25	82.5	0.789	∞
$CH_3(CH_2)_3CH_2OH$	Pentyl alcohol	-78.5	138.0	0.817	2.4
$CH_3(CH_2)_4CH_2OH$	Hexyl alcohol	-52	156.5	0.819	0.6
$CH_3(CH_2)_5CH_2OH$	Heptyl alcohol	-34	176	0.822	0.2
$CH_3(CH_2)_6CH_2OH$	Octyl alcohol	-15	195	0.825	0.05
$CH_3(CH_2)_7CH_2OH$	Nonyl alcohol	- 5.5	212	0.827	--
$CH_3(CH_2)_8CH_2OH$	Decyl alcohol	6	228	0.829	--
$CH_2{=}CHCH_2OH$	Allyl alcohol	-129	97	0.855	∞
$(CH_2)_4CHOH$	Cyclopentanol	-19	140	0.949	--
$(CH_2)_5CHOH$	Cyclohexanol	24	161.5	0.962	3.6
$C_6H_5CH_2OH$	Benzyl alcohol	15	205	1.046	4.0
Diols and Triols					
CH_2OHCH_2OH	Ethylene glycol	-12.6	197	1.113	∞
$CH_3CHOHCH_2OH$	Propylene glycol	-59	187	1.040	∞
$CH_2OHCH_2CH_2OH$	Trimethylene glycol	-30	215	1.060	∞
$CH_2OHCHOHCH_2OH$	Glycerol	18	290	1.261	∞

*∞ = totally soluble

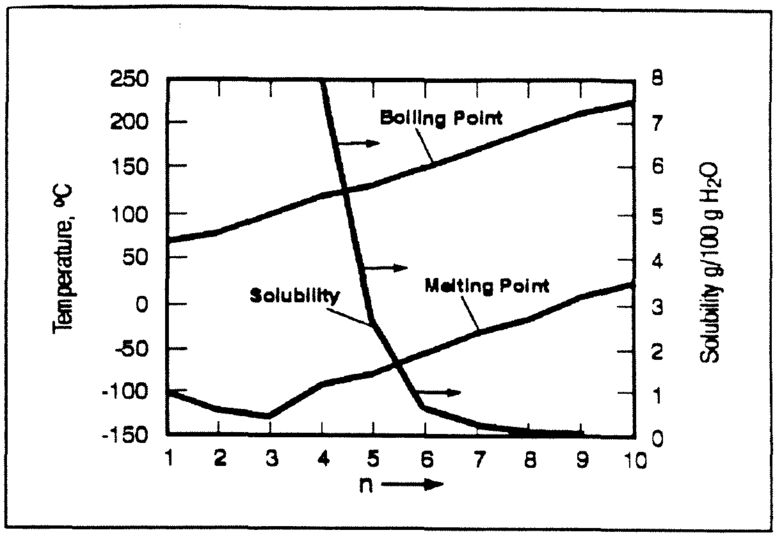


Figure 2-1., Boiling point, melting point, and water solubility of straight alcohols($C_nH_{2n+2}O$) versus n (n=number of carbon atoms in the alcohol molecule).

Hydrogen bonds are about 5 to 10 kcal/mol (20 to 40 kJ/mol*), and are stronger than most other intermolecular attractions. Hydrogen bonds are strong enough to have an important influence on such properties as boiling points, solubility, and many of the secondary structural characteristics of molecules.

Octane Number

The octane number is a numerical rating which indicates the tendency of an engine to knock when a motor fuel is used in a standard spark-ignition internal combustion engine. The higher the number, the less likely it is that the fuel will knock under full load conditions. In the United States, two different measures of octane are customarily used and then averaged: research (R) octane, which is the theoretical power rating, and motor (M) octane, which is the observed value in laboratory tests. The octane

---

*Mole (symbol "mol"): The quantity of a chemical substance that has a weight in mass units numerically equal to the molecular weight of that substance. In chemistry, moles are used as the standard unit of measure and for comparison of compounds. The mass units must be specified, e.g., atoms, molecules, ions, radicals, electrons, etc.

number is a measurement term used to identify the ability of a fuel to resist spontaneous combustion. Low octane gasoline may prematurely ignite due to the heat and compression inside the cylinder, causing a "knock" sound heard by the driver. This pre-ignition, while quite common in a car under a heavy load, accelerating, or driving up a long hill, can contribute to engine failure if it occurs frequently.

Policy Issue #2

As is discussed further in Section 5, alcohols and alcohol-based ethers have much higher octanes than that of most gasoline blends. The (R+M)/2 octane of ethanol is 97, that of methanol 98, MTBE 109, and ETBE 110. In contracts, U.S. gasoline is prepared in three octane blends: regular (87 (R+M)/2), mid-grade (89 (R+M)/2) and high test (92 or greater (R+M)/2). Alcohol fuels and alcohol-based ethers are greatly valued by gasoline blender and engine designers for their high octane number. The use of 10% ethanol will increase the octane value of a base gasoline from 2.5 to 3 octane points. [5]

The octane numbers of methanol and ethanol are listed in Table 2-3. The difference between the research and motor octane numbers is commonly taken as an indication of fuel sensitivity to changes in engine conditions. By this measure (106-92=14 octane numbers for methanol), these fuels are sensitive to changes in engine conditions.

Energy Density

In chemistry, moles are used as the standard unit of measure and for comparison of compounds. However, for engineering purposes mass and stored volume are preferred over the molar basis for expressing energy quantities. Heat release is viewed in the positive

Table 2-3 -- Properties of Oxygenates, Gasoline, and No. 2 Diesel Fuel

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Formula	CH_3OH	C_2H_5OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$	$(CH_3)_3COCH_3$	$(CH_3)_2(C_2H_5)COCH_3$	C_4 to C_{12}	C_8 to C_{25}
Molecular weight	32.04	46.07	60.09	74.12	88.15	102.18	100-105[a]	200 (approx.)
Composition, weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	85-88[a]	84-87
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	12-15[a]	13-16
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	0	0
Specific gravity, 60°F/60°F	0.796[b]	0.794[b]	0.789[b]	0.791[b]	0.744[n]	0.77[o]	0.72-0.78[a]	0.81-0.89[c]
Density, lb/gal @60°F	6.63[a]	6.61[a]	6.57[a]	6.59[a]	6.19[n]	6.41[o]	6.0-6.5[a]	6.7-7.4[c]
Boiling temperature, °F	149[b]	172[b]	180[b]	181[b]	131[b]	187[o]	80-437[a]	370-650[c]
Reid vapor pressure, psi	4.6[p]	2.3[p]	1.8[p]	1.8[p]	7.8[d]	1.5[o]	8-15[f]	< 0.2
Octane no. (see note 1)								
Research octane no.	106	106	---	---	117	108	88-98[f]	---
Motor octane no.	90	89	---	---	102	96	80-88[f]	---
Cetane no. (see note 1)	3	8	---	---	---	---	14	40-55
Water solubility, @70°F								
Fuel in water, volume %	100[b]	100[b]	100[b]	100[b]	4.3[b]	---	Negligible	Negligible
Water in fuel, volume %	100[b]	100[b]	100[b]	100[b]	1.4[d]	0.6[o]	Negligible	Negligible
Freezing point, °F	-143.5[b]	-173.2[b]	-127.3[b]	78.0[b]	-164.[b]	---	-40[f]	-40-30[f]
Refractive index, n_D@68°F	1.3286[b]	1.3614[b]	1.3772[b]	1.3838[b]	1.3689[b]	---	1.4-1.5[g]	1.4-1.5[g]
Viscosity								
Centipoise @68°F	0.59[k]	1.19[k]	2.38[k]	4.2 @ 78°F[k]	0.35[k]	---	0.37-0.44[e,q]	2.6-4.1
Centipoise @-4°F	1.15[k]	2.84[k]	9.41[k]	Solid[k]	0.60[k]	---	0.60-0.77[e,q]	9.7-17.6
Coefficient of expansion, @60°F 1 atmosphere, per °F	0.00067[j,a]	0.00062[j,a]	---	---	0.00078[d]	---	0.00067[e]	0.00046
Electrical conductivity, mhos/cm	4.4×10^{-7}[h]	1.35×10^{-9}[h]	---	---	---	---	1×10^{-14}[h]	1×10^{-12}
Flash point, closed cup, °F	52[p]	55[p]	53[p]	52[p]	-14[d]	---	-45[a]	165[c]
Autoignition temperature, °F	867[a]	793[a]	750[a]	892[a]	815[d]	---	495[a]	600 (approx.)
Flammability limits, volume %								
Lower	7.3[p]	4.3[p]	2.0[p]	2.4[p]	1.6[d,j]	---	1.4[a]	1.0
Higher	36.0[p]	19.0[p]	12.0[p]	8.0[p]	8.4[d,j]	---	7.6[a]	6.0
Latent heat of vaporization								
Btu/gal @60°F	3,340[a]	2,378[a]	2,100[b]	1,700[b]	863[f]	---	900 (approx.)[a]	710 (approx.)
Btu/lb @60°F	506[a]	396[a]	320[b]	258[b]	138[f]	---	150 (approx.)[a]	100 (approx.)
Btu/lb air for stoichiometric mixture @ 60°F	78.4[a]	44.0[a]	31.1[b]	23.2[b]	11.8	---	10 (approx.)[a]	8 (approx.)

Table 2-3 -- Continued

Property	Methanol	Ethanol	IPA	TBA	MTBE	TAME	Gasoline	No. 2 Diesel Fuel
Heating value (see note 2)								
Higher (liquid fuel-liquid water) Btu/lb	9,750^{a}	12,800^{a}	14,500^{g}	15,500^{g}	18,290^{g}	---	18,800-20,400	19,200-20,000
Lower (liquid fuel-water vapor) Btu/lb	8,570^{a}	11,500^{a}	13,300^{g}	14,280^{g}	15,100^{g}	15,690^{o}	18,000-19000	18,000-19,000
Lower (liquid fuel-water vapor) Btu/gal @60°F	56,800^{i}	76,000^{i}	87,400^{i}	94,100^{i}	93,500^{i}	100,600^{i}	109,000-119,000	126,000-130,800
Gaseous fuel-water vapor Btu/lb @60°F	9,080^{a}	11,900^{a}	---	---	---	---	19,000-19,300	---
Heating value, stoichiometric mixture								
Mixture in vapor state, But/cubic foot @68°F	94.5^{a}	94.7^{a}	---	---	---	---	95.2^{a}	96.9^{c,s}
Fuel in liquid state, Btu/lb of air	1,330^{a}	1,280^{a}	---	---	---	---	1,290^{a}	---
Specific heat, Btu/lb-°F	0.60^{k}	0.57^{k}	0.61^{k}	0.72^{k}	0.50^{k}	---	0.48^{l}	0.43
Stoichiometric air/fuel, weight	6.45^{i}	9.00^{i}	10.3^{i}	11.1^{i}	11.7^{i}	12.1^{i}	14.7^{i}	14.7
Volume % fuel in vaporized stoichiometric mixture	12.3^{a}	6.5^{a}	---	---	2.7^{j}	--	2.0^{a}	---
Ratio moles product/moles charge	1.06^{i}	1.07^{i}	1.07^{i}	1.07^{i}	10.7^{i}	1.07^{i}	1.05^{i,m}	1.06^{i,r}
Ratio moles product/moles $O_2 + N_2$	1.21^{i}	1.12^{i}	1.10^{i}	1.10^{i}	1.10^{i}	1.09^{i}	1.08^{i,m}	1.07^{i,r}

---

1. Laboratory engine Research and Motor octane rating procedures are not suitable for use with neat oxygenates. Octane values obtained by these methods are not useful in determining knock-limited compression ratios for vehicles operating on neat oxygenates and do not represent octane performance of oxygenates when blended with hydrocarbons. Similar problems exist for cetane rating procedures.

2. The higher value is cited for completeness only. Since no vehicles in use, or currently being developed for future use, have powerplants capable of condensing the moisture of combustion, the lower heating value should be used for practical comparisons between fuels.

[a] "Alcohols: A Technical Assessment of Their Application as Motor Fuels," API Publication No. 4261, July 1976.

[b] Handbook of Chemistry and Physics, 62nd Edition, 1981, The Chemical Rubber company Press, Inc.

[c] "Diesel Fuel Oils, 1987," Petroleum Product Surveys, National Institute for Petroleum and Energy Research, October 1987.

[d] ARCO Chemical Company, 1987.

[e] "MTBE, Evaluation as a High Octane Blending Component for Unleaded Gasoline," Johnson, R. T., Taniguchi, B. Y., Symposium on Octane in the 1980's, American Chemical Society, Miami Beach Meeting, September 10-15, 1979.

[f] "Status of Alcohol Fuels Utilization Technology for Highway Transportation: A 1981 Perspective," Vol. 1, spark-Ignition Engine, May 1982, DOE/CE/56051-7.

[g] API Research Project 44, NBS C-461.

[h] Lang's Handbook of Chemistry, 13th Edition, McGraw-Hill Book Company, New York, 1985.

[i] Calculated.

[j] Pour Point, ASTM D 97 from Reference c.

[k] "Data Compilation Tables of Properties of Pure Compounds," Design Institute for Physical Property Data, American Institute of Chemical Engineers, New York, 1984.

[l] Petroleum Product Surveys, Motor Gasoline, Summer 1986, Winter 1986/1987, National Institute for Petroleum and Energy Research.

[m] Based on isooctane.

[n] API Monograph Series, Publication 723, "Tert-Butyl Methyl Ether," 1984.

[o] BP America, Sohio Oil Broadway Laboratory.

[p] API Technical Data Book -- Petroleum Refining, Volume I, Chapter I. Revised Chapter I to first, Second, Third, and Fourth Editions, 1988.

[q] "Automotive Gasolines," SAE Recommended Practice, J312 May 1986, 1988 SAE Handbook, Volume 3.

[r] Based on cetane.

[s] "Internal Combustion Engines and Air Pollution," Obert, E. F., 3rd Edition, Intext Educational Publishers, 1973.

sense, with this quantity generally referred to as the calorific value. But on a mass basis, the term "specific energy" in units of Btu/lb is used and, on a volume basis, the term "energy density" (energy per unit volume) is adopted in units of Btu/gallon.

Policy Issue #3

Because of their lower calorific value, alcohol fuels generally have a lower energy density than gasoline. This is a major consideration in the design of neat alcohol vehicles, since they will need larger storage tanks if they are to have the same range per tankful as gasoline-powered automobiles. However, this is offset slightly by the higher efficiency and octane of these fuels.

Energy density for methanol, ethanol and gasoline is listed in Table 2-3.

Efficiency and Performance

When blended with gasoline in proportions of up to 25% (by volume), the greater volumetric efficiency and higher octane number of ethanol offset its lower calorific value (26.6 MJ/kg versus 44.0 MJ/kg for gasoline). At blends above 25%, the engine's power and fuel consumption begin to be affected. Nevertheless, higher percentages of alcohol in motor fuels are feasible via a lean limit control system. This system requires some electronic sensing and engine modification. [6] With specially designed engines, pure alcohol delivers 18% more power per litre than gasoline, but it is consumed at a rate which is 15-20% higher than gasoline. Therefore, from an energy point of view, the two factors effectively cancel, leaving neither fuel with a clear advantage.

Boiling Point

As shown in Table 2-4 [7], alcohols have much higher boiling points than comparable hydrocarbons. This is due to the strong hydrogen bond, which contributes to increasing the molecular mass of alcohols. Since boiling of a liquid depends on the separation of molecules as they move from the liquid to the gas phase, more energy (a higher temperature) is required to break the hydrogen bond among alcohol molecules to accomplish the phase change.

As shown in Figure 2-2 [8], gasoline is composed of a number of compounds having boiling points ranging from approximately 27-225°C (80-437°F). Unlike gasoline, methanol and ethanol are single compounds that boil at 64.7°C (149°F) and 78.3°C (173°F), respectively. In fuel applications, alcohols lack the light fractions with boiling points near 38°C (100°F) which are essential for starting spark-ignited engines in severe cold.

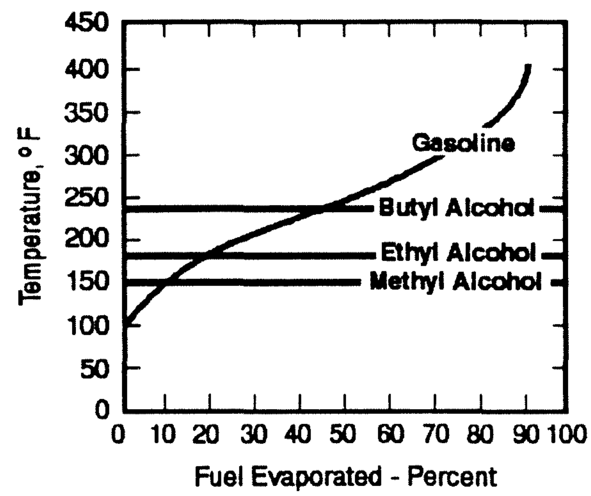


Figure 2-2., ASTM distillation curves for gasoline and alcohol.

Table 2-4. **Comparison of Some Physical Properties of Alcohols and Hydrocarbons of Similar Molecular Weight**

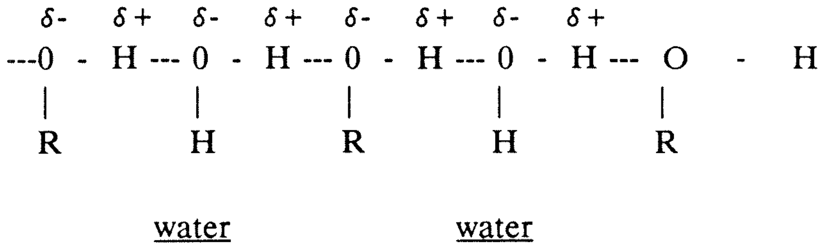
Alcohol		Hydrocarbon				
Name	Formula	Name	Formula	Molecular Weight*	Boiling Point °C	Melting Point °C
Methanol	CH_3OH			32	65	-98
		Ethane	CH_3CH_3	30	-89	-172
Ethanol	CH_3CH_2OH			46	78.5	-117.3
		Propane	$CH_3CH_2CH_3$	44	-42.2	-189.9
Propanol	$CH_3CH_2CH_2OH$			60	-97.2	-127
		Butane	$CH_3(CH_2)_2CH_3$	58	-0.6	-135
Pentanol	$CH_3(CH_2)_3CH_2OH$			88	138	-79
		Hexane	$CH_3(CH_2)_4CH_3$	86	69	-95
Decanol	$CH_3(CH_2)_8CH_2OH$			158	228	6
		Undecane	$CH_3(CH_2)_9CH_3$	156	196	-26

---

*Molecular weight is the sum of the atomic weights that make up a molecule. Atomic weight is the average mass of the atoms of a given element, relative to the mass of a carbon-12 atom, which is taken to be exactly 12.

Solubility in Water

The hydroxyl group of an alcohol molecule is capable of forming a strong hydrogen bond with a molecule of water:



$$\begin{array}{cccccccccccccccccccc}
 & \delta- & & \delta+ & & \delta- & & \delta+ & & \delta- & & \delta+ & & \delta- & & \delta+ & & & & \\
--- & 0 & - & H & --- & 0 & - & H & --- & 0 & - & H & --- & 0 & - & H & --- & O & - & H \\
 & | & & & & | & & & & | & & & & | & & & & | & & \\
 & R & & & & H & & & & R & & & & H & & & & R & & \\
 & & & & & \underline{\text{water}} & & & & & & & & \underline{\text{water}} & & & & & &
\end{array}$$

Consider the methanol molecule: the hydroxyl group alone accounts for about half of the total molecular weight. Therefore, methanol will be completely soluble in water, as noted earlier in Table 2-2.

Policy Issue #4

> Ethanol and propanol and other low molecular weight alcohols are completely soluble in water. This strong affinity for bonding with water is one of the most striking characteristics of low molecular weight alcohols. In neat alcohol fuels, the tendency to absorb water has some operational characteristics (primarily in fuel-line freezing in very cold weather. In low-level alcohol/gasoline blends, however, small amounts of water will cause the mixture to separate into distinct phases. This is a problem not only for vehicle driveability, but for the bulk storage and shipping of the blended fuel. Current gasoline storage tanks and pipeline facilities contain small but significant levels of water, making them unsuitable for alcohol/gasoline blends.

In alcohol molecules with longer hydrocarbon chains, the hydroxyl group represents a smaller fraction of the total molecular weight. Therefore, the solubility of alcohols in water gradually decreases as the hydrocarbon portion of the molecule lengthens, as shown earlier in Figure 2-1. As a matter of fact, long-chain alcohols are more "alkane-like" and therefore are less like water. As a result, long-chain alcohols such as iso-propanol, 1-butanol, n-decanol, etc., can be used as additives to prevent phase separation in methanol/gasoline and ethanol/gasoline blends.

Latent Heat of Vaporization

Fuel is usually supplied to the engine manifold and air stream in liquid form. It is heated there and converted to a vapor prior to combustion. The latent heat of vaporization is the amount of heat required to vaporize a unit quantity of a fuel, generally measured at one atmosphere of pressure and at the boiling point of the liquid. The latent heat of vaporization of gasoline is approximately 900 Btu/gal. The vaporization of gasoline in a stoichiometric mixture of liquid gasoline and air (without external heating) results in an air temperature reduction of approximately 22°C (40°F).

Policy Issue #5

The latent heat of vaporization of methanol and ethanol are 3,340 and 2,378 Btu/gal., respectively; several times that of gasoline. Therefore, vaporization of these fuel alcohols produces a much larger temperature drop. However, with the same heat addition per unit mass of charge, the percent of the alcohol evaporated in the manifold will also be less. Because of its greater evaporative cooling effect, alcohol reduces the charge temperature and thus usually improves the engine volumetric efficiency.

Alcohols have a much lower molecular weight than gasoline, and therefore their vapor occupies proportionately more volume than an equal mass of gasoline vapor. It is the high latent heat of vaporization which is primarily responsible for the increased power outputs with alcohol, and which leads to the popularity of methanol as a blending constituent for automobile racing fuels. The latent heats of vaporization of gasoline, methanol and ethanol are shown in Table 2-3.

Stoichiometric Air/Fuel Ratio

When the fuel and air react in an engine cylinder to produce combustion products, the number of moles of product is different than the number of moles of reactant. For example, consider the complete combustion of ethanol with the stoichiometric (chemically correct) amount of air:

$$\begin{array}{ccccccccccc} \text{Ethanol} & + & \text{Oxygen} & + & \text{Nitrogen} & \rightarrow & \text{Carbon Dioxide} & + & \text{Water} & + & \text{Nitrogen} \end{array}$$

$$C_2H_5OH + 30_2 + 3\,(79/21)\,N_2 \rightarrow 2\,CO_2 + 3H_20 + 3 \times 3.76N_2$$

$$\begin{array}{llllllll} \text{Moles:} & 1 & +\,3 & +\,11.3 & \rightarrow 2 & + & 3 & +\,11.3 \\ & \Sigma & = & 15.3 & \Sigma & & = & 16.3 \\ & & & & & & & \\ \text{Weights:} & 46 & +\,96 & +\,316 & \rightarrow 88 & + & 54 & +\,316 \\ & \Sigma & = & 458 & \Sigma & & = & 456 \end{array}$$

The $\frac{\text{lb air}}{\text{lb fuel}} = \frac{412}{46} = 9.0$

This combustion reaction is exothermic and results in the liberation of 11,911 Btu/lb of ethanol burned from the vapor state. For the quantities represented by the combustion equation, the energy release by the ethanol in vapor state is 11,911 Btu/lb x 46lb /mol. = 548,000 Btu/mol. The energy release per standard cubic foot of stoichiometric volume, will be:

$$\frac{548{,}000 \text{ Btu/mol. ethanol}}{(1 + 3 + 11.3) \text{ mols. reactants} \times 378 \frac{\text{std. ft}^3}{\text{mol.}}}$$

$$= 94.7 \text{ Btu/ft}^3$$

From Table 2-3, the energy release per cubic foot of methanol (in vapor state) is nearly the same: 94.5 Btu/ft^3. The value for octane vapor is 95.4 Btu/ft^3. For gasoline, the energy release will vary quite a bit for different gasolines, but the average value is almost the same as that for ethanol. Therefore, it is interesting that gasoline and alcohols, which in many aspects are quite different, have nearly equal energy of combustion per unit volume of stoichiometric mixture. From this we may conclude that these fuels used in an engine under the same conditions with the same fraction of the stoichiometric mixture and fully vaporized fuel, will produce nearly the same power.

When compared to methanol and gasoline, ethanol is the fuel producing the largest number of moles of product per mole of reactant and will produce the greatest pressure in the cylinder after combustion. The greater pressure taken alone would result in an increase in engine power. [9]

However, a modern engine may not (and usually does not) ingest its mixture with the fuel already evaporated. In fact, the fuel may even be entirely liquid, as in the case of direct injection engines.

Under such conditions, the number of moles of product should be examined on the basis of the number of moles of air inducted since the fuel occupies very little of the volume. When the fuel enters the cylinder in the liquid state, we find enhanced power output from methanol and a slightly increased output from ethanol when compared with gasoline. Similar calculations were made for methanol, gasoline, isooctane and benzene, and the resultant stoichiometric data are compiled in Table 2-5. [10]

Table 2-5. Combustion of Alcohols and Hydrocarbons in Air

Fuel	Reaction Equation	Stoichiometric Air-Fuel Ratio (Lb./Lb.)	Volume % Fuel In Vaporized Stoichiometric Mixture	Ratio Moles Product Moles Charge	Ratio Moles Product Moles $O_2 + N_2$
Methanol	$CH_3OH + 1.5O_2 + 5.66N_2 =$ $CO_2 + 2H_2O + 5.66N_2$	6.45	12.3	1.061	1.209
Ethanol	$C_2H_5OH + 3O_2 + 11.3N_2 =$ $2CO_2 + 3H_2O + 11.3N_2$	9.00	6.5	1.065	1.140
Benzene	$C_6H_6 + 7.5O_2 + 28.3N_2 =$ $6CO_2 + 3H_2O + 28.3N_2$	13.2	2.7	1.014	1.042
Isooctane	$C_8H_{18} + 12.5O_2 + 47.2N_2 =$ $8CO_2 + 9H_2O + 47.2N_2$	15.1	1.6	1.058	1.075
Gasoline	$C_nH_{2n} + 1.5nO_2 + 5.66nN_2 =$ $nCO_2 + nH_2O + 5.66nN_2$	14.7	2.0	1.047	1.070

ENDNOTES:

1. Solomons, T.W.G. *Organic Chemistry*. 4th Ed. John Wiley & Sons, Inc., pp. 349-393, 1988.

2. Pine, S.H., J.B. Hendrickson, D. J. Cram, and G.S. Hammond. *Organic Chemistry*. 4th Ed. McGraw Hill Book Co., pp. 44-48, 1980.

3. Roberts, John D., and Marjorie C. Caserio. *Organic Chemistry*. French Edition by J.M. Conia, Paris, Ediscience, pp. 294-302, 1967.

4. American Petroleum Institute, "Alcohols: A Technical Assessment of Their Application as Fuels," API Publication No. 4261, Second Edition, July 1988.

5. Johnson, Larry. "Vehicle Performance and Air Quality Issues of 10% Ethanol and 90% Gasoline Blends." Paper presented at the "International Forum on Energy Engineering." The 24th Intersociety Energy Conversion Engineering Conference. Washington, D.C. August 6-11, 1989.

6. Rothman, Harry, Rod Greenshields, and Francesco Rosillo Calle. *Energy From Alcohol. The Brazilian Experience*. The University Press of Kentucky, Lexington, 1983.

7. Roberts, John D., op.cit.

8. Bolt, Jay A. "A Survey of Alcohol as a Motor Fuel." SAE/PT-80/19.

9. Wyman, Charles E., and Norman D. Hinman. "Ethanol: Fundamentals of Production from Renewable Feedstocks and Use as a Transportation Fuel." 11th EtOH. New/AP, 1990.

10. American Petroleum Institute, "Alcohols: A Technical Assessment of Their Application as Fuels." API Publication No. 4261, July 1976.

Section 3

THE INTERNAL COMBUSTION ENGINE

Quick Reference Data

In a spark-ignition (SI) engine, the fuel/air mixture is compressed to a pressure and corresponding temperature (400°-600°C) generally below its auto-ignition threshold, with the mixture being ignited by a spark shortly before the piston reaches top-dead-center.

In a compression-ignition (CI) engine, air is compressed to a sufficiently high temperature (700°-900°C) to cause auto-ignition of fuel upon injection into the cylinder shortly before the end of the compression stroke.

Principal Design Parameters for an SI Engine

- **Compression Ratio (CR):** increasing CR increases fuel economy with two drawbacks: increased tendency to knock and higher NO_x emissions.
- **Combustion Chamber Design:** recent research has focused on faster burning designs, i.e., compact chamber, centrally located spark plug, high turbulence swirl induction, and four/five valves per cylinder.
- **Valve Timing:** the opening and closing of the intake and exhaust valves for the exchange of gases in the cylinders of a four-stroke, internal combustion engine. Ideally, a larger valve overlap (a very short time in which both the intake and exhaust valves are slightly open) is needed at high speeds for performance, and a smaller overlap is needed at idle and slow engine speeds to lower emissions.
- **Fuel Management:** sequential port fuel injection has shown favorable results over carburetion when used in an alcohol-burning engine (especially for methanol) because the mean effective pressure and thermal efficiency improve significantly over most of the operating range.

The Key Operating Parameters for SI Engines

- **Equivalence Ratio:**
    - At lower equivalence ratios (lean burn conditions), engines operate more efficiently.
    - Lean burn conditions, while providing better thermal efficiency and lower hydrocarbon (HC) and CO emissions, produce higher NO_x emissions.

- **Spark Advance:** optimum spark setting will depend on rate of flame development and propagation and the length of the flame path across the combustion chamber.
    - As the spark is advanced, HC emissions increase up to the lean misfire limit.
    - As the timing is advanced, combustion temperature is increased and NO_x formation increases.
    - The influence of ignition timing on fuel consumption is opposite to the influence it exerts on pollutant emissions.
- **Exhaust Gas Recirculation (EGR):**
    - Increasing amount of EGR decreases NO_x emissions, but increases HC emissions and fuel consumption.
    - Increasing amount of EGR requires advancing the spark timing as the equivalence ratio decreases.

Key Design Parameters for Alcohol Combustion

- Higher octane
- Greater enthalpy of formation
- Lower flame temperature
- Extended lean limit of operation

Useful Terms and Definitions (also see Glossary)

- **Adiabatic:** occurring without loss or gain of heat.

- **Compression Ratio (CR):** the maximum cylinder volume divided by the minimum cylinder volume.

- **Enthalpy Requirement:** the additional heat input required by the engine's fuel induction system to achieve the required degree of fuel vaporization for smooth operation.

- **Equivalence Ratio:** measure of the actual fuel/air mixture to the stoichiometric fuel/air ratio.

- **Exhaust Gas Recirculation (EGR):** the recirculation of exhaust gases to the combustion chamber to reduce the peak combustion temperature for the reduction of NO_x emissions.

- **Maximum Brake Torque (MBT)**: the timing associated with a particular fuel for a particular combustion chamber; aside from the fuel/air mixture, the moment of ignition has the greatest influence on pollutant emissions.

- **Octane**: identifies the ability of a fuel to resist spontaneous combustion or pre-ignition; the higher the octane the less likely that a fuel will prematurely ignite (knock).

- **Spark Advance:** the optimal spark setting, an operating parameter dependent on the rate of flame development and propagation within the combustion chamber.

- **Stoichiometry** (of fuel/air): the proportion required between fuel and air for a specific fuel to allow complete combustion of the chemical reactions to occur (i.e., the proportions that are exactly right).

Key Issues and Implications

Issues and Implications

Issue #1: *Optimization of Spark Ignition Engines for Alcohol Fuels by Increasing Compression Ratios (CRs).*

Increasing the compression ratio increases fuel economy by improving thermal efficiency. Because of their higher octane ratings and lean burn characteristics, alcohol fuels allow the use of higher CR.

Implications of Higher Compression Ratios (Regardless of Fuel Used):

- Higher fuel economy
- Increased tendency to knock
- Higher temperature in the combustion chamber, resulting in lower HC and CO emissions and higher NO_x formation.

Proposed Solutions:

- By increasing the volumetric content of alcohol in gasoline, an engine can operate at higher CRs without knock. Dedicated alcohol engines have been found to operate smoothly at CRs of up to 12.5 - 13.5, while production gasoline engines are limited to CRs of 8-12.
- Alcohols have inherently lower flame temperatures than gasoline and, under lean burn conditions, tend to produce less NO_x.

Detailed Information: Refer to pages 3-3 and 3-4.

Issue #2: *The Opportunities for Optimized Engine/Vehicle Design Provided by the Inherent Characteristics of Alcohol Fuels*

Alcohol fuels have a number of characteristics which can improve the performance of internal combustion engines. Relative to gasoline, methanol and ethanol have higher octane ratings, greater heat of vaporization, and lower flame temperatures. They have also been shown to possess an extended lean limit of operation.

Implications of Unique Characteristics of Alcohol Fuels:

- The use of alcohol fuels in production vehicles designed for gasoline will not take full advantage of the beneficial characteristics of those fuels.
- A flexible fuel vehicle (FFV), by definition, must be designed as a compromise between the characteristics of gasoline and alcohol, and may not optimize the use of either fuel.

Proposed Solutions:

- To achieve the maximum benefits from alcohol fuels -- increased fuel efficiency, increased power, and reduced emissions -- the vehicles and vehicle engines should be redesigned to operate on neat alcohol fuels or high alcohol/gasoline blends.
- FFVs should be considered, at best, as a temporary bridge to dedicated fuel vehicles.

Detailed Information: Refer to pages 3-17 and 3-18.

Section 3
THE INTERNAL COMBUSTION ENGINE

- Engine Design
- Operating Parameters
- Key Design Parameters for Alcohol Combustion

Introduction

Internal combustion engines can be characterized by two primary design features: method of ignition and type of operating cycle. The method of ignition -- spark ignition or compression ignition -- dictates a host of other characteristics including the type of fuel used, the method of preparing the fuel/air mixture, the design of the combustion chamber and the combustion process, as well as load control, engine emissions and operating characteristics.

Recent alcohol fuel research conducted with particular engine types has varied considerably. Most research in the past five years has been conducted on four-stroke, spark-ignition engines operating on methanol blends, although considerable work has also been done on methanol-powered modified diesel prototypes to power mass transit buses because of reduced soot and particulate formation. [1] Work on test-bench, two-stroke spark ignition engines using methanol fuel has shown abnormal combustion (knock) characteristics even at low compression ratios and loads. [2]

The following discussion will focus on the operating characteristics of spark-ignited, four-stroke engines using alcohol fuels. These engines are the standard production engines used in passenger cars in the United States, and variations of these engines have been successfully used in Brazil for alcohol blends and neat fuels. Also, Compression Ignition (CI) or diesel engines cannot use alcohol fuels without ignition improvers or engine modifications, such as the addition of glow plugs, to assist combustion. Due to the limited amount of recent engine research available with ethanol, the data will focus on the use of methanol; however, because of the similarities between the two alcohol fuels, much of the research findings may also apply to ethanol.

Engine Design

In a spark-ignition (SI) engine, the fuel/air mixture is compressed to a pressure and corresponding temperature (400°-600°C) generally below its auto-ignition threshold. The mixture is then ignited by a spark shortly before the piston reaches top-dead-center (TDC). In a compression-ignition (CI) engine, air is compressed to a sufficiently high temperature (700°-900°C) to cause auto-ignition of the fuel upon injection into the cylinder shortly before the end of the compression stroke. [3] Fuels that are routinely used in SI engines generally have higher octane ratings[*] (see Section 2), while those used for CI engines have higher cetane ratings.[**]

Most internal combustion engines operate on the four-stroke cycle: each cylinder requires four strokes of its piston or two revolutions of the crankshaft to complete the sequence of events required to produce one power stroke. To obtain a higher power output from a given engine size, the two-stroke engine was developed. Each cylinder requires only two strokes of its piston or one revolution of the crankshaft to complete one power stroke. [4]

Automotive engine design requires tradeoffs between performance, emissions, and efficiency. Complete combustion is a theoretical concept that explains what *should* occur within the combustion chamber of an engine. Ideally, the products of that combustion process are carbon dioxide, water vapor, and nitrogen. Unfortunately, our inability to control combustion reaction rates over the wide ranges at which engines operate results in incomplete combustion and the formation of a broad range of pollutants. Since the mid-70s, catalytic converters have been employed in the United States to reduce the formation of pollutants by allowing combustion reactions to reach completion.

---

[*] A number that is used to measure the antiknocking properties of a liquid motor fuel.

[**] A measure of the ignition value of a diesel fuel.

The principal design parameters for a spark-ignition engine -- whether fueled by alcohol, alcohol-gasoline blends, or gasoline -- are compression ratio (CR), combustion chamber design, valve timing, and fuel management.

Compression Ratio

Compression ratio (CR) is defined as the maximum cylinder volume (when the piston is at the bottom of its reciprocating path) divided by the minimum cylinder volume (when the piston is at Top Dead Center or TDC). Increasing the compression ratio is a known method of increasing fuel economy by improving thermal efficiency. Because of their higher octane ratings, alcohol fuels allow the use of higher compression ratios. However, the introduction of high compression ratios has two potential drawbacks: an increased tendency to knock and higher NO_x emissions. [5] Alcohol blends can help solve the problem of knock at elevated compression ratios. Using a variable-compression ratio, single-cylinder engine, the effect of methanol content on the knock-limited compression ratio (KLCR) is shown below in Figure 3-1. [6]

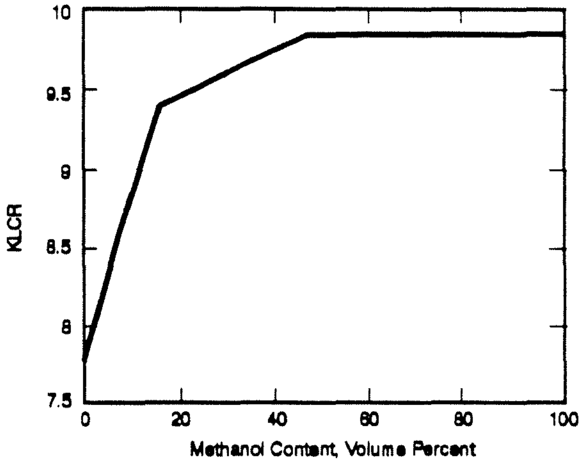


Figure 3-1., The effect of methanol content on Knock Limited Compression Ratio (KLCR).

Policy Issue #1

Because of their higher octane ratings and lean burn characteristics, alcohol fuels allow the use of higher compression ratios.

As the volumetric content of ethanol or methanol in the gasoline blend is increased, the engine can operate at higher CRs without knock. [7] Current gasoline passenger automobile engines produced in the United States have CRs ranging from 8-12 with race engines limited to 14. Dedicated alcohol engines have been found to operate smoothly at CRs up to 12.5-13.5 [8,9], although alcohol-fueled racing engines have been shown to withstand CRs up to 18. [10] As the CR is increased, the temperature in the combustion chamber increases, resulting in increased NO_x formation. However, as shown in Figure 3-2 [11], methanol has inherently lower flame temperatures than gasoline, and therefore tends to produce less NO_x.

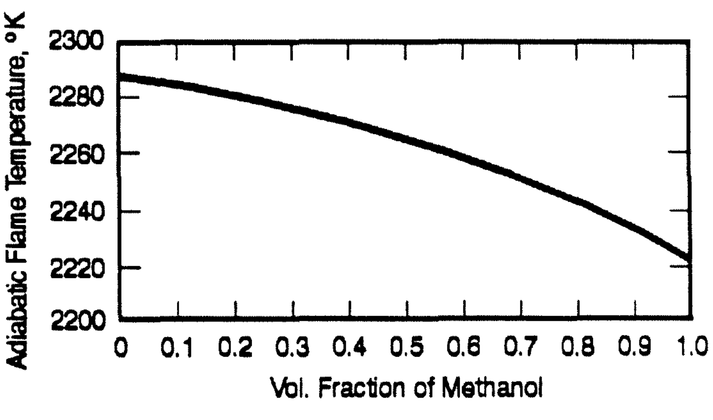


Figure 3-2., Adiabatic flame temperatures of indolene-methanol blends.

Combustion Chamber Design

Alcohol fuels, alcohol/gasoline blends, and gasoline can be burned in the same SI engine designs. There has been continuing debate among researchers over the optimum SI engine combustion chamber design for alcohol fuels. Recent innovations have focused on faster burning designs -- i.e., compact chambers, centrally located spark plugs, high turbulence swirl induction, and four and five valves per cylinder. A faster burning chamber with its shorter burn time permits operation with more excess air or leaner mixtures, and provides a more repeatable combustion pattern, thus providing lower cycle-by-cycle variability over the entire operating range. [12] A four or five valve per cylinder engine reveals flow areas quicker than a two valve for cylinder engine. Two or three valves have more perimeter than a single large one of equal area, and flow at low lift is proportional to perimeter. The influence of spark-plug position and 4-valve designs on fuel consumption and HC emissions is shown in Figure 3-3. [13]

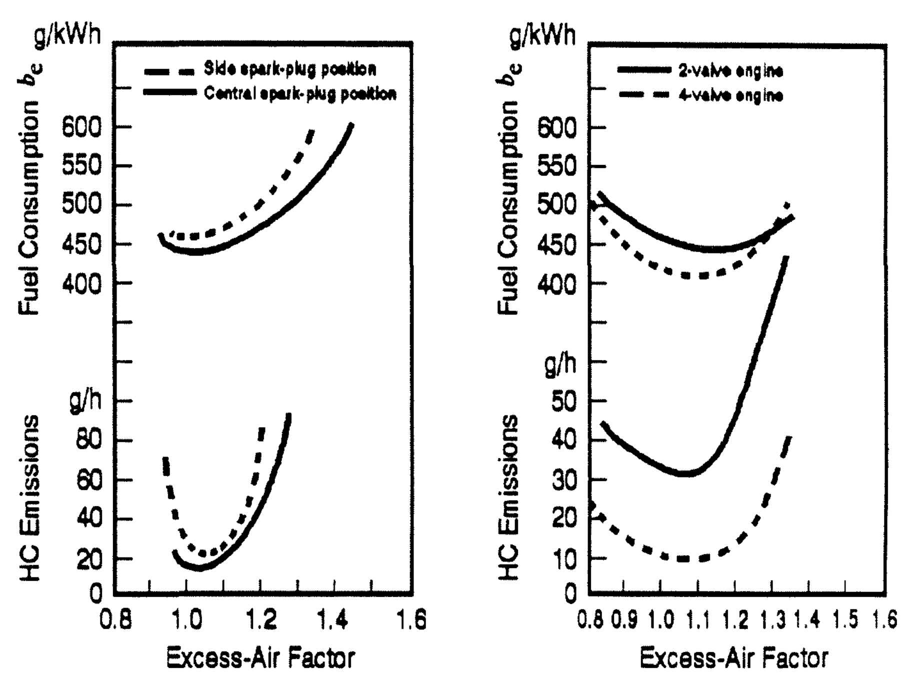


Figure 3-3., Influence of spark-plug location and valve configuration on fuel consumption and HC emissions.

Because of their ability to create more turbulence, compact chamber designs reduce the octane requirements of the fuel, therefore allowing higher compression ratios to be used resulting in lower unburned HCs and increased thermal efficiency. Because methanol has a faster burning velocity than gasoline as well as operating efficiently at higher compression ratios, it shortens the burn time and extends the stable operating limit regardless of combustion chamber geometry. Figure 3-4 [14] compares the faster laminar burning velocity of methanol to indolene, a common test reference gasoline.

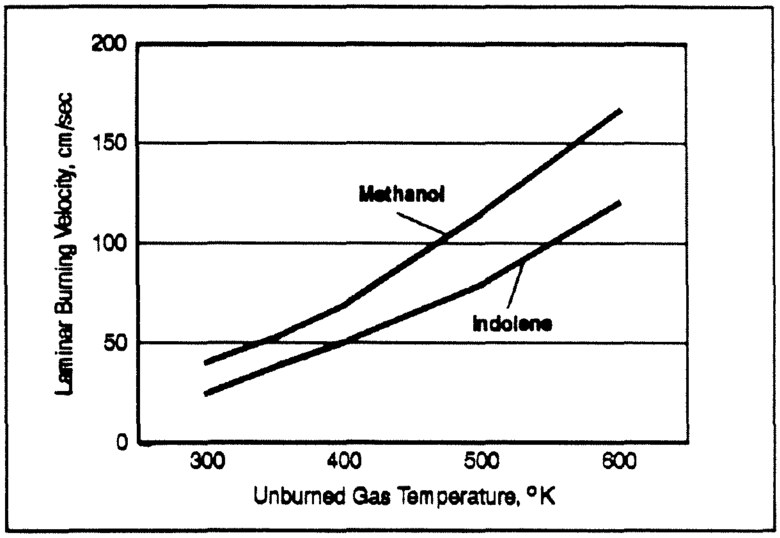


Figure 3-4., Experimental laminar burning velocities for methanol/ and indolene/air mixtures.

Valve Timing

The exchange of burned gas in the cylinder for fresh mixture occurs through the alternate opening and closing of the inlet and exhaust valves. The effect of changing an engine's valve timing for optimizing performance with alcohol fuels has not been thoroughly researched. The camshaft dictates the valve timing, i.e., the timing of opening and closing the valves in relation to each other. There is a short period of time near the beginning of the intake stroke in which the intake and exhaust valves are both slightly open called overlap, during which the residual gas content is determined. The residual gas content is the burned gas remaining in the cylinder that is not expelled while the exhaust valve is open. The amount of residual gas content has a direct effect on efficiency and the level of HC emissions. The residual gas content along with the exhaust gas recirculation (EGR) (used to control NO_x), effectively determine the stable operating limit of a particular engine. [15] The use of methanol allows greater tolerance to EGR and extends the stable operating limit of the engine. [16,17] Camshaft modifications to flatten the torque curve for methanol optimization have resulted in decreases in fuel economy. [18] On most cars, the valve timing is optimized for one engine speed, causing the rate of formation of HC pollutants and the volumetric efficiency to vary with engine speed. However, both Acura and Nissan [19] have produced cars with engines that incorporate variable valve timing. Although the two approaches are substantially different, the effects are the same: a large valve overlap at high engine speeds for power and a small overlap at low engine speeds for lower unburned hydrocarbon emissions, smoother idle, and improved fuel economy. For further information on valve timing research, refer to [20,21].

Fuel Management

Sequential port fuel injection has demonstrated superior fuel management characteristics versus carburetion when used on an alcohol-burning engine. This is true for both methanol and ethanol. As shown in Figure 3-5 [22], the mean effective pressure and the thermal efficiency improve significantly over most of the operating range. The higher constant thermal efficiency observed is typical of fuel injections' ability to extend maximum efficiency through a greater portion of the operating range.

The behavior exhibited above is typical of gasoline engines as well. However, because of methanol's much lower heating value it requires much higher mass flow rates for a stoichiometric air/fuel mixture than does gasoline. Due to the increased fluid flow through the intake manifold, more liquid methanol forms films on the intake manifold walls causing worse mal-distribution problems than are encountered with gasoline. [23] Ethanol's heating value

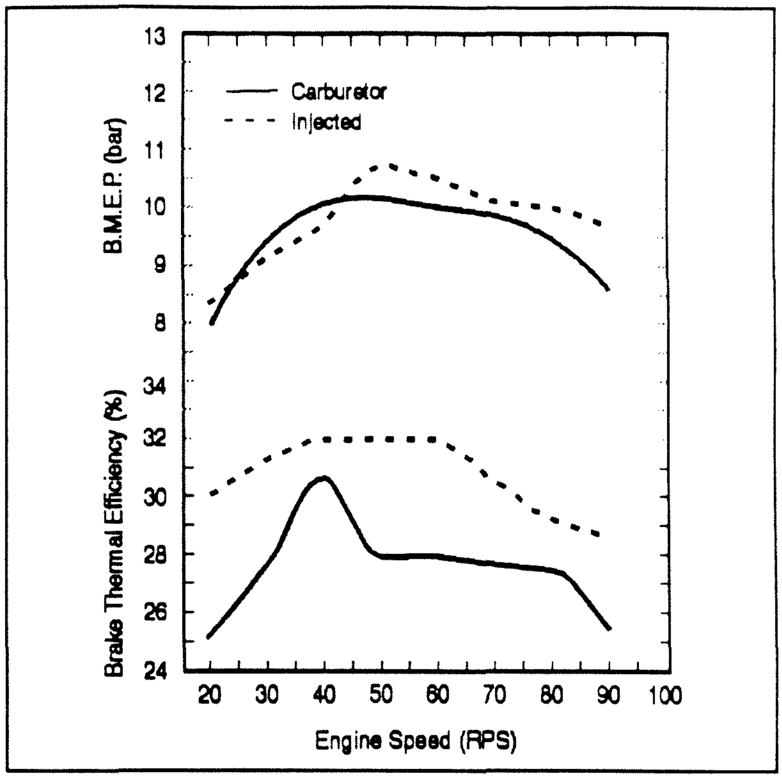


Figure 3-5., Comparison between carburetor and sequential fuel injection.

lies between that of methanol and gasoline. Because the use of ethanol requires less of a fuel flow increase than methanol, the positive effect of port fuel injection is thought to be greater for methanol than ethanol. The higher thermal efficiency for fuel injection shown above in Figure 3-5 [24] is attributed to better fuel distribution between cylinders.

Operating Parameters

The operating parameters for a SI engine vary according to its specific design and are very closely related to one another. Compromises exist between design goals and it becomes necessary to optimize accordingly. Some engines have been designed using lean-burn strategies to minimize HC and CO emissions while reducing fuel consumption while others are built strictly for performance. Catalytic after-treatment of exhaust is vital to ensure that emissions are kept to an absolute minimum. Because of the key role played by the catalytic converter in engine emission clean-up, it becomes necessary to separate emissions into two categories: "engine out" emissions and tailpipe emissions (after the catalyst). The key operating parameters are **equivalence ratio**, **spark advance** and **exhaust gas recirculation.** It is important to realize that the parameters are closely interrelated. Performance of a particular parameter can be compared by examining their effects on the specific fuel consumption, thermal efficiency, and torque.

Equivalence Ratio

The equivalence ratio (ϕ) is a measure of the actual fuel/air mixture $(F/A)_{actual}$ to the stoichiometric fuel/air ratio $(F/A)_s$. **Stoichiometry** is the proportion required between fuel and air for a specific fuel to allow complete combustion of the chemical reactions to occur. The excess air ratio is also used and is inverse of the equivalence ratio (ϕ^{-1}). Its purpose is to describe whether the engine is operating on a lean or rich fuel/air mixture. Both are defined below: [25]

Equivalence Ratio $$\phi = \frac{(F/A)_{actual}}{(F/A)_s}$$

Excess Air Ratio $$\lambda = \phi^{-1} = \frac{(A/F)_{actual}}{(A/F)_s}$$

For fuel-lean mixtures:	$\phi < 1, \lambda > 1$
For stoichiometric mixtures:	$\phi = \lambda = 1$
For fuel-rich mixtures:	$\phi > 1, \lambda < 1$

At lower equivalence ratios or lean burn conditions, engines operate more efficiently. Because of their oxygenated composition, alcohol fuels and alcohol-based ethers allow the use of leaner equivalence ratios. Figure 3-6 [26] shows the relation between equivalence ratio and thermal efficiency for methanol and gasoline.

The maximum efficiency attainable by a lean mixture of gasoline (27%) can be attained with rich mixtures of methanol. Work conducted on a test engine operating on ethanol produced similar results. [27] Because the efficiency values are measured at the fuel's knock limited compression ratio (KLCR), the second figure is included to discriminate between the effect of the fuel and the effect of KLCR on efficiency.

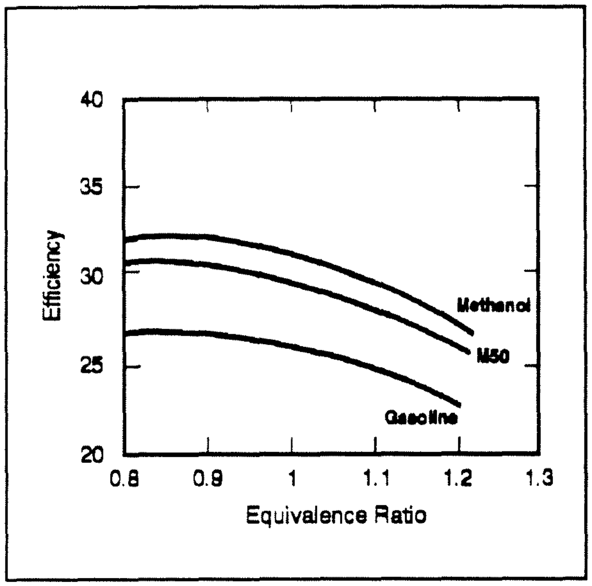


Figure 3-6-1., The effect of equivalence ratio and methanol content on brake efficiency.

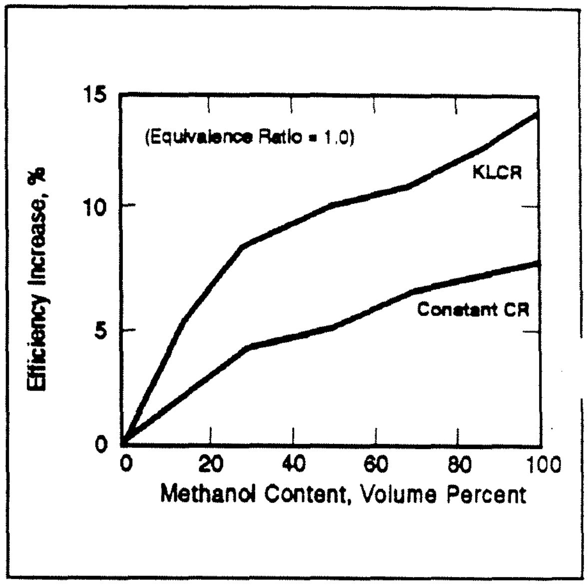


Figure 3-6-2., A comparison of efficiency increases due to methanol content at KLCR and constant CR.

Figure 3-7-1 [28] shows the relation between equivalence ratio and power for methanol and gasoline. The peak power achieved with gasoline was attained by the fuels containing methanol at much leaner conditions. Again, because an increase in compression ratio is accompanied by an increase in power, the right hand illustration in Figure 3-7-2 [29] shows the contribution of the compression ratio vs. the methanol fuel content.

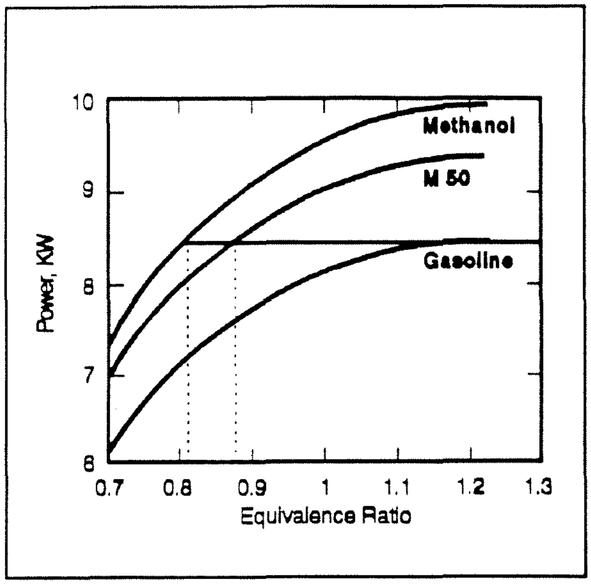


Figure 3-7-1., The effect of equivalence ratio and methanol content on power output.

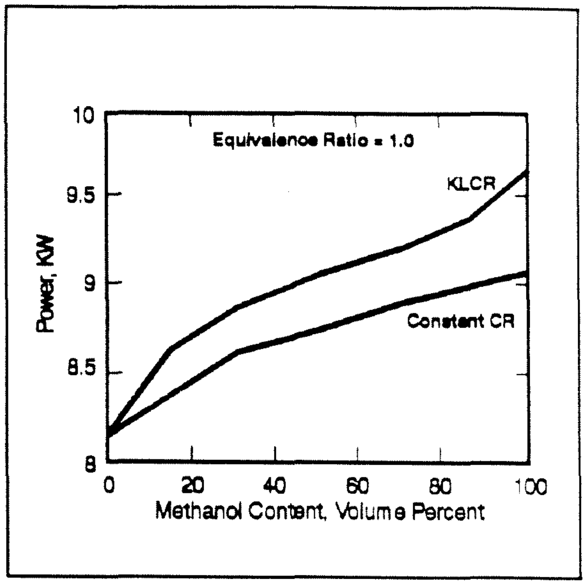


Figure 3-7-2., A comparison of power output due to methanol content at KLCR and constant CR.

One of the issues in modern engine design is the control of specific pollutants. Increasing the percentage of methanol and lowering the equivalence ratio decreases hydrocarbon and CO emissions but increases the creation of NO_x and formaldehyde, as can be seen in Figure 3-8. [30]

Lean burn strategies, while providing better thermal efficiency and lower hydrocarbon and CO emissions, produce higher NO_x emissions. Work conducted at Toyota has shown that using high swirl induction and lean burn with EGR to control NO_x is possible, at the expense of driveability. The Toyota researchers agree that additional experimentation is needed before these technologies are production-ready. [31]

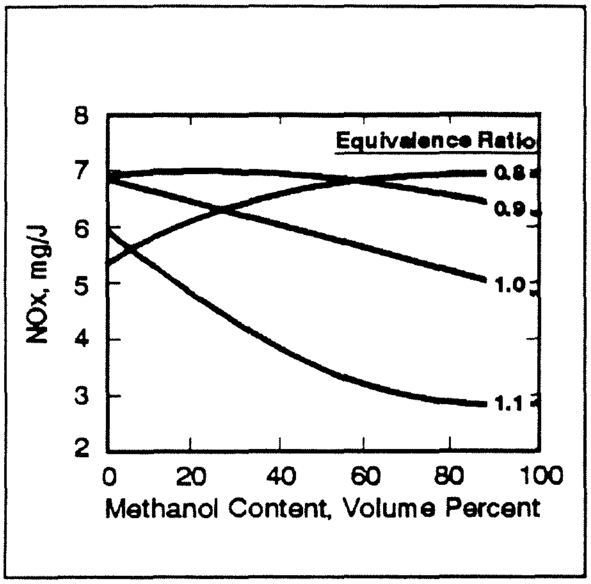


Figure 3-8-1., The effect of methanol content and equivalence ratio on NO_x emissions.

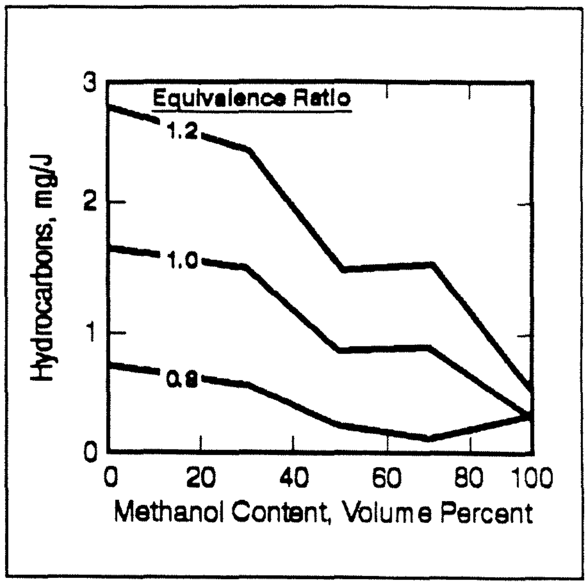


Figure 3-8-2., The effect of methanol content and equivalence ratio on HC emissions.

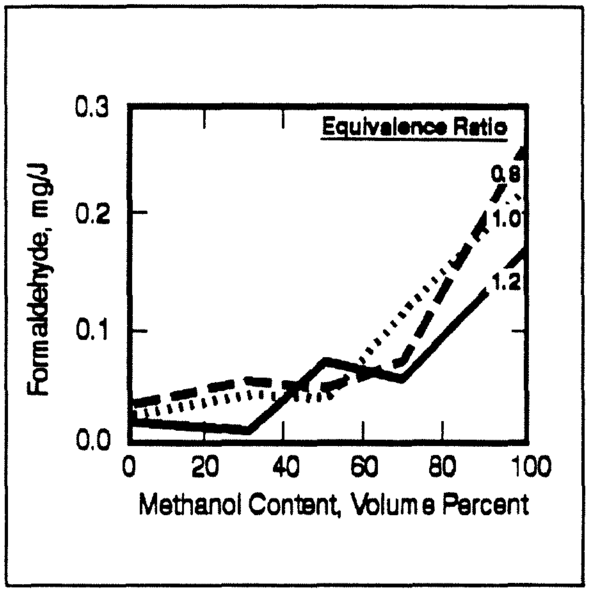


Figure 3-8-3., The effect of methanol content and equivalence ratio on formaldehyde emissions.

Spark Advance

The spark plug is fired before the piston reaches top dead center (TDC) on its compression stroke. The ignition point is presented as the "spark advance," in degrees of rotation of the crank shaft before TDC. Because of the time required for the flame development (combustion) process to build pressure in the cylinder, there is a maximum brake torque (MBT) timing associated with a particular fuel for a particular combustion chamber. [32] The optimum spark setting will depend on the rate of flame development and propagation and the length of the flame travel path across the combustion chamber. The use of both ethanol and methanol has shown to decrease the spark advance required for MBT. [33,34] As shown in Figure 3-9 [35] for methanol, as the percentage of alcohol increases in the gasoline/alcohol mixture, less spark advance is required and the MBT timing shifts toward Top Dead Center or TDC. This is an indication of methanol's higher burning velocity. In the drawing, DBTDC signifies Degrees Before Top Dead Center.

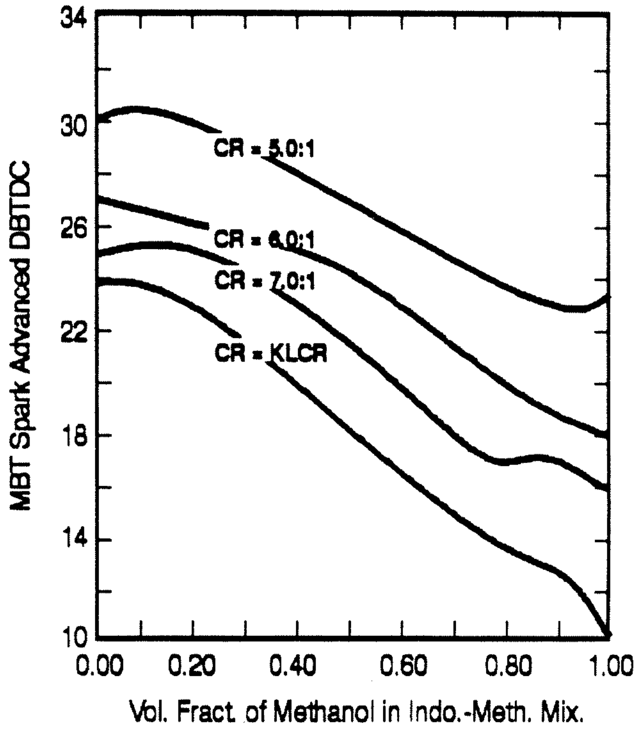


Figure 3-9., The effect of methanol content on MBT spark timing at different compression ratios.

The importance of proper ignition timing cannot be overemphasized. Aside from the fuel/air mixture, the moment of ignition has the greatest influence on pollutant emissions. As shown below in the set of drawings in Figure 3-10 [36], both HC and NO_x emissions are much higher at 50° before TDC than at 20°, for the range of equivalence ratios from 0.75 to 1.2. As the spark is advanced (away from TDC), HC emissions increase up to the lean misfire limit. As the timing is advanced, the combustion temperature is increased and NO_x formation increases. CO emissions are almost completely independent of ignition timing and are primarily a function of the fuel/air ratio.

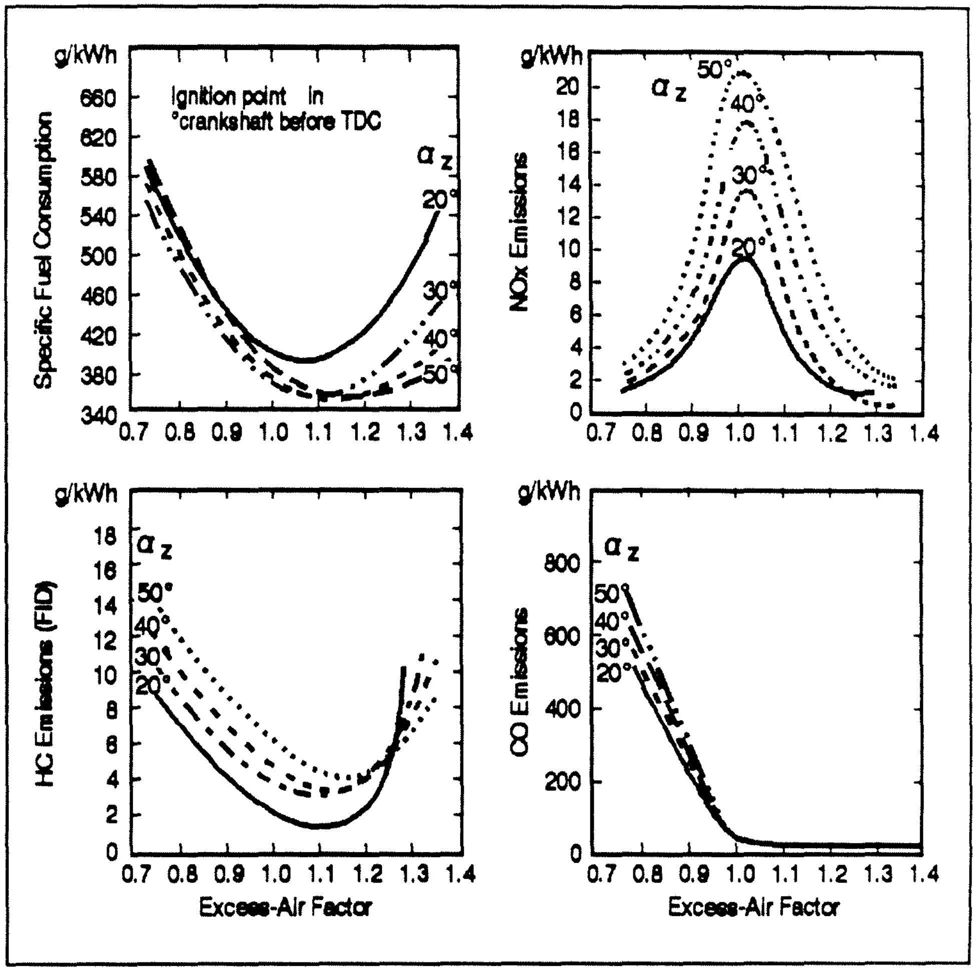


Figure 3-10., The influence of excess air ratio and ignition timing on pollutant emissions and fuel consumption.

The influence of ignition timing on fuel consumption is opposite to the influence it exerts on pollutant emissions. As the timing is advanced, specific fuel consumption goes down. At lean excess air ratios, the spark advance can be set for either high fuel efficiency or low emissions.

Exhaust Gas Recirculation (EGR)

EGR refers to the recirculation of exhaust gases to the combustion chamber to reduce the peak combustion temperature for the reduction of NO_x emissions. The lower flame temperature of alcohols produce less NO_x, reducing the EGR required for NO_x control. Because methanol is a faster burning fuel, its tolerance to EGR was theoretically found to be higher. [37,38] However, the reduction capabilities of NO_x with methanol were also found to be higher than gasoline. An actual prototype engine test revealed that 40% less EGR rate was needed with M-85 (85% methanol plus 15% gasoline) to achieve the same NO_x reduction as gasoline. [39] The maximum EGR rate in a gasoline or gasoline/alcohol fuel engine is limited by the increase in HC emissions that can be tolerated as well as the maximum burned gas fraction before stable combustion is lost.

The effect on specific fuel consumption (SFC) for a gasoline-powered engine varies with the excess air factor and EGR rate as shown in Figure 3-11. [40] Richer mixtures with higher EGR rates result in a higher SFC (i.e., poorer fuel economy).

Prototype engine work has revealed that engines operating on methanol behave similarly to the gasoline engines depicted in Figure 3-11. It is important to note that increasing EGR requires advancing the spark ignition as the equivalence ratio decreases, as shown in Figure 3-12. [41]

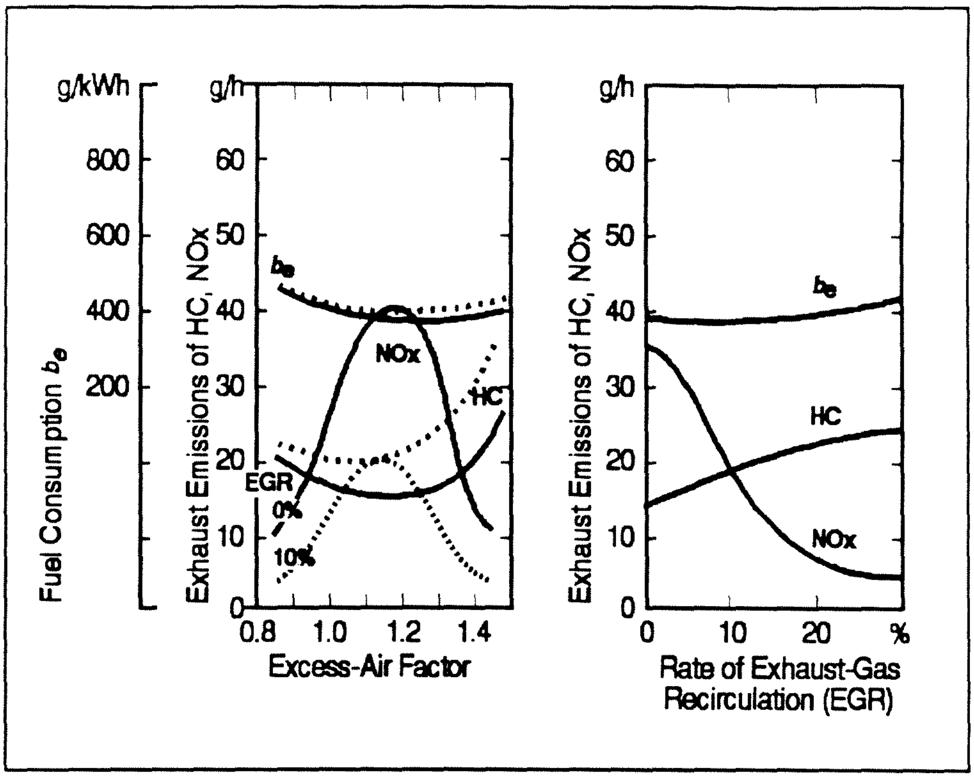


Figure 3-11., The influence of Exhaust-Gas-Recirculation (EGR) on pollutant formation and fuel consumption.

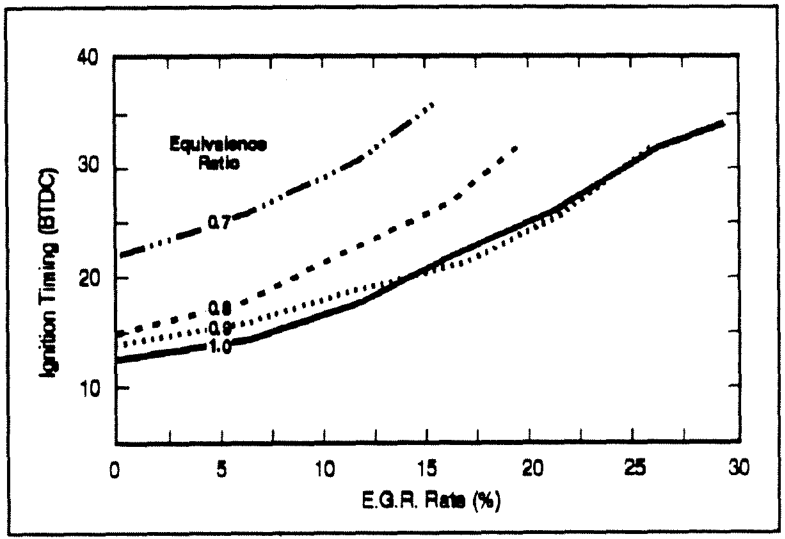


Figure 3-12., The effect of increasing EGR on ignition timing and equivalence ratio for a methanol fueled engine.

Key Design Parameters for Alcohol Combustion

Policy Issue #2

> Relative to gasoline, methanol and ethanol have higher octane, greater heat of vaporization, and lower flame temperatures. They have also been shown to exhibit an extended lean limit of operation.

By exploiting these characteristics, a methanol-fueled engine can operate at leaner fuel/air ratios than those burning gasoline to improve thermal efficiency and reduce the concentrations of both regulated and unregulated exhaust gas emissions. [42] A high compression, lean burn stratified charge engine may be the goal for designing an optimized methanol engine.

Stratified charge implies a heterogeneous fuel/air mixture distribution in the combustion chamber. Combustion is initiated in the fuel rich zone and spreads to the more lean regions. Stratified engines are very fuel efficient but due to the difficulty encountered in regulating the fuel/air mixture with today's oxygen sensors and three-way catalysts, research on this technology has been reduced. [43] Ricardo developed and tested a high compression ratio compact chamber engine with optimization for methanol. Employing a CR of 13:1 with lean burn strategy, fuel efficiency improvements of 10% were noted. For more detailed information, refer to [44].

Methanol's high heat of vaporization provides a lower intake temperature to the engine. A significant amount of heat is removed from the incoming air to vaporize the liquid methanol fuel. This cooling effect increases the charge density in the cylinder (since cooler gases are more dense than warmer gases), improving volumetric efficiency and increasing power. Unfortunately, this characteristic also is responsible for the difficulty associated with cold-starting methanol vehicles (see Section 6). In methanol combustion, the ratio of moles-of-product to moles-of-reactant are 1.209 times that of gasoline. [45] This results in higher cylinder pressure, which in turn results in a higher power output. These advantages are realized without significant alterations to the engine for methanol optimization. Using flexible fuel technology, Ford measured a 3% improvement in fuel efficiency on M-85 and a 5-7% increase in power over gasoline operation. Because flexible fuel vehicles are designed to operate on gasoline as well as methanol, they cannot be optimized to take full advantage of methanol's properties. Ethanol's heat of vaporization is slightly less than methanol's. Similar increases in efficiency and cold start problems occur when operating on ethanol.

Clearly, certain negative effects of methanol combustion exist that will have to be further researched before dedicated vehicles are mass-produced. While the combustion of methanol releases less hydrocarbons than gasoline, it is still uncertain what effect unburned methanol emissions have on air quality. Figure 3-13 [46] shows that formaldehyde levels have been found to be significantly higher than gasoline.

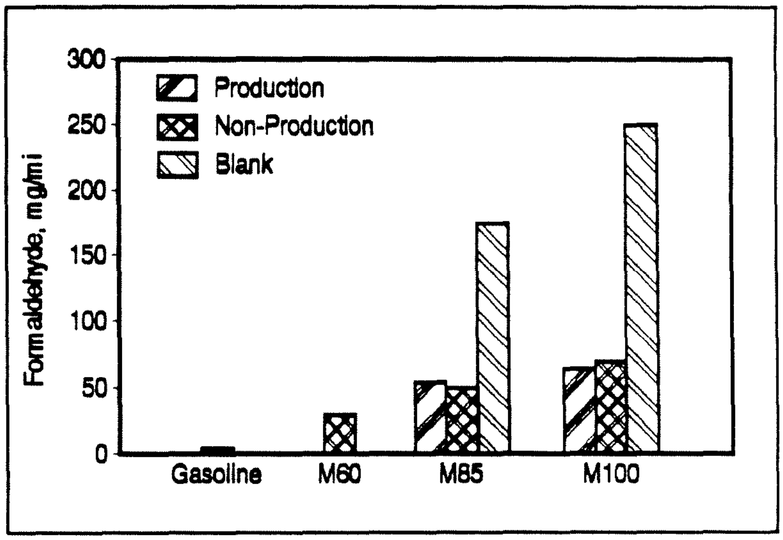


Figure 3-13., Comparison of formaldehyde emissions from production and non-production catalysts aged to 50K miles.

Greatly increased engine wear at cold temperatures has been observed with methanol as a fuel (when compared to gasoline, ethanol, and ethanol/water mixtures), and this is multiplied when water is added to the methanol fuel as shown in Figure 3-14 [47] below. For further information refer to [48].

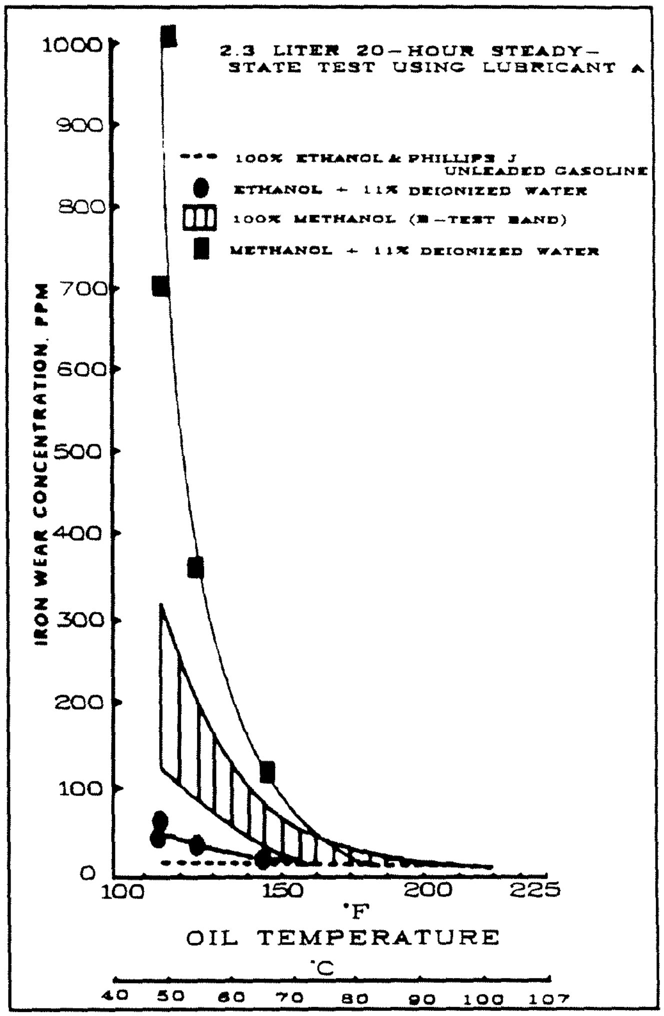


Figure 3-14., Effect of oil temperature on engine iron wear with various fuels.

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Section 4

VOLATILITY OF TRANSPORTATION FUELS

Quick Reference Data

Boiling Point or Range at One Atmosphere Pressure:

Ethanol	78°C (172°F)
Methanol	65°C (149°F)
Gasoline	27-225°C (80-437°F)

Reid Vapor Pressure

Fuel	RVP (psi)
Ethanol	2.3
ETBE	4.4
Methanol	4.6
MTBE	7.8
Gasoline	8-15
Diesel	0.4

Note: An increase in RVP of a vehicle fuel also increases the vehicle's evaporative emissions. In the U.S., RVP is controlled seasonally by federal regulations, with values ranging from 9.0 in summer to 15.0 in winter.

RVP of Alcohol/Gasoline Blends

		Alcohol Blending Agent			
% of Gasoline	% of Alcohol/Ether	Ethanol	ETBE	Methanol	MTBE
100	0	9.00	9.00	9.00	9.00
95	5	10.10	8.80	12.30	9.40
90	10	10.00	8.60	12.40	9.20
85	15	9.90	8.30	12.30	9.10
80	20	9.75	8.10	12.20	9.10
75	25	na	7.90	na	na
70	30	9.50	na	12.05	na
50	50	8.70	na	11.4	8.80
30	70	7.00	na	10.00	na
10	90	4.30	na	7.20	8.10
0	100	2.30	4.40	4.60	7.80

Useful Terms and Definitions (also see Glossary)

- **Distillation Curves:** The reference to plotting a line connecting the percentages of gasoline that evaporate at various temperatures. Distillation curve is used as an important control for fuel volatility (vaporization) standards.
- **Reid Vapor Pressure (RVP):** A method of determining vapor pressure of gasoline and other petroleum products. Widely used in the petroleum industry as an indicator of the volatility (vaporization characteristics) of gasoline.
- **Vapor/Liquid (V/L) Ratio:** A test to determine a fuel's tendency to vapor lock (i.e., the temperature required to create a V/L ratio of 20).
- **Vapor Lock:** The inability of a fuel system to supply the required quantity of fuel to the engine because of the formation of excessive vapor in the system.
- **Volatility:** A fuel's ability to vaporize or change from liquid to vapor.

Key Issues and Implications

Issue # 1: Increased RVP for Low Level Alcohol/Gasoline Blends

The addition of low levels (less than 20%) of alcohol to gasoline leads to an increase in the RVP of the resultant gasoline blend; the increase is particularly large with methanol/gasoline blends.

- Use of low-level alcohol/gasoline blends especially with methanol could increase evaporative emissions and contribute to ozone problems.

Proposed Solutions:

- The use of high percentage alcohol blends or neat alcohol fuels will eliminate this problem, since alcohols by themselves have lower RVPs than gasoline.

Detailed Information: Refer to page 4-9.

Issue # 2: Low Volatility of Neat Alcohol Fuels

Pure or neat alcohol fuels are less volatile (possess lower Reid Vapor Pressures or RVP) than gasoline.

Implications of Alcohol's Low Volatility:

- Neat alcohol fuels will have much lower evaporative emissions than gasoline. The evaporative emissions from gasoline and other volatile hydrocarbons are significant contributors to the formation of urban ozone; thus neat alcohol fuels offer a significant opportunity for mitigating urban ozone problems.
- Lower RVP contributes to cold start problems. As a result, some neat alcohol fuels require additives or cold start subsystems.

Detailed Information: Refer to pages 4-8 through 4-9.

Issue # 3: RVP as a Transportation Fuel Emissions Benchmark

RVP is used by the U.S. EPA as a benchmark to set volatility limits in motor gasoline. Current allowable summer RVP in many regions of the U.S. is 9.0 psi.

Implications of the Use of RVP in Emissions Control:

- As a regulatory tool, volatility has become a very important measure of fuel acceptability.
- Currently, gasohol (10% alcohol, 90% gasoline) is allowed by EPA to have an RVP waiver of one point (gasohol can have an RVP 1 psi higher than gasoline), primarily in recognition of the benefits of gasohol in reducing CO emissions.
- Due to the substantial increase in RVP caused by even small additions of methanol to gasoline (as well as other concerns such as corrosion in conventional vehicles), there is currently no use of low-level methanol/gasoline blends.

Detailed Information: Refer to pages 4-7 through 4-8.

Issue # 4: The Low RVP of Alcohol-Based Ether/Gasoline Blends

Alcohol based ethers (ETBE/MTBE) have low RVPs. When blended with gasoline in low levels, ethers do not contribute to an increase in RVP as do low molecular weight alcohols (ethanol and methanol).

Implications of the Low RVP of Ether/Gasoline Blends:

- There is likely to be substantial increases in the use of MTBE and ETBE as octane enhancers in reformulated gasoline, partly because they do not increase RVP and therefore do not contribute to ozone formation.

Detailed Information: Refer to pages 4-10 through 4-12.

Issue # 5: Changes in the Gasoline Distillation Curve by the Addition of Small Amounts of Alcohols

Due to their low boiling points, low molecular weight alcohols (such as methanol and ethanol) vaporize more readily than many of the components of gasoline. This is particularly true of methanol.

Implications of the Low Boiling Point of Alcohols

- In older automobiles, methanol/gasoline blends can fractionate in the intake manifold, leading to different fuel mixtures in different cylinders (and therefore driveability problems)
- The lower boiling point is not considered a problem for gasoline blends using alcohol-based ethers, ethanol and higher molecular weight alcohols and has not caused difficulty for millions of U.S. cars currently operating on gasohol or on premium gasolines using MTBE as an octane enhancer.

Proposed Solutions:

- Modern fuel injection systems minimize the problem of blend fractionation and premature vaporization.

Detailed Information: Refer to pages 4-7 through 4-8.

Section 4
VOLATILITY OF TRANSPORTATION FUELS

- Reid Vapor Pressure
- Distillation Curves
- Vapor/Liquid Ratio

Introduction

A fuel's ability to vaporize or change from liquid to vapor is referred to as its **volatility**. Gasoline and other liquid fuels such as alcohols are used in a variety of engines with large variations in operating conditions and under a wide range of atmospheric temperatures and barometric pressures. Therefore, the volatility characteristics of a spark ignition (SI) engine fuel are of prime importance.

Fuels that do not vaporize readily may cause hard starting of cold engines and poor vehicle driveability during warm-up and acceleration. Conversely, fuels that vaporize too readily at higher operating temperatures will cause too much vapor to form causing a decrease in fuel flow to the engine (known as "vapor lock"). These extremes of difficult starts on the one hand and vapor lock on the other can be minimized by changing fuel volatility specifications for seasonal, geographical, and elevation considerations. [1] Therefore, it is important that a fuel's tendency to evaporate is controlled to certain standards.

While a theoretical description of the effects of volatility on vehicle performance is needed to describe differences in fuel types, actual vehicle driveability can be controlled by optimizing engine control parameters. A fuel's tendency to vaporize is measured by three methods: Reid Vapor Pressure (RVP), distillation curves, and Vapor/Liquid ratio. [2] Since gasoline is a mixture of hydrocarbons, it does not have a single boiling temperature. Neat alcohols have single boiling points because they are homogeneous.

Because of the "non-ideal" properties of alcohol/gasoline blends, current standard volatility measurements are not well suited to compare gasoline to alcohol blends. The volatility characteristics of neat alcohols and alcohol/gasoline blends compared to gasoline will be the focus of this discussion.

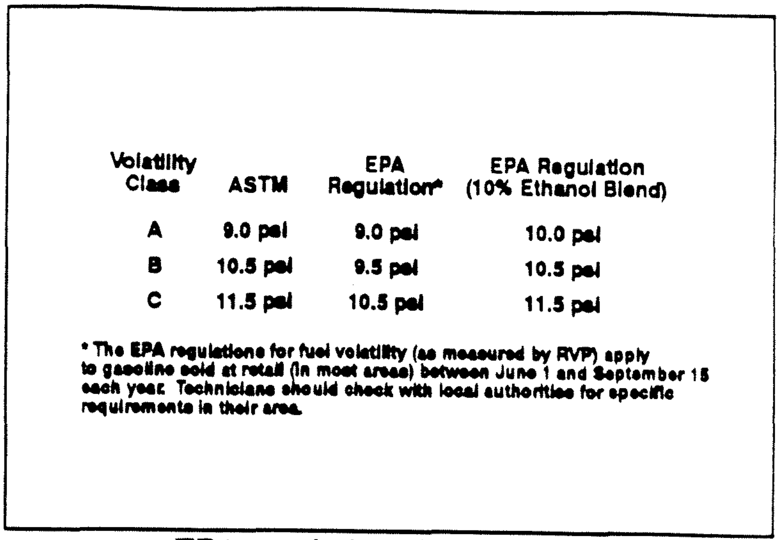
Reid Vapor Pressure

The Reid Vapor Pressure or RVP (ASTM D 323) is a measurement of a fuel's front-end volatility. The determination of RVP is performed by submerging a fuel sample (sealed in a flask) in a 100°F water bath. More volatile fuels will vaporize more readily, producing higher pressure readings. Less volatile fuels will not create as much vapor, therefore creating lower pressure readings.

Policy Issue #1

In the United States, the RVP of gasoline and gasoline/alcohol blends is controlled seasonally by federal air quality regulations, with values ranging from 9.0 in the summer to as high as 15.0 in the winter. Because an increase in RVP also increases vehicle evaporative emissions, the EPA has issued regulations setting maximum RVP levels during summer months for various fuel classes as shown below in Figure 4-1. [3]

Because the addition of 10% ethanol results in an increase in RVP, a 1.0 psi waiver has been granted by the EPA for gasohol. Although low level alcohol blends have higher RVP values than regular gasoline, they are given an RVP waiver because they contribute to the reduction of CO production.



Volatility Class	ASTM	EPA Regulation*	EPA Regulation (10% Ethanol Blend)
A	9.0 psi	9.0 psi	10.0 psi
B	10.5 psi	9.5 psi	10.5 psi
C	11.5 psi	10.5 psi	11.5 psi

* The EPA regulations for fuel volatility (as measured by RVP) apply to gasoline sold at retail (in most areas) between June 1 and September 15 each year. Technicians should check with local authorities for specific requirements in their area.

Figure 4-1. EPA regulations for summertime volatility.

RVP values are given below for various fuels and components [4,5].

FUEL	RVP (PSI)
Methanol	4.6
Ethanol	2.3
MTBE	7.8
ETBE	4.4
Gasoline	8-15
Diesel	0.4

Policy Issue #2

Neat ethanol and methanol have significantly lower RVPs than gasoline. This means they tend to evaporate less readily. Since evaporative emissions are a major source of ozone formation, particularly in the summertime, neat alcohol fuels can play a major role in reducing urban air pollution.

When alcohols are blended with gasoline, the resulting alcohol/gasoline blends exhibit very non-ideal blending conditions, i.e., they do not obey Rault's Law.

Policy Issue #3

The addition of low levels of alcohols (5-25%) to a 9 psi gasoline causes a marked increase in RVP (see Figure 4-2 and Table 4-1 below). This is particularly true for

As the percentage of alcohol in the blend increases, however, the RVP values decrease down to the base value of the alcohol fuel.

Not all of the oxygenates increase the RVP of a gasoline stock when added as a blending agent. ETBE actually reduces RVP at low concentrations, while MTBE increases the RVP only negligibly in the common 0-20% blending range, as is shown in Table 4-1. [6,7]

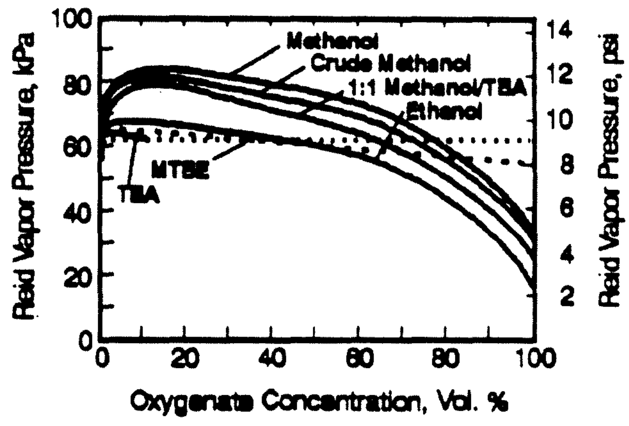


Figure 4-2., The effect of oxygenate concentration on Reid Vapor Pressure (RVP).

Table 4-1. RVP of Alcohol/Gasoline Blends

% of Gasoline	% of Alcohol/Ether	Alcohol Blending Agent			
		Ethanol	ETBE	Methanol	MTBE
100	0	9.00	9.00	9.00	9.00
95	5	10.10	8.80	12.30	9.40
90	10	10.00	8.60	12.40	9.20
85	15	9.90	8.30	12.30	9.10
80	20	9.75	8.10	12.20	9.10
75	25	na	7.90	na	na
70	30	9.50	na	12.05	na
50	50	8.70	na	11.4	8.80
30	70	7.00	na	10.00	na
10	90	4.30	na	7.20	8.10
0	100	2.30	4.40	4.60	7.80

Policy Issue #4

Low levels of ethers such as ETBE and MTBE have proven to have negligible effects on RVP (see Table 4-1). In the near term, this will be important in the reformulation of gasolines to reduce urban air pollution caused by existing vehicles. It is expected that gasoline refiners will make extensive use of ETBE and MTBE and other alcohol-based ethers to provide octane to base gasoline without increasing evaporative emissions or affecting driveability.

The negative effects of low fuel volatility on vehicle driveability are well documented. [8] However, a number of factors besides the volatility of the fuel can influence the experimental measurement of RVP. The RVP of a fuel has been found to decrease as the fuel level in the tank decreases, and this effect is more pronounced for fuels or blends with higher RVPs [9]. There is great debate among researchers as to the validity of using RVP in determining cold start performance for alcohol/gasoline blends. Recent work has shown the cold starting ability is also influenced by a fuel's excess air ratio. [10]

Distillation Curves

The distillation test (ASTM D 86) is used to determine fuel volatility across the entire boiling range of gasoline. More volatile (faster vaporizing) components evaporate at lower temperatures, less volatile (slower vaporizing) ones evaporate at higher temperatures. The plotting of these evaporation temperatures is referred to as a distillation curve.

At atmospheric pressure, neat methanol and ethanol are single compounds that boil at 64.7°C (148°F) and 78.3°C (173°F), respectively. MTBE boils at 55°C (131°F). As such, they lack a boiling curve or distillation curve. Gasoline, on the other hand, is a mixture of compounds that boils over a range of temperatures -- generally 27-225°C (80-437°F). [11] Thus, methanol, ethanol, and the other oxygenates have constant volatilities, while the volatility of gasoline can be tailored over a range of temperatures by adjusting the relative amounts of different hydrocarbons in the mixture. The heterogenous characteristics of gasoline and diesel fuel become apparent upon comparison to the homogeneous qualities of methanol and ethanol (see Figure 4-3). The difference in volatility between the oxygenates and gasoline is an important factor in the performance of gasoline/oxygenate blends in automobile engines with respect to starting, warm up, vapor lock, and other driveability characteristics.

The ASTM specification sets temperature ranges at which 10%, 50%, and 90% of the fuel will be evaporated. Each of these points affect different areas of vehicle performance. The 10% evaporated temperature must be low enough to provide easy cold starting but high enough to minimize vapor lock as well as hot driveability problems. The 50% evaporated temperature must be low enough

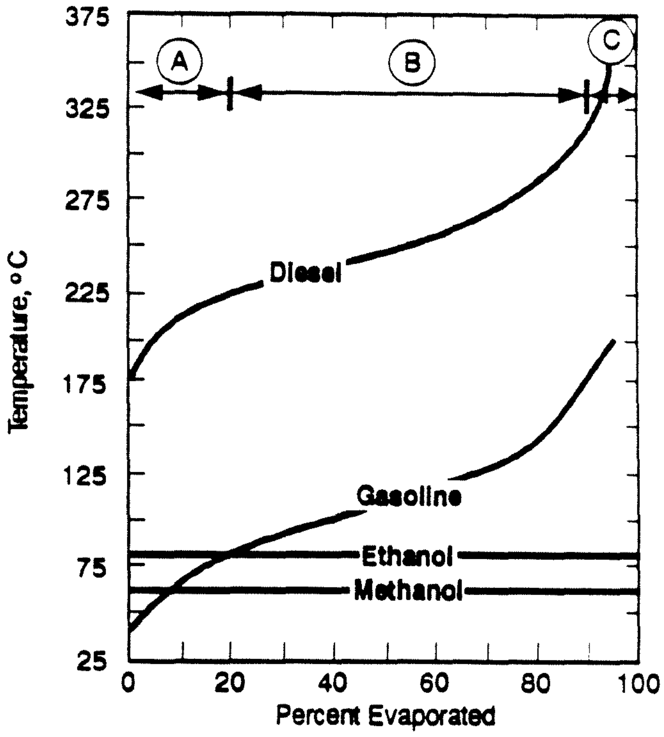


Figure 4-3., Distillation curves for various fuels.

to provide good warm up and cold weather driveability without being so low as to contribute to hot driveability and vapor locking problems. The 90% and end point evaporation temperatures must be low enough to minimize crankcase and combustion chamber deposits as well as spark plug fouling and dilution of engine oil. Figure 4-3 [12] depicts the distillation curve of gasoline in relation to diesel, neat ethanol and neat methanol. The curve can also be divided into the sections shown; A= Front End (0-20% evaporated), B= Mid-range (20-90% evaporated), and C= Tail End (90-100% evaporated). Clearly, diesel is shown to be a much less volatile fuel than gasoline, whereas only the front end volatility (less than 10% and 20% evaporation of methanol and ethanol, respectively) of neat alcohols are generally less volatile than gasoline.

- *Low Level Alcohol Blends*

Adding alcohols to gasoline causes an increase in vapor pressure and depresses the boiling temperature, as shown in Figure 4-4 [13] and 4-5 [14]. For additional information, refer to [15,16,17]. However, some researchers have found the addition of low levels of alcohols raise the front-end section of the curve. [18] The distillation curve of these blends show that most of the alcohol vaporizes at its boiling point, giving the so-called "alcohol flat" in the distillation curves.

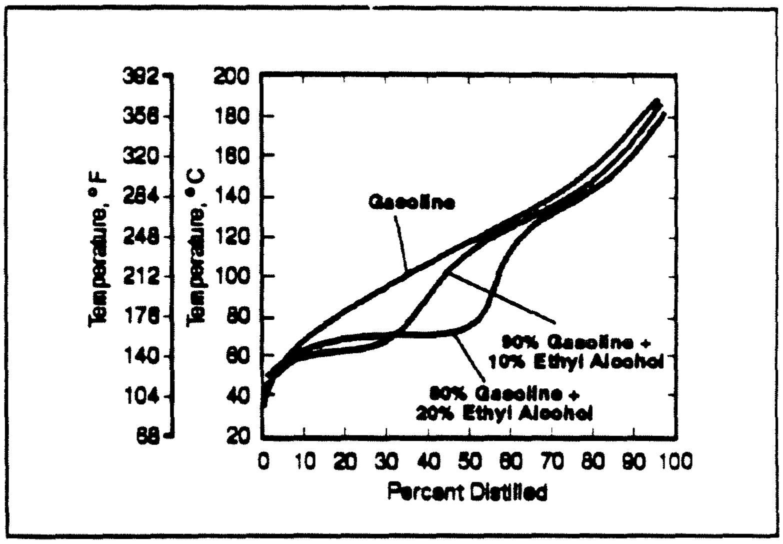


Figure 4-4., ASTM distillation curves for gasoline and ethyl alcohol blends.

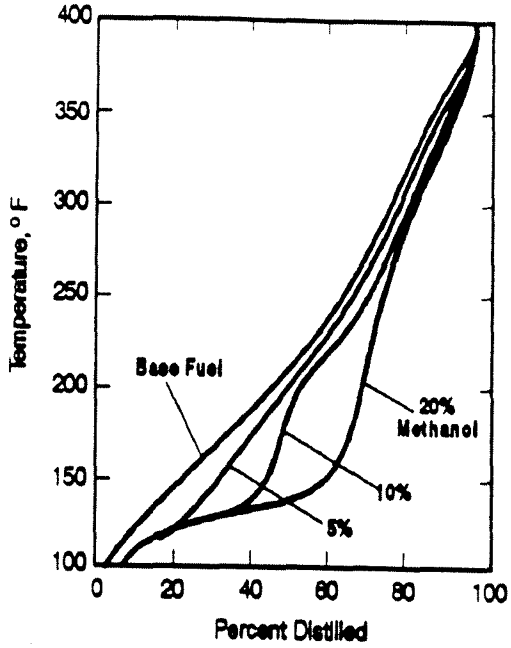


Figure 4-5., Methanol depresses gasoline's distillation temperature.

Lower molecular weight alcohols have the greatest effect on boiling point depression. Methanol causes the largest changes; its effects can be observed even when accompanied by a cosolvent. Ethanol and higher molecular weight alcohols such as TBA exert much smaller changes on the distillation characteristics, while ethers such as ETBE and MTBE have little or no effect at all.

From a typical equilibrium vapor composition curve (Figure 4-6), it is apparent that in the flat region, alcohol vapors exist at concentrations disproportionate to the alcohol concentration in the blend. At a volumetric concentration of methanol of 5% or greater, over 50% of the resulting vapor at 46°C (115°F) is methanol, as shown in Figure 4-6. [19]

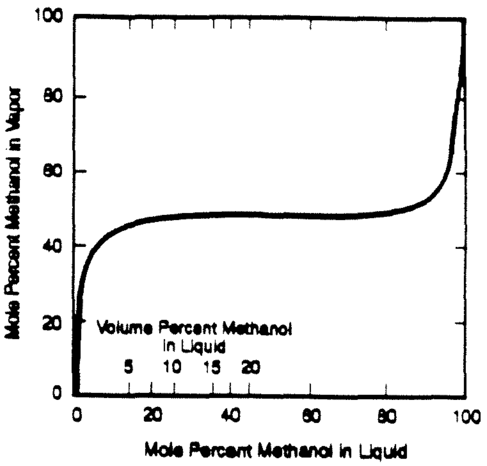


Figure 4-6., Low concentrations of methanol in blends produce much higher concentrations in vapors.

Policy Issue #5

The addition of methanol to gasoline increases the fuel's tendency to vapor lock. The high concentration of methanol in vapors above dilute gasoline/methanol blends and the flat area created in a blend's distillation curve also indicate that the blend could fractionate in the intake manifolds of automobile engines (particularly those equipped with carburetors rather than modern fuel injection systems).

If fractionation of the blend *does* occur in the intake manifold, the methanol concentration in the fuel-air mixture could vary significantly among the individual cylinders, leading to operational problems. The effects of ethers such as MTBE on the distillation curve is found to be minimal, as shown in Figure 4-7. [20]

- *Higher Alcohol Blends*

Greater concentrations of methanol in gasoline blends have very significant effects on the shape of the distillation curve, as shown below in Figure 4-7. [21] The front end temperatures increased, indicating possible cold start problems; the mid range temperatures have been decreased indicating possible driveability problems; and the end point temperatures decreased, implying less crankcase and combustion deposits.

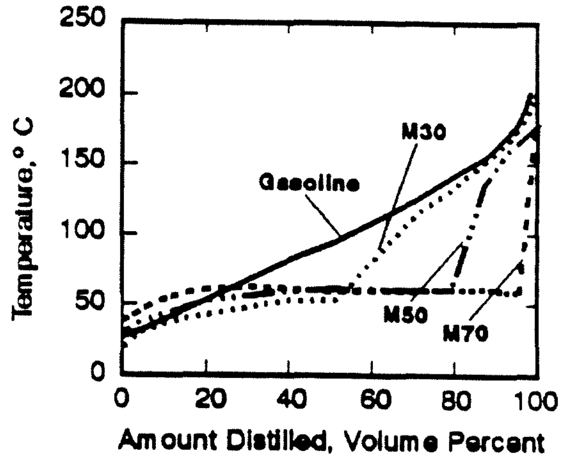


Figure 4-7., The effect of high level methanol blends on the distillation curve for gasoline.

Because ethanol has a higher boiling point than methanol, its effect on the gasoline curve would be less than methanol. To summarize, the effect of increasing the percentage of alcohol on the distillation curve is to flatten it around the alcohol's boiling temperature as shown earlier in Figure 4-3. [22] It is important to realize that the distillation curve, RVP and the vapor/liquid ratio are all related to one another.

Vapor/Liquid Ratio

The Vapor/Liquid (V/L) Ratio (ASTM D 2533) is a test used to determine the temperature required to create a vapor-liquid ratio of 20. More volatile fuels require less heat, while less volatile fuels require a greater degree of heat to create the same ratio. The V/L ratio assists in defining a fuel's tendency to vapor lock. Vapor lock is defined as the inability of the fuel system to supply the required quantity of gasoline to the engine because of the formation of excessive vapor in the system. [23] As the V/L ratio increases, the RVP decreases within a given test sample. Because of the non-ideal effect of alcohol blending, some researchers suggest that higher V/L ratios should be considered for the test procedure in judging a blend's performance. [24] They suggest that in comparing the temperature values at V/L ratios of 20, it becomes clear that the temperature varies according to alcohol content, being lower than gasoline for low level blends and higher for high level blends. However, in studies comparing temperatures at V/L ratios of 50 [25], it is clear that the temperature required is less for blends than for gasoline.

In conclusion, because of the non-ideal properties of alcohol/ gasoline blends, current standard volatility measurements may not be well suited for comparing gasoline to alcohol blends.

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25. Ibid.

Section 5

COMPATIBILITY OF ALCOHOLS WITH OTHER FUELS IN BLENDS

Quick Reference Data

Impacts of Gasoline Composition on Methanol Solubility

Gasoline Composition (Volume %)			Minimum Temp. at Which 10% Methanol will Dissolve	
Saturates	Aromatics	Olefins		
100	0	0	27°C	(80°F)
65	21	14	7°C	(44°F)
43	2	55	-7°C	(20°F)
20	78	2	-16°C	(4°F)

Note: Ethanol and higher alcohols dissolve much more readily in hydrocarbons than methanol and can be added to a methanol/gasoline blend to increase methanol's solubility.

Low Temperature Solubility of Methanol in Gasoline

Aromatics in Gasoline (Volume %)	Methanol Solubility (Volume %)	
	-23° to -18°C (-10° to 0°F)	0° to 3°C (32° to 37°F)
16	2-3	5-10
28	5-10	15-20
31	5-10	>50
42	>50	>50

Effects of Adding Alcohol (Ethanol or Methanol) to Gasoline

- Increased volatility
- Volumetric expansion (small but measurable)
- Increased octane

Octane Ratings of Liquid Fuels

Compound	Octane Rating (R+M)/2
Gasoline	87-94
Ethanol	97
Methanol	98
MTBE	109
ETBE	110

Energy Content/Volume

Percent by Volume			
Ethanol (99.5%)	Gasoline (100%)	Lower Heating Value (Btu/gallon)	Relative Heating Value (Gasoline = 1)
0	100	109,000	1.000
10	90	105,662	0.969
20	80	102,324	0.938
30	70	98,986	0.908
100	0	76,000	0.697

Means for Overcoming Phase Separation

- Maintaining warm fuel mixture temperatures and low water content
- Using chemical additives
  - cosolvent alcohols
  - surfactants

Useful Terms and Definitions (also see Glossary)

- **Aromatics:** High octane blending components that have a benzene ring in their molecular structure. Commonly used term for the BTX group (benzene, toluene, xylene). Aromatics are hydrocarbons.

- **Azeotrope**: A liquid mixture that is characterized by a constant minimum or maximum boiling point which is different than that of any of the components. Azeotropes distill without change in composition.

- **Benzene Ring:** structural arrangement of atoms believed to exist in benzene and other aromatic compounds showing six carbon atoms in symmetrical hexagonal fashion.

- **Hydrogen Bond**: A bond between the hydrogen atom of one molecule and a pair of unshared electrons on the electronegative atom of another molecule.

- **Hydroxyl**: the chemical group or ion OH that consists of one atom each of hydrogen and oxygen, is neutral or positively charged and is characteristic especially of alcohols.

- **Octane Number (Rating)**: A measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the grater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

    - ***Motor Octane:*** the octane as tested in a single cylinder octane test engine at more severe operating conditions. Motor Octane Number affects high speed and part throttle knock and performance under load, passing, climbing hills, etc. Motor Octane is represented by the designation M in the (R+M)/2 equation and is the lower of the two numbers.

    - ***Pump Octane:*** a term used to describe the octane as posted on the retail gasoline dispenser as (R+M)/2 and is the same as Antiknock Index.

    - ***Research Octane:*** the octane as tested in a single cylinder octane test engine operated under less severe operating conditions. Research Octane Number affects low-to-medium speed knock and engine run-on. Research Octane is represented by the designation R in the (R+M)/2 equation and is the higher of the two numbers.

- **Olefins**: unsaturated open-chain hydrocarbons containing at least one double bond; member of the ethylene series.

- **Phase Separation**: the formation of layers due to the presence of water within a low level alcohol-gasoline blend, with most of the hydrocarbons in the upper layer and water, alcohol, and some aromatic hydrocarbons in the lower level. This condition can lead to driveability problems.

- **Solubility:** the amount of a substance that will dissolve in a given amount of another substance and is typically expressed as the number of parts by weight dissolved by 100 parts of solvent at a specified temperature and pressure or as percent by weight or by volume.

Key Issues and Implications

Issues and Implications

Issue #1: Solubility of Methanol in Gasoline

Methanol is not completely soluble in those gasolines which contain low levels of aromatic compounds, particularly at low ambient temperatures. New efforts to reformulate gasoline are likely to result in reduced levels of aromatic compounds in gasoline (primarily because of the carcinogenic character of these compounds), which may exacerbate this problem.

Implications of the Low Methanol Solubility:

- In flexible fuel vehicles (FFVs), as you switch between methanol (M85) and reformulated (low aromatic content) gasolines, solubility problems may occur.

Solutions to the Solubility Problem:

- In order to avoid operational problems with FFVs, it may be necessary to use ethanol or "higher" alcohols (which dissolve more readily in gasoline) as additives to methanol fuels to improve solubility with gasoline.

Detailed Information: Refer to pages 5-2 through 5-3.

Issues and Implications (Continued)

Issue # 2: Phase Separation

In alcohol/gasoline blends, the presence of water (even in small amounts) can lead to "phase separation" -- the formation of layers within the fuel or storage tank, with most of the hydrocarbons in the upper layer and water, alcohol, and some aromatic hydrocarbons in the lower level. This problem is most pronounced in low-level alcohol blends and at low ambient temperatures.

Implications of Phase Separation:

- **Phase separation of blends can lead to fuel line freezing or poor driveability.** In flexible fuel vehicles (FFVs), the presence of water in the fuel mixture can cause the optical fuel sensor to malfunction, which could lead to driveability problems.

Potential Solutions :

- A number of approaches are available to prevent phase separation, including: improved maintenance of gasoline storage and distribution systems; the use of additives (such as higher or "heavy" alcohols or surfactants) that will prevent separation even when water is present in a blend; and water removal facilities at fuel dispensing stations.

Detailed Information: Refer to pages 5-7 through 5-10.

Section 5
COMPATIBILITY OF ALCOHOLS WITH OTHER FUELS IN BLENDS

- Solubility in Gasoline
- Creation of Mixtures Having Different Properties than Constituent Fuels
- Bonding with Water and its Implications
- Alcohol/Gasoline Separation
- Methods to Overcome Phase Separation

Introduction

Although ethanol and methanol are completely soluble in water, their solubility in gasoline varies depending on both temperature and gasoline composition. Adding ethanol or methanol to gasoline results in mixtures having different properties than the constituent fuels. In addition, alcohol/gasoline blends have less energy content than pure gasoline. In relatively dilute blends (less than 20%), alcohols contribute to:

- increasing the octane number and the vapor pressure of the blend,
- depressing the boiling temperature of gasoline; and
- a small but measurable volume expansion.

Alcohol/gasoline blends are sensitive to the presence of small amounts of water, even at room temperature. Because of their polar structure, ethanol and methanol molecules actively associate with water molecules through hydrogen bonds.

This can result in the separation of the gasoline/alcohol blend into two phases. Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water and small quantities of aromatic hydrocarbons. A strategy to prevent the occurrence of phase separation of alcohol/gasoline blends is presented at the end of this section.

Solubility in gasoline

Gasoline is a mixture of petroleum-derived hydrocarbons and specialized additives. Its composition varies, depending on the desired octane rating, the nature of the base petroleum feedstock, the season of the year, and a variety of other factors. Over the past 20 years, there has been a pronounced trend in the United States toward the use of more aromatic hydrocarbons (benzene, toluene and xylene) in the gasoline pool. Although these compounds vaporize readily and are inexpensive to produce, aromatic hydrocarbons pose serious health hazards and contribute to urban air pollution. Therefore, efforts to "reformulate" gasoline normally include a major reduction in the percentage composition of aromatics. Alcohols and alcohol-based ethers blend more easily with certain types of gasoline components than others. This is particular true for low molecular-weight alcohols such as methanol.

Policy Issue #1

Methanol and non-aromatic hydrocarbons are not very soluble in each other, and solubilities decrease as temperature is lowered. In addition, the solubility of methanol in gasoline is affected by the chemical nature of the hydrocarbons making up the gasoline. Methanol dissolves less readily in paraffinic hydrocarbons (such as n-octane, n-hexane and cyclohexane) than it does in aromatic hydrocarbons (such as benzene and toluene).

Solubility is not a problem for alcohol/gasoline blenders today, since ethanol and high aromatic feedstocks are used. However, if methanol is used as an octane enhancer in the future, solubility maybe jeopardized in cold climates, as shown in Table 5-1 below. [1]

Table 5-1
Solubility of Methanol in Gasoline

Aromatics in Gasoline, Volume Percent	Methanol Solubility, Volume Percent -23° to -18°C (-10° to 0°F)	Methanol Solubility, Volume Percent 0° to 3°C (32° to 37°F)
16	2-3	5-10
28	5-10	15-20
31	5-10	>50
42	>50	>50

Gasoline Composition Saturates	Gasoline Composition Aromatics	Gasoline Composition Olefins	Minimum Temperature at which 10% Methanol will Dissolve, °C (°F)
100	--	--	27 (80)
65	21	14	7 (44)
43	2	55	-7 (20)
20	78	2	-15 (4)

For gasolines with 16% aromatics, for example, 5-10% methanol is soluble at temperatures above 0°C (32°F), and 2-3% is soluble at temperature as low as -23°C (-10°F). This will be important for methanol blending with reformulated gasolines, which are expected to contains as little as 20% aromatics (current gasolines contain 30-34% aromatics on average). In addition, flexible fuel vehicles (FFVs) will have to have the ability to switch readily from one fuel (such as M85) to another (such as reformulated gasoline). Both fuels will be present in the fuel tank after the switch is made. Therefore, issues of solubility and fuel compatibility will be more important for FFVs than for dedicated fuel (i.e., M85) automobiles. The addition of cosolvents and other additives can help resolve this potential problem.

Ethanol and higher alcohols such as isopropanol and 1-butanol dissolve more readily in hydrocarbons found in gasoline than does methanol, and they can be added to a methanol/gasoline blend to increase methanol's solubility. Discussions of gasoline/alcohol "blends" generally refer to gasoline/ethanol combinations (because of the difficulties associated with blending lower concentrations of methanol in gasoline) or gasoline mixed with other oxygenates such as alcohol-based ethers (MTBE and ETBE).

Creation of Mixtures Having Different Properties than Constituent Fuels

Volume Change of Alcohols/Gasoline Blends

When ethanol and methanol are added to gasoline, a small but measurable volume expansion effect occurs, as illustrated in Figure 5-1. [2] The expansion of a gasoline/methanol blend reaches a maximum value of about 0.2% over a broad range of concentrations from about 20 to 80% methanol. Ethanol/gasoline blends reach about the same maximum expansion but peak sharply at about 10-20% ethanol content. Expansion values for gasoline/ethanol blends as high as 0.55% with a 12.5% concentration of ethanol have been observed.

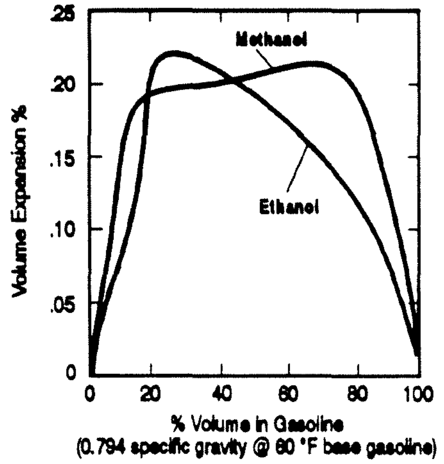

Figure 5-1., Volume increase for gasoline/ethanol and gasoline/methanol blends.

Increased Octane Rating

Alcohols and alcohol-based ethers have much higher octane ratings than most gasolines as seen in Table 5-2 below. [3]

Table 5-2. Octane ratings of gasoline and oxygenates

Compound	**Octane Rating (R+M)/2**
Gasoline	87
Ethanol	97
Methanol	98
MTBE	109
ETBE	110

When blended with gasoline, alcohols and alcohol-based ethers contribute to increasing the octane number of the blend. In fact, the "blending" octanes of alcohols are higher than their octane ratings would indicate. Methanol has a blending octane of 115 at 5% volume in gasoline, and ethanol is rated at 111 at 10% in gasoline. [4] The use of 10% ethanol will increase the octane number of a base gasoline from 2.5 to 3 octane points. [5] The influence of alcohol additions on four base gasoline stocks -- straight run, catalytically cracked, thermally cracked, and polymer gasoline -- is shown in Figure 5-2. [6]

In addition to the octane data shown, the curves in Figure 5-2 reveal that the greatest improvement in octane number from alcohol addition is obtained for gasoline stocks of the lowest octane number (straight run and thermally cracked), as would be expected.

Reduced Energy

Since the heating value (also called "energy content/volume") of ethanol is 76,000 Btu/gal or about two-thirds of that of gasoline (109,000 - 119,000 Btu/gal), blends of these fluids will also have less energy than gasoline, as shown in Table 5-3. [7]

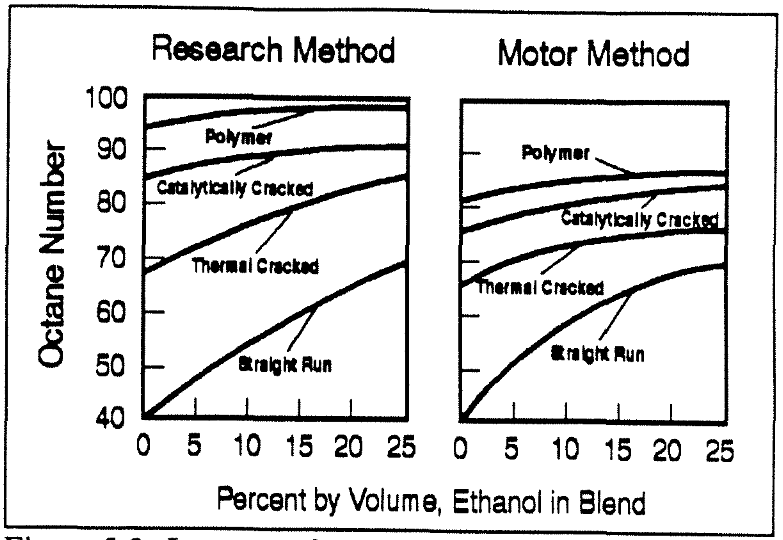

Figure 5-2., Increase of octane ratings of several gasoline stocks with the addition of ethanol.

Table 5-3 Calorific Values of Ethanol-Gasoline Blends

Percent by Volume Ethanol (99.5%)	Gasoline (100%)	Lower Heating Value Btu/gal	Relative Heating Value (Gasoline = 1)
0	100	109,000	1.000
10	90	105,662	0.969
20	80	102,324	0.938
30	70	98,986	0.908
100	0	76,000	0.697

This reduced energy per unit of volume will require increased fuel flow rates for proper engine operation. When fuels of different heating value are being considered, the energy of the fuel per unit volume is as equally important as the air-fuel mass ratio. Therefore, if a high percentage alcohol/gasoline blend is substituted for gasoline in an automobile, larger metering jets may be required to maintain the same percent of the stoichiometric air for combustion, or the same equivalence ratio. Up to 20% ethanol blends are normally accommodated by current production vehicles without modifications, and flexible fuel vehicles are designed to accept any alcohol/gasoline mixture ratios without difficulty.

Bonding with Water and its Implications

Low-molecular weight alcohols such as methanol and ethanol are completely soluble in water. Because of their polar structure, the alcohol molecules actively associate with water molecules through hydrogen bonds. The hydrogen bonds are strong enough to prevent the separation of the water/alcohol mixture by distillation.

Distillation of a solution of ethanol and water will not yield ethanol more concentrated than 95%. A mixture of 95% ethanol and 5% water boils at a lower temperature (78.15°C) than either pure ethanol (boiling point or bp = 78.3°C) or pure water (bp = 100°C). Such a mixture is called an "azeotrope." Pure ethanol is often obtained by adding benzene to the mixture of 95% ethanol and water and then distilling this solution. Benzene forms a different azeotrope with ethanol. This azeotrope boils at 64.9°C, leaving behind the water (along with traces of ethanol). Eventually, pure ethanol (also called absolute or neat alcohol) is produced by continued distillation after the benzene azeotrope is vaporized.

The earlier difficulty of producing water-free (anhydrous or absolute) alcohol explains why older engine tests were usually run with alcohol containing some water. In more recent years, it has become practical to produce alcohol with less than 0.1% water at an acceptable cost, ending the use of the 95% product in fuel applications.

Alcohol/Gasoline Separation

The solubility of methanol and ethanol in gasoline in the presence of even a small quantity of water is very limited. Even at room temperatures, only 1-2% of water can be tolerated for 25-40% alcohol mixtures before phase separation occurs and this tolerance drops sharply at lower temperature and at lower alcohol contents, as shown in Figures 5-3 and 5-4. [8,9] Although both of fuel alcohols have low water tolerance, methanol is somewhat less tolerant of water than ethanol in the 10-20% blending ratios.

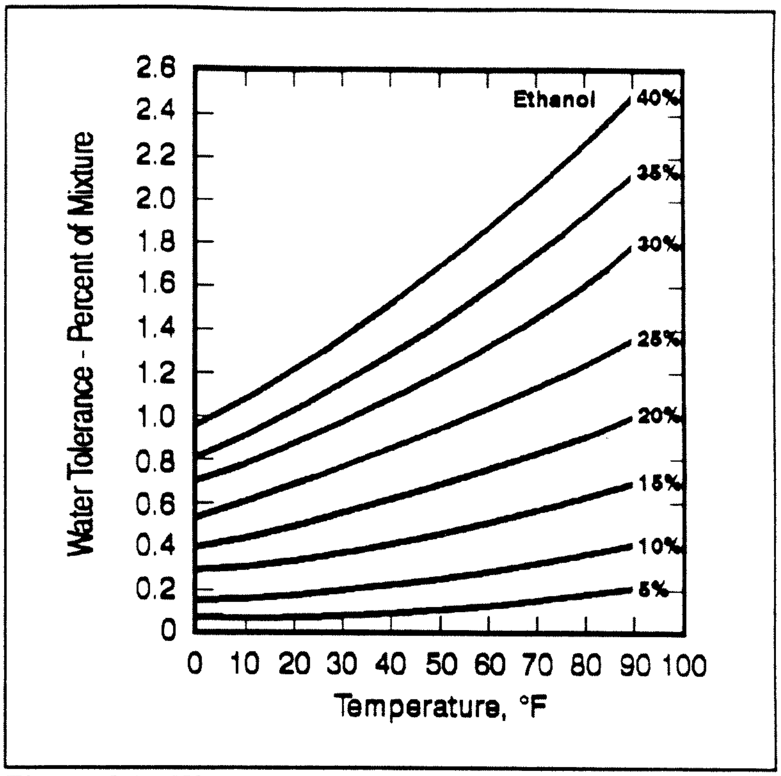

Figure 5-3., Water tolerance of ethanol/gasoline blends.

Policy Issue #2

When small amounts of water are added to ethanol/gasoline or methanol/gasoline blends, hydrogen bonds form between the water and alcohol molecules, and the blend separates into two phases. Paraffinic hydrocarbons (such as n-hexane and cyclohexane) predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons. The beginning of this separation is characterized by a cloudiness or "haze" in the mixture. The ability of the blend to carry moisture without separation increases when more alcohol is present, and when temperature is increased. Phase separation was a serious problem in early years of gasohol (10% ethanol, 90% gasoline) usage because the older one-stage distillation process did not remove all of the water. Under winter conditions, phase separation could lead to frozen fuel lines and difficult starting. Current production practices routinely produce anhydrous or water-free fuel ethanol, largely eliminating the problem of phase separation.

The amount of water that can be tolerated by a 25% ethanol/gasoline blend at room temperature is about 1%. If twice this amount is added to a sample of 25% blends, most of the alcohol will separate from the gasoline in a few seconds and settle to the bottom of the container. The interface between ethanol and gasoline will be sharply defined. Given the current limited use of fuel ethanol in the United States and modern production techniques, water intrusion has not been a serious issue.

For methanol, however, the presence of water is a more serious problem. Data on the water sensitivity of methanol/gasoline blends are given in Figure 5-4. A blend containing 10% methanol must be protected against water in concentrations greater than about 0.05 - 0.2% (depending on the fuel's temperature) or the blend will separate. To create a national production and distribution system, new dedicated pipelines and storage tanks will be required. Gasoline as conventionally transported, however, is often exposed to water in volumes greater than 1 percent.

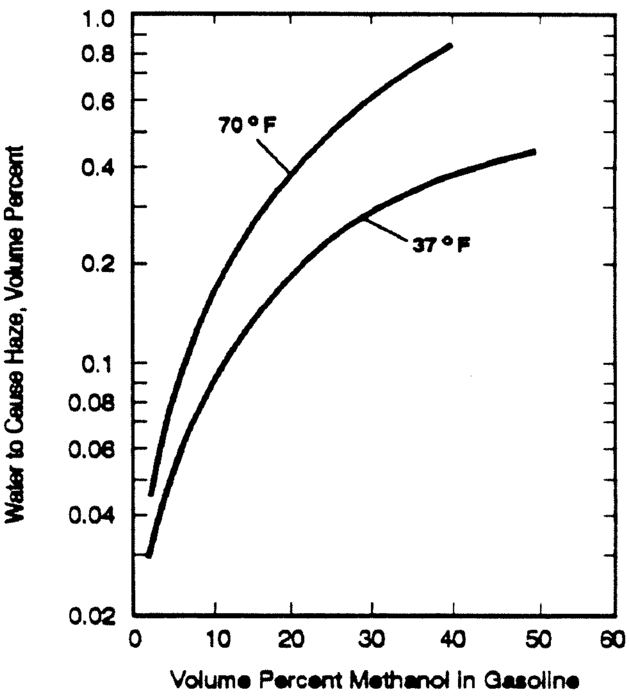

Figure 5-4., Methanol/gasoline blends tolerate little water.

The evidence of water intrusion in the existing fuel distribution system has been well documented. [10] Some of this water results from the condensation of moisture from the air in vented and partially filled tanks, and when products containing water are shipped by pipeline. But most of the water contamination is thought to result from precipitation penetrating the seals of floating roofs of bulk storage tanks.

Methods to Overcome Phase Separation

Considerable research has been undertaken in the last two decades to identify efficient means to stabilize alcohol/gasoline blends while preserving the other favorable characteristics of the fuel. [11,12,13,14] Several strategies have been proposed to monitor and control phase separation, and are presented in a recent review paper. [15]

Policy Issue #2

Keeping the mixture temperature high and the water content low improves the compatibility of gasoline/water/alcohol mixture. The phase separation problem can be effectively controlled by current technology, but at a substantial cost. The use of chemical additives to prevent phase separation has been extensively studied and successfully applied. The most popular additives are cosolvent alcohols (C_2-C_{12}) and various commercial noniomic surfactants and various anionic fatty acid surfactants. Among cosolvents alcohols, linear alcohols are more efficient than branched ones, and their efficiency increases with the carbon chain length. Iso-propanol, 1-butanol, n-decanol and palmitic acid have been suggested by several authors as the most cost-effective phase separation inhibitors.

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Section 6

ENGINE AND VEHICLE OPERATION ISSUES

Quick Reference Data

Heat of Vaporization/ Low Ambient Temperature Starting

	Btus/lb
Gasoline	150
Ethanol	396
Methanol	506

Existing Vehicle Warranties

The warranties of most passengers vehicles sold in the United States cover the following fuel concentrations in gasoline:

Ethanol	10%
Methanol	3-5%
MTBE	15%

Flexible Fuel Vehicle Mileage/Range

(1987 Crown Victoria)

	Miles per gallon	Range (18 gallon tank)
Gasoline 100	16.0-17.4	288-313
M25	14.3-15.5	257-279
M50	11.9-12.7	214-229
M85	9.2-10.2	166-184
M100	8.5-8.8	153-158
E85	12.2-12.8	220-230
E95	11.8-11.9	212-214

- Fuel economy: Due to higher heating value, straight gasoline provides higher mileage per gallon than any alcohol blend or neat fuel.
- Fuel efficiency: Alcohol fuels are more thermodynamically fuel efficient than gasoline, i.e., alcohols use fewer Btus per mile traveled than gasoline.

Useful Terms and Definitions (also see Glossary)

- **Enthalpy Requirement:** The additional heat input required by the engine's fuel induction system to achieve the fuel vaporization for smooth operation.
- **Vapor Lock:** Reduced fuel flow to the engine due to increased vapor formation, generally caused by high operating temperatures.

Key Issues and Implications

Issues and Implications

Issue # 1: *Cold Weather Starts and Warm-up with Neat Alcohol Fuels and High-Level Blends*

Low ambient temperatures can affect vehicle cold start and warm-up operations when neat and high-level blends of alcohol fuels are used, due to the greater latent heat of vaporization of alcohol fuels.

Implications of Cold Starting Problem:

- Neat alcohols must be blended with other fuels or must have additional equipment installed in the fuel system to facilitate starting.
- For low level alcohol/gasoline blends, cold start and warm-up operations are really not problems since these blends perform essentially the same as unblended gasoline.

Potential Solutions

- Numerous options are available to mitigate these problems, ranging from the use of fuel additives to cold start mechanical subsystems.

Detailed Information: Refer to pages 6-4 through 6-6.

Issue # 2: *Low vapor pressures of alcohol fuels*

Neat alcohols and high-level alcohol/gasoline blends have characteristically low vapor pressures and flat distillation curves.

Implications of Low Vapor Pressure:

- As the percentage of alcohol in the fuel increases, vehicles could have an increased potential for vapor lock at high ambient temperatures. However, recent test results have not shown this to be the case.

Potential Solutions:

- The use of additives and adjustments to fuel flow pressure seems to mitigate any potential problems.

Detailed Information: Refer to page 6-9.

Issue # 3: *Lower Energy Density of Alcohol Fuels*

Alcohol fuels contain less energy (Btus) per gallon than gasoline, so as the alcohol content of a fuel increases, the overall driving range for a given vehicle tends to decrease.

Implications of Lower Energy Density:

- Bigger fuel tanks or more frequent fill-up will be required with alcohol fuels. However, this is partially offset by the fact that alcohols are more thermally efficient (i.e., require fewer Btus/mile) than gasoline.

Detailed Information: Refer to pages 6-10 through 6-13.

Section 6
ENGINE AND VEHICLE OPERATION ISSUES

- Low Ambient Temperature Starting
- High Temperature Performance
- Vehicle Range

Introduction

Proper operation of a vehicle depends on several factors. In addition to the quality of the delivered vehicle, adherence to scheduled factory maintenance is important in assuring proper operation. **Vehicles designed to run on gasoline are generally warranted to operate on low level ethanol, methanol and ether blends.** The majority of the world's automobile manufacturers warrant their vehicles to operate properly with oxygenated blends according to the limits below:

Ethanol	10%
Methanol	3-5%
MTBE	15%.

For a complete listing of warranties refer to [1].

Of the alcohol-blending agents available, methanol is the most controversial. Several automobile manufacturers specifically warn the consumer against the use of blends containing methanol in their production vehicles. This is due primarily to concerns about accelerated engine wear, and possible incompatibility with fuel system components.

Vehicles designed to run on higher blends of alcohols than the low levels noted above often exhibit certain driveability problems. Driveability can refer to a fuel's volatility characteristics as well as to any method for judging the overall performance of a particular vehicle. Alcohol-fueled vehicles have been reported to have difficulties with low ambient temperature starting, high temperature performance, and reduced vehicle range. An additional area of concern, fuel system component failures, is examined in Section 7.

Low Ambient Temperature Starting

Methanol and ethanol have much greater latent heat of vaporization values than gasoline (i.e., they require more heat/gram to vaporize completely). Whereas the value for gasoline is approximately 150 Btu/lb (348.9 kJ/kg), the values for neat alcohols are: methanol - 506 Btu/lb (1176 kJ/kg); and ethanol - 396 Btu/lb (921.1 kJ/kg). [2] Consequently, the warm-up period is extended and acceptable driveability during this phase of engine operation is more difficult to achieve.

The effect is more pronounced as the ambient temperature drops and the proportion of alcohol or alcohol-based ether in a blend increases. The testing methods for cold starting among researchers vary considerably, with the testing temperature and the definition of a successful start being key differences. Recent research has shown that low ambient temperatures affect both low level blends as well as neat alcohol vehicles.

- Low Level Blends

Traditionally, the midpoint of a gasoline's ASTM distillation curve has been used as a principal cold-weather driveability control parameter. This method is important because it provides the basis on which gasoline producers can set their specifications to ensure proper driveability performance throughout the vehicle population. Because of non-ideal volatility behavior of alcohol fuels, researchers have defined a new volatility parameter termed "enthalpy requirement". [3] It is defined as the additional heat input required by the engine's fuel induction system to achieve the required degree of fuel vaporization for smooth operation. Initial testing has proven it to be equivalent to the ASTM midpoint parameter for gasoline operation. Whereas the "E100" ASTM midpoint parameter has under-predicted the driveability performance problems with low-level (20% methanol, 10% MTBE) blends, the Standard Enthalpy Requirement Parameter (SER) works equally well with hydrocarbon and oxygenated blends.

The effect of low temperatures on low-level alcohol blends is unclear. Theoretically, a 10% ethanol blend raises the RVP of a blend by 1 psi. Raising the Reid Vapor Pressure (RVP) in the winter is a typical method of improving cold startability. However, because of the leaning effect of the alcohol, the overall effect will depend on the vehicle fuel system. The leaning effect will be more noticeable in older open-loop carbureted vehicles. Newer vehicles are equipped with more precise fuel metering methods (fuel injection and closed-loop control) which calibrate themselves for slight differences in oxygen content. Fleet results are varied. For more information, refer to [4,5]. Mixtures of 10% ethanol - 90% gasoline are in widespread use in a number of U.S. regions with severe winters, and no major difficulties in cold-winter starting has been reported. However, work at Volkswagen (Figure 6-1), has shown that a blend containing 3.7% oxygen by weight, obtained by mixing 3% methanol and 5% ethanol, produced disruptions in driveability in a carbureted "Polo" sedan which were not acceptable. [6]

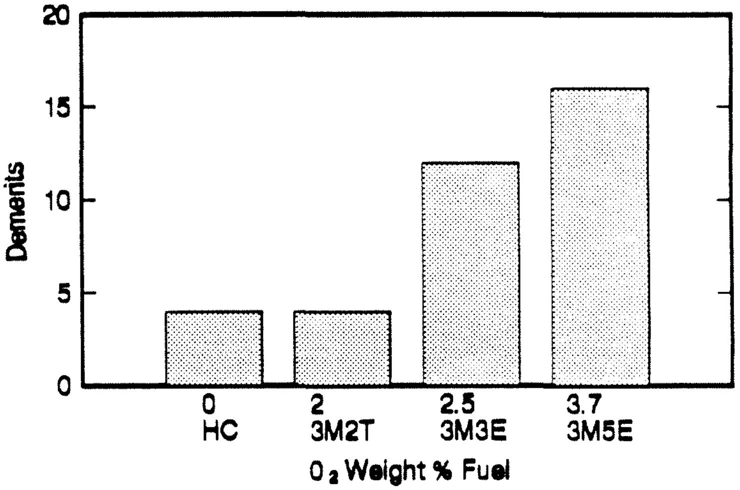

Figure 6-1., Driveability demerits with oxygenated components.

Neste Oy of Finland tested MTBE blends up to 25% down to -25°C. Their temperature data show that the cranking time increases as the MTBE concentration increases and the temperature decreases. The authors conclude based on a demerit rating scale that MTBE does not detract from vehicle performance. [7]

- High Level Blends

Policy Issue #1

The effect of low temperatures on neat and high level blends is very clear: they become difficult to start. Much effort has been spent on increasing the reliability of cold starting for these fuels.

To aid in starting neat alcohol fueled vehicles at low temperatures, many have experimented with the use of "add-on" technology such as dual fuels, fuel heaters, dissociation of methanol into hydrogen and CO, and dehydration of methanol into dimethyl ether and water. [8,9]

Auto manufacturers such as Ford believe that the additional hardware needed for such systems is not a practical solution [10]. Instead, through the use of cold start engine calibrations they can achieve cold start on M-85 down to -20°F (-29°C). [11]

General Motors has successfully cold started a port fuel injected, 2.5L spark ignition engine down to -20°F (-29C) using 10.5 psi RVP M-85 fuel without heaters or auxiliary fuel injectors. The engine used an exponential decay algorithm for the amount of fuel injected into the cylinders during cranking, along with a high current ignition system. [12]

The cold start limits of neat (i.e., 100% pure) alcohols compared to seasonal gasoline blends are shown below in Figure 6-2. [13] As mentioned before, a fuel's ability to start at low temperatures depends on its RVP. RVP is normally measured at a temperature of 38°C, and at that temperature a typical winter blend has an RVP of .9 bar. Figure 6-2 shows the reduction of vapor pressure with temperature. At a given vapor pressure, methanol has a lower temperature threshold than ethanol.

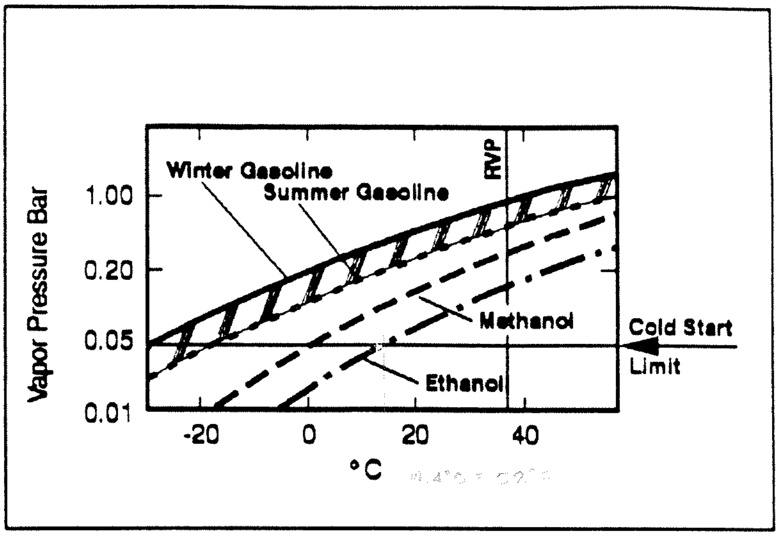

Figure 6-2., Vapor Pressure of ethanol, methanol, and gasoline dependence on temperature.

The addition of front-end volatility enhancing agents improves cold starting of high level alcohol blends. Additives tested by researchers include gasoline, butane, isopentane, and dimethyl-ether. Volkswagen found that the addition of 8% by volume of isopentane extended the cold start limit of methanol from +10°C to approximately -20°C, as shown in Figure 6-3. [14]

Figure 6-4 [15] below shows how gasoline, butane, isopentane and dimethyl-ether affect the limit temperature of cold startability. The additives are arranged in the order of their ability to extend the cold start limit. The L, M, and H following the methanol content designate low, medium, and high RVP regular gasoline blends. For example, RGM85M refers to a M85/15% regular gasoline blend of medium volatility. An isopentane M-90 blend was found to extend the limit to -32°C. The cold temperature limits decrease significantly with small additions of the above mentioned additives.

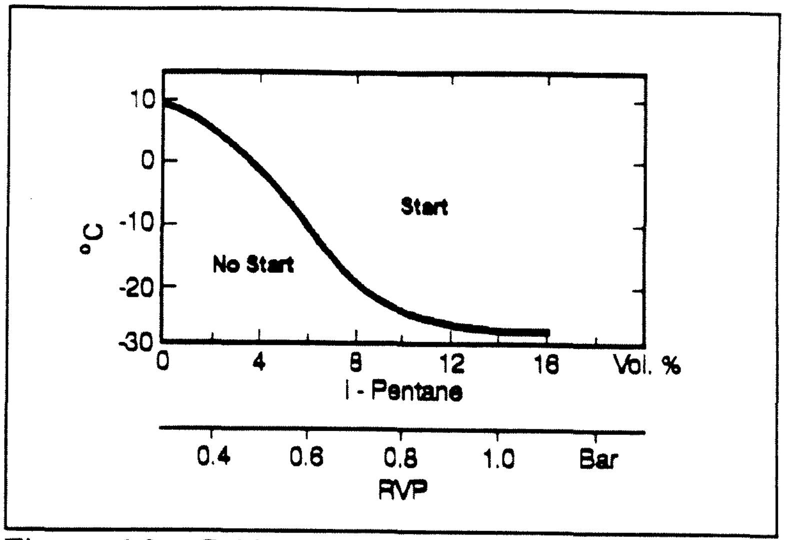

Figure 6-3., Cold start performance of methanol/i-pentane blends.

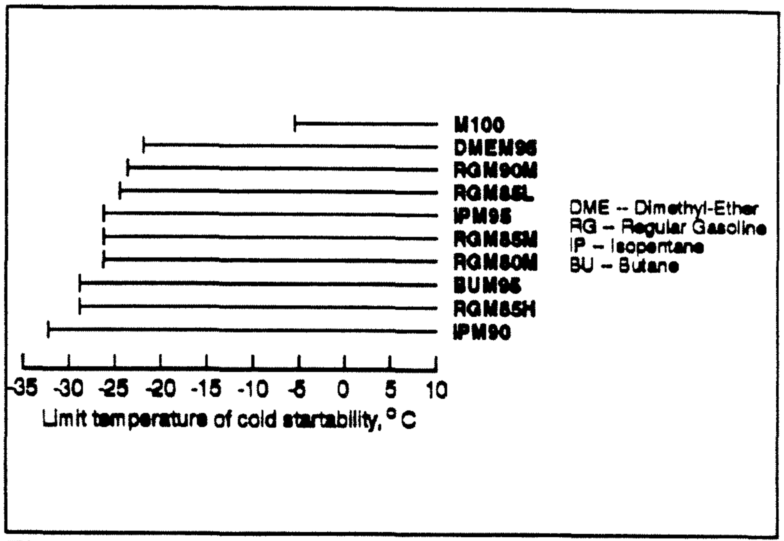

Figure 6-4., Effect of additives to methanol on cold start temperature limits.

High Temperature Performance

When gasoline as well as alcohol blends in a vehicle are exposed to high operating temperatures, vapor tends to form in fuel pumps, fuel rails, lines and carburetors. If too much vapor is formed, a decrease in fuel flow can occur to the engine resulting in symptoms of vapor lock. These include stalling, hesitation, loss of power or complete stoppage followed by difficult restarting. Vapor lock can become a real problem as temperatures rise above the boiling points of fuels upon shutdown of an engine, making restarting very difficult. Proper engine design techniques can help alleviate the problem. New fuel injection systems operate at higher pressures to minimize vapor formation during the pressure drops that occur during fast acceleration. Because of their lower heating values, alcohol fuels require fuel injection systems to deliver an increased amount of fuel per unit time, requiring even higher pressures than gasoline-fueled vehicles. [16]

- *Low Level Blends*

High temperature performance of unmodified present day vehicles on low-level alcohol blends is generally not a problem. As previously mentioned, the majority of the world's auto manufacturers state in their 1990 car warranties that the use of low-level alcohol blends is acceptable. However, they caution that if driveability problems are encountered, one should discontinue use. Because of the RVP increase associated with 10% ethanol blends, high temperature operation of vehicles can increase the possibility of vapor lock conditions. Research has shown varying degrees of severity, dictated by vehicle fuel control technology. [17,18] Because closed-loop system technology allows for slight variations in fuel air ratio, little or no negative driveability effects are encountered due to leaning caused by the ethanol. Older open-loop, carbureted vehicles experience more driveability problems associated with ethanol leaning effects.

Work at Toyota has shown that the Fuel Evaporative Vapor Index (FEVI), used to predict a fuel's tendency to vapor lock, fails to predict this possible deterioration in driveability when using low-level methanol blends. The reason for this discrepancy is that, compared to gasoline, the volatility of blended fuels increases at a greater rate as the temperature approaches the actual operating temperatures of 100°C. Figure 6-5 [19] shows that hot start cranking time increases as the percentage of methanol increases.

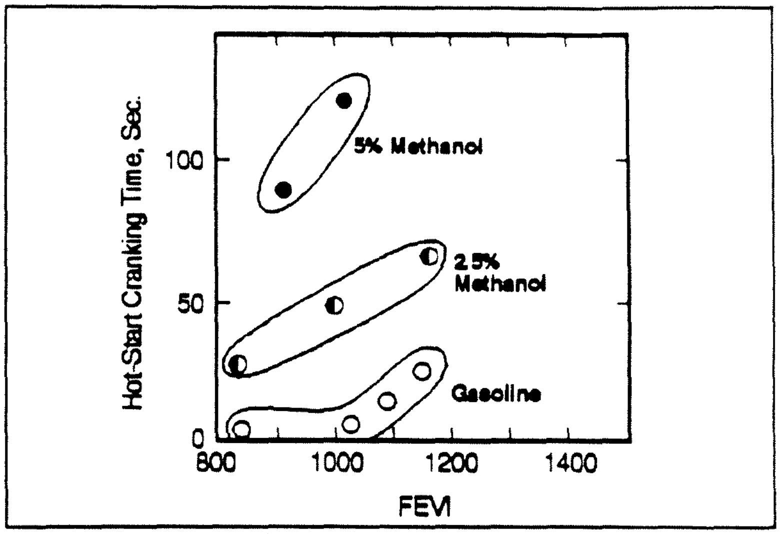

Figure 6-5., Relationship between cranking time and FEVI for low level methanol blends.

Compared to methanol, ethanol should produce less of a negative effect because of its lower volatility. Toyota's warranty, typical of most major manufacturers including the three largest U.S. automakers, states: "If driveability problems are encountered (poor hot starting, vaporizing, engine knock, etc.), discontinue use". [20] Clearly the effect of low-level alcohol blends during high operating conditions depends on the specific fuel system and fuel being used.

- High Level Blends

Policy Issue #2

High operating temperatures increase the possibility of vapor lock as the percentage of alcohol increases. This is due to the volatility characteristics, low RVP, and flat distillation curves (see Section 4, Figure 4-3) of neat methanol and ethanol.

While the first generation Bank of America carbureted vehicles had difficulties with vapor lock [21], the newer fuel injected dedicated neat alcohol fuel vehicles and flexible fuel vehicles or FFVs do not seem to exhibit these problems. The California Air Resources Board (CARB) describes driveability and performance to be generally very good and excellent for their dedicated alcohol fuel VW, Toyota, Ford FFV* Crown Victorias, and GM VFV* Corsicas. These vehicles generally operate on M85 blends containing a 40% aromatic-based gasoline. [22] The high level of aromatics is added to increase the RVP to aid in cold weather starting. Seasonally, gasoline blenders change the mixture of components in their fuels. Winter gasoline generally has more volatile additives to increase the ease of cold weather starting. In fall and spring, the arrival of unseasonally warm weather can adversely affect the performance of cold weather blends. High operating temperatures may lead to vapor lock in the engines running on a cold weather blend. [23] Similarly, high-alcohol blends require the use of very volatile additives to provide the volatility needed for cold weather operation. These blends are equally susceptible to vapor lock during unseasonably warm weather.

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[*] Ford Motor Company has adopted the term "Flexible Fuel Vehicle" or FFV for its prototype multi-fuel vehicles, while General Motors uses the term "Variable Fuel Vehicle" or VFV. We will adopt the most common usage and refer to all vehicles designed to operate on gasoline, alcohols, and gasoline/alcohol blends as flexible fuel vehicles or FFVs.

Vehicle Range

Policy Issue #3

The effect of alcohol content on a vehicle's range is well known. Alcohols have less energy content/unit volume than gasoline. As the alcohol content of a fuel increases, the overall range for a given vehicle tends to decrease.

Because ethanol has a higher heating value and greater air/fuel requirement than methanol, its overall vehicle range if tested in the same vehicle would fall between that of gasoline and methanol. The decrease in overall vehicle range when using methanol is clearly shown in Figure 6-6 below. [24] The vehicle is a Ford Flexible Fuel Vehicle (FFV) Crown Victoria which can operate on any blend methanol/gasoline or ethanol/gasoline blend.

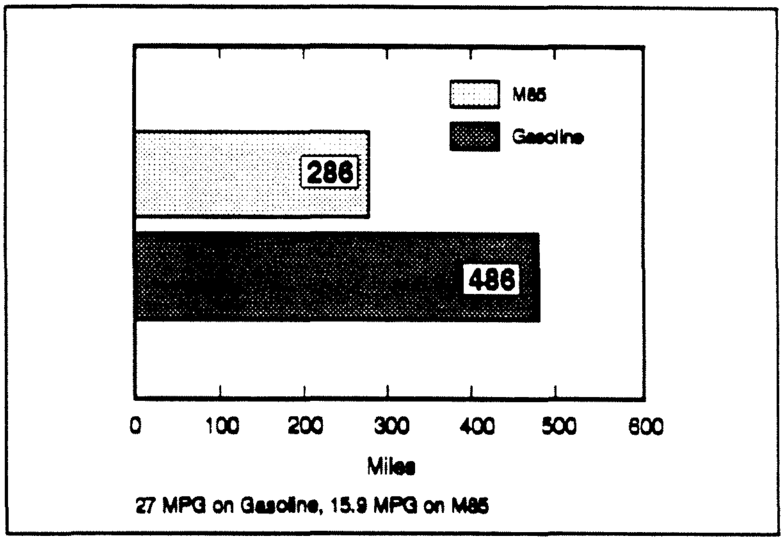

Figure 6-6., FFV vehicle range on M-85 and gasoline.

Differences in a particular vehicle's range are primarily dictated by the fuel economy of the vehicle/fuel combination. Fuel efficiency is an additional energy-based parameter used to describe a particular fuel.

Fuel economy is measured in units of distance per unit volume of fuel, either miles per gallon or kilometers per liter (or gallon). A recent study conducted by the State of Colorado describes their oxygenated fuels program in which 1.8 million vehicles travelled over 4.8 billion miles. The state found a decrease of 1-3% in fuel economy for the newest closed-loop technology vehicles operating on a 10% ethanol blend. This slight decrease is due primarily to the 3% lower Btu/gallon value of a 10% ethanol blend. [25,26] The California Air Resources Board or CARB has been periodically testing methanol fueled prototypes since 1980. [27] In Brazil the majority of the fleet operates on neat ethanol, although the Brazilian consumer has the option of purchasing 22% ethanol/ 78% gasoline vehicles as well. [28] Table 6-1 is a compilation of fuel economy figures from CARB and the Brazilian Motor Vehicles Manufacturers Association. [29,30]

Table 6-1

Vehicle	Fuel	Fuel Econ. (MPG)	Gasoline Equiv. MPG
		CARB DEDICATED	
81 VW	M85	12.8-16.0	22.6-28.3
81 VW	M85	12.0-15.1	21.2-26.7
83 ESCORT	M85	12.6-13.7	22.3-24.2
83 ESCORT	M85	13.6-14.7	24.0-26.0
83 ESCORT	M85	13.6-17.0	24.0-30.0
83 ESCORT	M85	13.1-17.2	23.1-30.4
85 CAMRY	M85	15.0-17.2	26.5-30.4
86 CAMRY	M85	16.0-16.2	28.3-28.6
86 CARINA	M85	18.1-20.5	32.0-36.2
87 CROWN VICTORIA	M85	9.7-10.0	17.1-17.7
88 CORSICA	M85	11.4-12.0	20.1-21.2

U.S. CARB MULTIFUEL

87 FFV CROWN VICTORIA	GAS	16.0-17.4	---
	M25	14.3-15.5	16.4-17.8
	M50	11.9-12.7	16.0-17.1
	M85	9.2-10.2	16.2-18.0
	M100	8.5- 8.8	17.4-18.0
	E85	12.2-12.8	17.3-18.1
	E95	11.8-11.9	7.5-17.7
88 VFV CORSICA	GAS	19.8-22.3	---
	M25	17.8-18.4	20.4-21.1
	M50	15.2-16.4	20.4-22.0
	M85	11.6-12.5	20.5-22.1
	M100	11.0	22.5

BRAZIL				GAS. EQUIV.	
		CITY	HGWY	CITY	HGWY
86 FIAT PREM.	E95	20.0	29.8	29.7	44.3
	GAS	27.7	40.4		
86 ESCORT	E95	23.3	32.4	34.7	48.2
	GAS	29.4	44.0		
86 CHEVETTE	E95	21.1	27.3	31.4	40.6
	GAS	25.8	33.8		
86 VW GOLF	E95	20.9	28.7	31.1	42.7
	GAS	27.0	35.5		

* CARB mileage figures collected under FTP test procedure.

Due to the wide a variety of factors which affect fuel economy, comparisons between vehicle types do not give accurate conclusions about a fuel's ability to provide greater mileage. However, in a FFV or VFV, straight gasoline with its higher heating value, provides higher mileage per gallon than any alcohol blends or neat fuels. Moreover, the CARB figures for the FFV Crown Victoria show ethanol to provide more miles per gallon than methanol, illustrating its higher Btu/gallon value.

The flexible fuel vehicle is clearly a compromise, designed to operate on the gasoline which is available everywhere in the United States and to operate reasonably well on alcohol fuels and blends. Vehicles designed specifically to operate on ethanol or methanol would not have to make these design compromises. They would take full advantage of the higher power and greater efficiency of alcohol fuels, would use the higher compression ratios, and other design decisions that would increase the mileage and performance of alcohol fuels above shown in Table 6-1.

Fuel efficiency is measured thermally instead of volumetrically. Alcohol fuels are more thermodynamically fuel efficient than gasoline. This comparison is made in units of energy per unit mile travelled (typically Btus/mile). [31] Comparing the average values of the FFV Crown Victoria on gasoline, methanol and ethanol in Table 6-2, we see the higher efficiency of both methanol and ethanol over gasoline.

Table 6-2

Fuel	MPG	Heating Value Btu/Gal)	Btu Mile	Improvement
Gasoline	16.7	116,000	6945	----
Methanol	8.7	56,800	6528	6.0%
Ethanol	11.8	76,000	6440	7.2%

The example is meant for illustrative purposes, to explain the concept of comparing the efficiency of fuels using the energy required per unit mile. Actual experiments by General Motors have shown alcohol to be slightly more fuel efficient than gasoline (for more information refer to). [32] Results can vary considerably depending on the heating values used and differences in volatility enhancement additives.

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Section 7

CLEANING AND CORROSION CHARACTERISTICS OF ALCOHOL

Quick Reference Data

Materials Subject to Degradation from High Concentration of Alcohols

- lubricating oils
- terne steel (in gas tanks)
- cylinder walls, fuel pumps, carburetors
- polymers, elastomers, rubbers, plastics (hoses)
- polymethane
- cork gasket material
- leather
- polyester bonded fiberglass laminate

Additives to Prevent Corrosion from Alcohols

- Higher alcohols to minimize phase separation
- Corrosion inhibitors
- Acid neutralizers in lubricants
- Surface treatment of engine parts (nitriding and chrome plating)

Useful Terms and Definitions (also see Glossary)

- **Corrosion:** a gradual wearing away or alteration by a chemical or electrochemical.

- **Formic Acid:** a colorless, pungent liquid acid (HCOOH) that is made by acidification of sodium formate. Formerly obtained from ants, spiders, etc. Synthetically, it is formed in the combustion chamber during the combustion of methanol or water-contaminated ethanol. Also known as methanoic acid.

- **TAME** (Tertiary Amyl Methyl Ether): an ether formed by the reaction of methanol and either isoamylene or isopentalene.

- **Terne Metal:** sheet iron or steel coated with an alloy of about 4 parts lead to 1 part tin.

Key Issues and Implications

Issue #1: Alcohol Combustion Characteristics and Acid Formation

At low engine temperatures, the combustion of methanol (or water-contaminated ethanol) produces water vapor and formaldehyde, which in turn produces formic acid inside the engine.

Implications of Combustion Characteristics and Acid Formation:

The water vapor and formic acid formed during low-temperature combustion of methanol (or other alcohols contaminated with high percentages of water) can oxidize metal engine components and reduce the lubricating ability of engine lubricating oil. Oxidation and reduced lubrication will lead to accelerated wear of engine parts such as cylinder walls, crankshafts, and bearings.

Proposed Solutions:

- Use of acid neutralizers in lubrication oil.
- Surface treatment of engine parts (such as soft nitriding crankshafts or plating cylinder bores with chrome).
- More frequent replacement of lubrication oil or higher quality synthetic oils or a redesign of conventional engine lubrication oils.

Detailed Information: Refer to pages 7-2 through 7-4 and 7-9 through 7-11.

Issue # 2: Alcohol Fuels as Reactive Solvents

Unlike gasoline, alcohols have a fairly strong solvent property that can harm some materials in engine fuel systems; can lead to lubrication failures in engines; and can loosen deposits in gas tanks and pipelines.

Implications of Alcohol's Solvent Capabilities:

- For 10% or less ethanol blends, there are no implications -- all automobiles sold in the U.S. now use fuel system components designed to use this blend under warranty.
- Premature degradation of certain common engine/fuel system materials.
- Reduced lifetimes or lower effectiveness of engine lubricants.
- Loosening of pre-existing deposits in storage tanks and pipelines.

Proposed Solutions:

- Fuel system components must be selected which are immune to the solvent action of alcohols--materials are available that can withstand this solvent action. For fuels containing high percentages of methanol fuel, solutions appear to have been found, although further testing and data is needed to verify performance.
- For higher percentage alcohol (especially methanol) fuels, there are a number of options for preventing corrosion, including: use of stainless steel or anodized aluminum components and the use of "higher alcohols" (those with more carbon in their molecular make-up) additives to act as corrosion inhibitors.
- Further investigation is needed on pipeline maintenance procedures to minimize deposits susceptible to alcohol solvent action.

Detailed Information: Refer to pages 7-4 through 7-9.

Section 7

CLEANING AND CORROSION CHARACTERISTICS OF ALCOHOL

- Solvent Characteristics of Alcohols and Alcohol Blends
- Influence on the Combustion Chamber
- Effects of Alcohols on Various Materials
- Influence on Fuel Distribution System
- Vehicle Failures
- Additives Required to Prevent Corrosion

Introduction

The different chemical structures of alcohol fuels (ethanol or methanol) and gasoline necessitate significant changes to current vehicle technology. A joint research effort by 14 major U.S. oil companies and three of the largest auto companies is currently focusing on experimental and commercial production of flexible fuel vehicles. These are specifically designed to run on high level alcohol blends as well as on conventional petroleum-based fuels. Unfortunately, the reliability and durability of flexible fuel vehicles depends on alcohol solvent and corrosion properties. Unlike gasoline, alcohols are strong solvents and are more highly corrosive. Methanol has been found to be more corrosive than ethanol, both in material degradation and the formation of acid within the combustion chamber, which reduces the effectiveness of the lubricating oil. The solvent effects of alcohol fuels on both the fuel distribution system and vehicle are addressed in this section, as well as the corrosion sensitivity of various metals and non-metals found in current vehicle and fuel distribution systems. Finally, a strategy to minimize the corrosive effects of alcohol fuels is also presented.

Solvent Characteristics of Alcohols and Alcohol Blends

Alcohols, because of their high polarity and the ability to form hydrogen bonds, are used as excellent solvents in the chemical industry. However, this solvent characteristic can cause problems when the alcohol is used as a fuel. These problems may occur in the fuel distribution system as well as in the combustion chamber.

Influence on the Combustion Chamber

A liquid fuel, while burning on a cold surface, can dissolve significant amounts of its combustion products. As discussed earlier, alcohols have much higher latent heats of vaporization than gasoline. Therefore, if the alcohol inducted into an automobile's cylinder is not sufficiently vaporized, the liquid fraction of the alcohol (ethanol or methanol) can act as a solvent for its combustion products. These products are corrosive (including formic acid, for example), degrading the lubricants and greatly increasing wear on cylinder walls.

Combustion residues from neat methanol include water, unburned alcohol, formaldehyde, formic acid, and methylenehydroxy-peroxide. In addition to these constituents, relatively low concentrations of acetaldehyde and acetic acid are found in combustion residues of ethanol, isopropanol, n-propanol and n-butanol. Methanol combustion residues contain substantially higher concentrations of formaldehyde and formic acid than the higher molecular weight alcohols, but all alcohol combustion residues contained about the same levels of methylenehydroxy-peroxide. The concentrations of combustion products in combustion residues, particularly formaldehyde, formic acid and methylenehydroxy-peroxide, tended to increase as the coolant temperature was raised. [1,2,3,4,5]

A number of studies have been undertaken which deal with the corrosion and wear within the engine chamber caused by the use of either methanol/gasoline or ethanol/gasoline blends. [6]

The formic acid and the water formed by the methanol combustion are the principal causes of corrosion and wear. Because the hydrogen-to-carbon or H/C ratio of methanol is higher than that of gasoline, a large amount of water vapor is formed by methanol combustion. Theoretically, 23 mol % of water is formed from methanol combustion compared to 13 mol % of water from gasoline. This explains the increased tendency for water to accumulate in the lubricant oil when the engine is fueled with methanol. At oil and water temperatures of around 40°C (while the engine is warming up), the volume of water condensed from methanol combustion is twice as great as that from gasoline, as illustrated in Figure 7-1. [7]

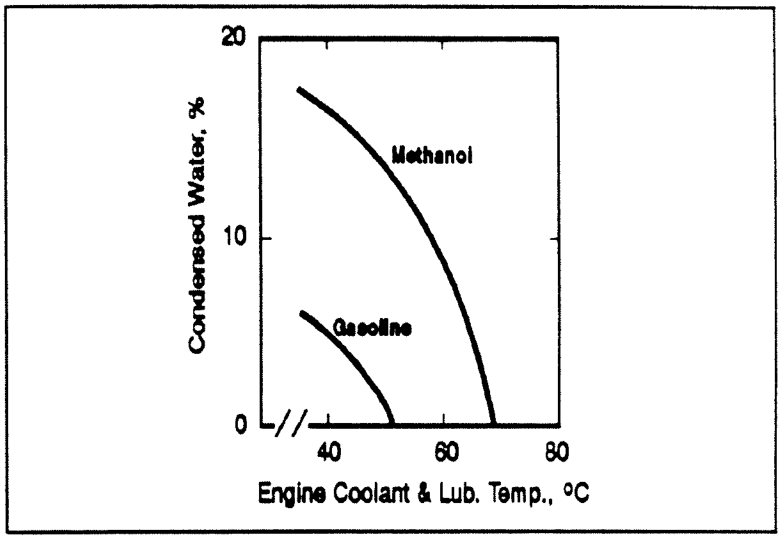

Figure 7-1., **Condensed** water from methanol and gasoline **combustion.**

This partial oxidation of methanol produces formaldehyde, which converts easily to formic acid.

$$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O \text{ (formaldehyde)}$$

$$HCHO + \frac{1}{2}O_2 \rightarrow HCOOH \text{ (formic acid)}$$

When methanol is burned in a cast iron container, the formic acid and methylene hydroxy-peroxide in the residue oxidize the metal and form rust.

In the studies examined, the wear rates with unleaded gasoline and anhydrous ethanol were in the normal range; however, when the ethanol contained 11% water, the wear increased significantly as the engine temperature was reduced. Considerably greater wear rates were observed with anhydrous methanol, and those increased dramatically when the methanol contained 11% water.

Effects of Alcohols on Various Materials

A variety of metals have been identified as potentially sensitive to degradation by methanol/gasoline blends in the range of 10-15% methanol. [8] These include: (a) terne steel, which is used in fuel tanks, (b) magnesium, and (c) aluminum, which is used in carburetors and fuel pump bodies.

Terne steel is a sheet steel that is hot dipped in a tin-lead solution to retard corrosion; it is almost exclusively used in automotive fuel tanks. Uniform corrosion leads eventually to a removal of the protective terne lining the fuel tank, which in turn leads to accelerated corrosion of the fuel tank steel itself. Presence of water contamination leads not only to more uniform corrosion but tends to increase the tendency toward pitting corrosion which can lead to fuel tank perforation in a short period of time. Fleet test results using terne metal in the gas tanks have not shown any catastrophic failure of the tanks due to corrosion by gasoline/methanol blends under 15% methanol.

However, observations of a galvanic corrosion in methanol/gasoline blends has been reported. [9] This is a corrosion due to the presence of electrical currents in methanol/gasoline blends, currents created by rear-mounted fuel pumps. Gasoline is known to be a relatively good electrically insulating liquid due to the general non-polar nature of the constituents hydrocarbons. Methanol, unlike gasoline, is very polar and conducts electricity much better. Therefore, the presence of methanol in a fuel blend would be expected to increase the tendency and extent of galvanic corrosion.

Several non-metals used in fuel systems have been responsible for most reported failures of vehicles fueled with methanol/gasoline blends. These include a large number of different polymers, elastomers, rubbers, plastics, etc. Other investigators have shown no problems in operation of methanol/gasoline blends. [10] Sensitive non-metals include natural rubber (not used in current vehicles), polyurethane (used as fuel lines in some vehicles), cork gasket material, leather, polyester-bonded fiberglass laminate, PVC, and certain other plastics (polyanides and methyl-methacrylate). Non-metals resistant to methanol include Buna N and Neoprene rubber, polyethylene, nylon and polypropylene. Contradictory results have been reported on a very large number of non-metals, including Nitrile and Viton. [11]

The effect of ethanol/gasoline and methanol/gasoline blends on the rate of fuel hose permeation has been investigated. [12] Fuel permeation rate through a fuel hose is a function of several parameters: (1) fuel aromatic content, (i.e., the greater the aromatics by volume, the greater the permeation); (2) hose material type and composition; (3) percent volume of alcohol; and, (4) type of alcohol. With an SAE 30 R 7 hose, 10% ethanol/gasoline blends increase the permeation rate about 25%, while 15% methanol/gasoline blends will increase the permeation rate 63%. Similarly, with an SAE 30 R 8 hose, 10% ethanol/gasoline blend will increase the permeation rate approximately 151%, while a 15% methanol/gasoline blend will increase the permeation rate 342%.

Influence on Fuel Distribution System

When ethanol or methanol, either pure or blended with gasoline, is shipped through a common carrier pipeline, it may loosen some of the deposits which have precipitated out from previous shipments and line the inner surfaces of pipe. This would not only result in contamination of the alcohol/gasoline blend and damage compressors and pressure maintenance units, but might possibly contaminate the next product sent through the pipeline as well. [13] **In contrast, alcohol-based ethers (such as ETBE, MTBE, and TAME) are considered by pipeline operators to be "pipeline-fungible"; that is, they can be shipped in pipelines interchangeably with gasoline and crude oil (without affecting the pipelines or subsequent shipments.**

Vehicle Failures

Experimental and commercial conversions of production vehicles to alcohol fuel have been performed for many years. Brazil instituted a large-scale alcohol fuel program in 1975. More than 11.9 million vehicles have been produced to operate on neat and 22% ethanol blends. In the United States, numerous research reports have been written in the past decade describing the negative effects of neat alcohol and high-level alcohol blends. **The corrosive properties of high-level alcohol blends or neat alcohols necessitate significant modifications to current U.S. vehicle technology.** After only 2 years Brazil was able to overcome almost all problems associated with alcohol fueled vehicles, indicating that the technology is available. Failures reported to date with flexible fuel vehicles (FFV) vehicles designed specifically to accommodate high-level alcohol blends as well as gasoline-based fuels, indicate that further reliability testing is needed if their reliability is to be similar to gasoline fueled cars.

Early Retrofits to Production Vehicles

In 1982 the Bank of America (BOA) converted 416 primarily carbureted vehicles to operate on low concentration blends (up to 18%) as well as neat methanol. The BOA reported negative effects of methanol on elastomers, carburetors, fuel lines, fuel pumps, fuel level sending units, terneplate gas tanks, as well as accelerated wear data from various internal engine components. [14] For further information on failures in older designs, refer to [15].

Maintenance data released by the California Air Resources Board (CARB) show intermittent fuel system problems causing inaccurate emissions measurements. While some changes were due to developmental reasons, the majority of the problems were due to clogging of injectors caused by the corrosive reactions between methanol and various fuel system components. Parts replaced by Ford on their carbureted and fuel injected 1983 Escorts included carburetors, fuel injectors, catalysts, EGR valves, oxygen sensors, fuel pumps, computer chips, and temperature sensors. Two Toyota test vehicles had their fuel injectors replaced twice because of driveability problems before they had logged 25,000 miles. One vehicle experienced engine failure after 43,500 miles. [16]

Current Modifications to Vehicles (M-85)

One U.S. automaker performed the following fuel system modifications to a 1988 production model to prevent the corrosion problems of high-level methanol blends [17],

- Stainless steel fuel tank with stainless flame arrestors in the fill and vent tubes to prevent ignition by an external source.
- Methanol-resistant float level potentiometer with a corrosion protection circuit.
- Higher flow methanol-tolerant fuel injector and fuel pump to handle higher flow rates.
- Stainless fuel lines with accompanying teflon fuel hoses.
- Anodized aluminum fuel injection rail and modified pressure regulator.

In addition, the necessary on-board hardware was provided to change the engine operating parameters to optimize the combustion of M-85. These modifications are typical for conversions of conventional vehicles to high-level alcohol blends.

Lubrication Failures

The use of neat methanol in current engine designs presents lubrication requirements substantially different than those of gasoline. Research has shown that using the same conventional mineral oil used in current engines severely increases upper cylinder bore wear, valve train wear and connecting rod bearing wear [18]:

	Gasoline	Methanol
Valve Train Cam Wear (mils)	0.5	2.7
Cylinder Bore Wear (mils)		
Longitudinal	0.9	9.3
Transverse	2.7	16.1
Connecting Rod Bearing (mg)	63	189

Preliminary experiments have demonstrated the ability of higher quality synthetic oils to reduce the severity of the wear associated with methanol combustion. Further work will be needed on lubrication composition to prevent the conversion of engine oil to an oil/methanol/water emulsion. This breakdown of the oil's lubricating properties is thought to be responsible for the higher wear. [19]

FFV Failures

Data reported by CARB indicate the replacement of original fuel injectors in 1987-1988 Crown Victorias FFVs with an improved injector virtually eliminated the injector fouling problems experienced initially. In addition, the replacement of the fuel pumps with stainless steel units has provided trouble-free operation with the exception of increased noise. Mileage accumulation varies from 23,000-41,000 miles (as of Nov. 1988). [20]

Multi-fuel vehicles utilize sensors to determine the alcohol/gasoline ratio in the particular blend being used. These systems can operate on ethanol as well as methanol blends. Currently there are optic and dielectric type sensors being used by Ford, General Motors, and Chrysler. The previously cited CARB analysis of the Ford Crown Victorias FFVs noted several failures of the cars' optical sensors, indicating the need for more development work in that area.

A recent SAE report describes the errors associated with both measuring systems. The optic sensor has inherently greater error due to the change in refractive index associated with different hydrocarbon constituents and the effect of deposits building on the fuel/optic interface. Although the dielectric measuring technique requires a temperature compensation function for variations in capacitance with respect to temperature, the error associated with this sensor is 5%. [21] The effect of water content on sensor performance is still not known. The authors indicate that both systems need to be further developed to assure durability and reliability.

Additives Required to Prevent Corrosion

Inhibitors and Higher Alcohols

Corrosion inhibitors are used in conventional gasolines to retard corrosion in metal fuel systems components. Higher alcohols, especially C_4 (i.e., iso-butyl or tert-butyl) alcohols, can be used to prevent or minimize phase separation in water-contaminated alcohol/gasoline blends. [22,23] The prevention of phase separation would have definite benefits for overall driveability as well as in corrosion of water-sensitive components such as aluminum.

Acid Neutralizers in Lubricant Oil

One of the functions of an engine oil is to protect surfaces against various chemical attacks. In particular, acids produced during combustion of gasoline/alcohol blends are neutralized by certain oil additives. Examples for acid neutralizers are zinc dialkyldithiophosphates and sulfonates, and calcium sulfonate. As seen in Figure 7-2 [24], the use of an acid neutralizer in lubricant oil in methanol-fueled vehicles provides significantly reduced wear but still is twice that of a gasoline engine. More frequent oil changes may be required to overcome this problem.

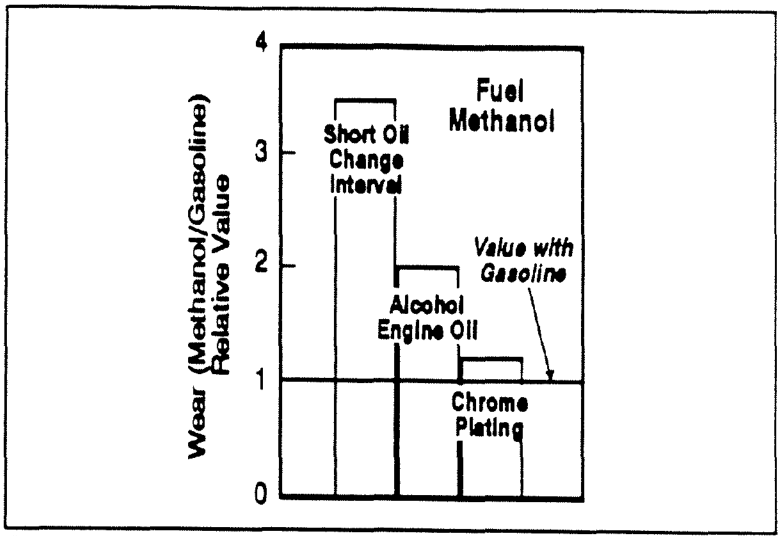

Figure 7-2., Effect of counter-measures on cylinder bore corrosive wear.

Surface Treatment of Engine Parts

By treating the crankshaft with soft nitriding and by plating the cylinder bores with chrome, wear with methanol fuel can be virtually reduced to the level of a gasoline engine (Figure 7-2). The chrome plating was electrically pitted in order to make it sufficiently rough to retain the oil film. [25]

Shorter Lubricant Oil Change Intervals

Although the basic compounds required for preventing oxidization and deterioration are contained in the oil, as the total engine operating hours increases, the basic compounds are neutralized and the lubricant oil shows increased acidity. Experimental results confirm that the main cause for the corrosive wear in methanol-fueled engines is accumulation of formic acid in the lubricant oil. Shorter lubricant oil change intervals reduce corrosive wear significantly, as shown in Figure 7-3. [26]

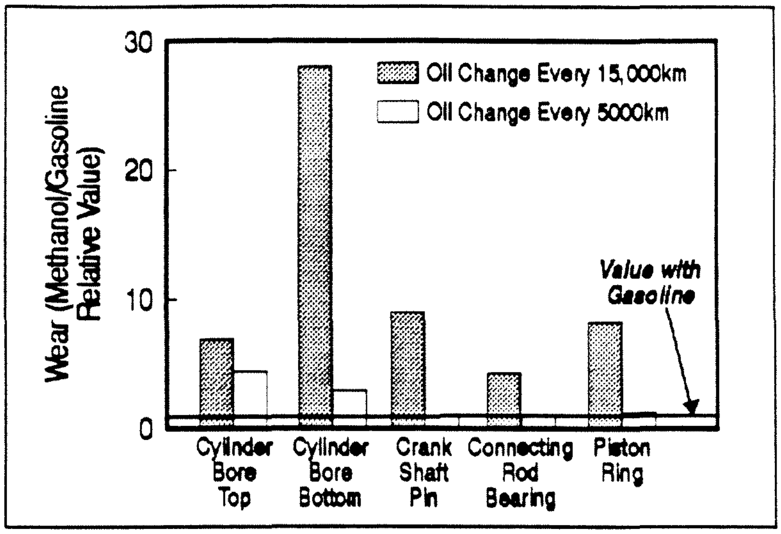

Figure 7-3., Effect of short oil change interval on wear.

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Section 8

NEW DIRECTIONS FOR REFORMULATING ALCOHOL FUELS TO OVERCOME OPERATIONAL PROBLEMS

Quick Reference Data

Cetane Numbers

Diesel = 45 to 55
Ethanol = 8
Methanol = 3

Electric Conductivity

(mbo/cm)	
Gasoline	1×10^{-14}
Diesel Fuel	1×10^{-12}
Ethanol	1.35×10^{-9}
Methanol	4.4×10^{-7}

Viscosity

	Centipoise	
	20°C	-20°C
Methanol	0.59	1.15
Ethanol	1.19	2.84
Diesel Fuel	9.7	1.15

Useful Terms and Definitions (also see Glossary)

- **Cetane Number (Rating)**: a measure of the ignition value of a diesel fuel (i.e., the percentage by volume of the hydrocarbon cetane ($C_{16}H_{34}$) in a mixture of cetane and 1-methylnaphthalene that gives the same ignition lag as the fuel oil being tested).

Issues and Implications:

Issue #1: Low Cetane Numbers of Fuel Alcohols

Neat alcohol fuels will not self-ignite in existing compression ignition (diesel) engines.

Implications of Low Cetane Numbers:

- Alcohols cannot be used in existing diesel engines to replace diesel fuel without modifying the engine or adding supplemental additives.

Proposed Solutions:

- The use of additives in alcohol fuels currently appear to be much more promising than modifying the diesel engine (such as using continuously operating glow plugs). "Ignition improver" additives that have shown significant success include peroxides, nitro-compounds (Avocet™), nitrocellulose, or nitrates. For example, the addition of 7.5% Avocet™ to methanol has resulted in similar combustion characteristics to diesel fuel when burned in a diesel engine.

Detailed Information: Refer to pages 8-2 through 8-4.

Issue #2: Phase Separation of Alcohol/Gasoline Blends

Implications of Phase Separation:

- Loss of cold weather driveability
- Potential fuel line freezing

Proposed Solutions:

- In addition to improved alcohol storage and shipping techniques to prevent water contamination, gasoline/alcohol blends can be reformulated to avoid phase separation by introducing additives such as "higher" alcohols, various nonionic surfactants, and various anionic fatty acid surfactants.

Detailed Information: Refer to pages 5-7 through 5-10 and 8-4.

Issue #3: Electrical Conductivity

The comparatively high electrical conductivity and high oxygen content of fuel alcohols can contribute to corrosion and wear problems as well as chemical degradation of materials in a vehicle's fuel system.

Implications of High Conductivity of Alcohol Fuels:

Current flows from rear-mounted fuel pumps can induce galvanic corrosion.

Proposed Solutions:

- Selecting materials compatible with the properties of alcohols will help alleviate these problems.
- Using corrosion inhibitor additives and higher alcohols (such as 1-butanol or n-decanol) as cosolvents with fuel alcohols inhibits corrosion of water-sensitive materials such as aluminum.

Detailed Information: Refer to pages 7-4 through 7-5 and 8-5.

Issue #4: Viscosity

Ethanol and methanol have low viscosity which may lead to lubrication problems, especially in diesel fuel engines modified to run on alcohol fuels.

Implications of Low Viscosity:

Increased wear due to less effective lubrication.

Proposed Solution:

- Use of higher alcohols as additives may be needed to improve lubricity.

Detailed Information: Refer to pages 8-6.

Issue #5: Cold Weather Starts

Neat alcohol-fueled engines have proven difficult to cold start, especially at ambient temperatures below 10°C (50°F).

Implication of Cold Weather Starting Problems:

- Prolonged engine cranking
- Battery wear

Proposed Solutions:

- Neat alcohols will require either "reformulated" mixtures using some form of additive (such as gasoline, dimethyl ether (DME)), or some other cold start subsystem.

Detailed Information: Refer to pages 8-6.

Section 8

NEW DIRECTIONS FOR REFORMULATING ALCOHOL FUELS TO OVERCOME OPERATIONAL PROBLEMS

- Cetane Number
- Miscibility with Water and Hydrocarbon Fuels
- Electric Conductivity and Oxygen Content
- Viscosity
- Material Compatibility
- Safety Issues
- Cold Startability

Introduction

Ethanol and methanol have many important properties that make them quite different from gasoline and diesel fuel (see Table 2-4). **Modifications to certain properties of ethanol and methanol would improve their performance as alternative liquid transportation fuels.** Therefore, this section will focus on opportunities to modify specific properties of alcohol fuels to improve engine/vehicle performance. A number of technical alternatives are feasible. At the two extremes, one can either blend in one or more additives to the ethanol or methanol to improve its characteristics, or redesign the engine to take full advantage of the alcohol fuel's properties. Because of the cost and complexities involved in new engine design, most recent efforts and fleet tests have tended to modify an existing diesel/gasoline engine, test the use of an additive in the fuel, or both. In this section, the focus is exclusively on reformulations of the basic alcohol fuel, primarily through the addition of higher alcohols, to lessen or eliminate existing operational problems.

A set of requirements must be established for the properties of any additive. The additive must be physically and chemically compatible with the base alcohol fuel and have preferably have the same or higher specific energy content. Additives must not be readily removable from the fuel, significantly add to exhaust emissions, nor leave any residue. Moreover, additives should not complicate regulatory compliance, and should also be relatively inexpensive.

Cetane Number

Policy Issue #1

> Diesel engines use compression and heat to auto-ignite the fuel. The cetane number is a measure of the ignition value of diesel fuel. Most diesel fuel has a cetane numbers ranging from 45 to 55. The "low" cetane number of ethanol (8) and methanol (3) indicates an insufficient self-ignition quality for direct use of these alcohols in unmodified diesel engines.

Additives must be used with alcohol fuel to improve its self-ignition properties. [1,2] These additives are called "ignition improvers."

Figure 8-1 [3] shows the influence of the fuel's cetane number on the concentration required of the ignition improver to obtain the same ignition delay as a conventional diesel fuel (cetane number 52). Peroxides and nitro-compounds such as Avocet™ and nitrocellulose are suitable ignition improving additives for poor quality diesel fuels and for middle distillate fuels. In Sweden, 2% Avocet™ is also being tested as an additive to allow lignocellulosic ethanol to be used as a primary fuel in diesel buses. [4] Nitrates are also valuable additives for low cetane number fuels such as alcohols. Such additives can boost the performance of normally low cetane number fuels such as ethanol and methanol to those of commercial diesel fuels. For example, tests were made with methanol plus an ignition-improving additive consisting of a modified nitrocellulose (NC) combined with polyether to avoid solid deposits in the injection system. In comparison with conventional diesel operation, the combustion of the methanol plus the ignition improver exhibits nearly equal fuel consumption and ignition and ignition delay behavior. The enhanced methanol blend demonstrated much lower NO_x, soot, and particulate emissions when compared to conventional diesel fuel.

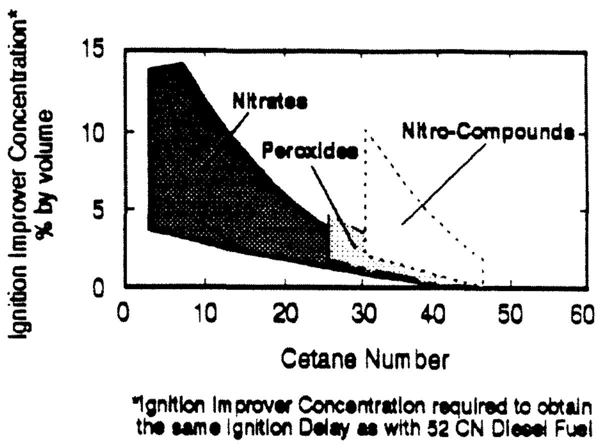

Figure 8-1., Ignition improver additives.

Of the commercial ignition improvers for alcohols, Avocet™ manufactured by ICI America, Inc. is one of the most popular and most widely tested. Avocet™ has a proprietary composition, but is known to contain a lubricant and corrosion inhibitor in addition to the active ignition improving compounds, which are nitrate esters; these components are diluted in methanol. The lubricant and corrosion inhibitor are present to protect the precise components of the diesel fuel injection systems, serving the same function as additives used to protect gasoline carburetor and fuel injection systems. Avocet™ is prepared in various concentrations by blending with chemical - grade neat methanol. The characteristics of Avocet™ are described below:

Appearance: Clear pale yellow liquid
Specific Gravity: 1.15
% Volatile by Volume: 25
Ingredients: Nitrate Ester and Methanol

The values used for methanol and Avocet™ in calculating the inputs for the emissions and carbon balance fuel consumption calculations are as follows:

	Methanol	Avocet™*
Specific Gravity	0.794	1.15
% Carbon by Wt.	37.5	35
% Hydrogen by Wt.	12.6	7
% Oxygen by Wt.	49.9	50
% Nitrogen by Wt.	--	8
Molecular Wt.	32.04	--

*Values provided by ICI America, Inc.

Avocet™ was recently used in a study to determine the performance and emissions of a Detroit Diesel Corporation 8V-71 transit bus engine operated on methanol. [5] The minimum amount of Avocet™ which enables the methanol fuel to have similar combustion characteristics to the baseline diesel fuel was 7.5%. Because methanol burns without smoke at relatively high fuel-to-air ratios, the engine could produce higher levels of power than when using the baseline diesel fuel. The combustion efficiency of this engine using ignition-improved methanol was essentially the same as when using the baseline diesel fuel. Gaseous emissions were essentially unchanged while total particulates were reduced for this engine using ignition-improved methanol relative to the baseline diesel fuel.

Miscibility with Water and Hydrocarbon Fuels

Policy Issue #2

> Miscible refers to the capacity of mixing fluids in any ratio without separation. Ethanol and methanol are completely miscible with water, but show very poor miscibility with gasoline/diesel fuels containing traces of water. As discussed earlier in Section 5, blending of gasoline or diesel with methanol/ethanol in the presence of water may lead to a phase separation problem.

This problem can be effectively controlled by the use of additives such as higher alcohols (C_2 - C_{12}), various commercial nonionic surfactants and various anionic fatty acids surfactants. Among them, **iso-propanol, 1-butanol, n-decanol and palmitic acid** have been the most often suggested. [6]

Electric Conductivity and Oxygen Content

Policy Issue #3

> The comparatively high electrical conductivity and high oxygen content of fuel alcohols can contribute to corrosion and wear problems as well as chemical degradation of materials in a vehicle's fuel system. Solving this problem requires the selection of alcohol compatible material for the fuel system. The use of corrosion inhibitors is also a good alternative.

The addition of higher alcohols, (such as 1-butanol or n-decanol) as cosolvants not only prevents the phase separation noted earlier but also inhibits the corrosion of water-sensitive materials such as aluminum. Other additives that have been demonstrated corrosion-inhibiting characteristics are calcium sulfonate, zinc dialkyl dithiophosphate, and Proal.™

Viscosity

Policy Issue #4

Viscosity is a measure of the resistance of a liquid to flow. The "viscosity index" is a measure of the constancy of the viscosity of a lubricant with changes in temperature, with higher values indicating viscosities that change little with temperature. The low viscosity of ethanol and methanol fuels suggests that lubrication problems with conventional fuel injection systems may be expected, especially in a diesel fuel engine. The use of higher alcohols as additives offers a better lubricity.

Cold Weather Startability

Policy Issue #5

Ethanol- and methanol-fueled spark ignition (SI) engines have proven difficult to start at ambient temperatures below approximately 10°C (50°F). This problem can be solved by mixing some additives for cold start improvement.

The cold startability of methanol and ethanol fuels improve greatly when a small amount of more volatile fuels such as **gasoline** is mixed in the alcohol. [7]

The use of **dimethyl ether (DME)** has been proposed to improve the cold starting performance of methanol-fueled SI engines. [8] DME could be generated on-board through catalytic dehydration of methanol, which is an exothermic reaction described by the following equation:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O + \text{Heat}$$

DME has a high vapor pressure, between that of propane and butane, (as shown in Figure 8-2 [9]). It also has wide flammability limits, 3.4 - 18.0 vol %, and is therefore capable of promoting engine cold starting to below -30°C (-22°F).

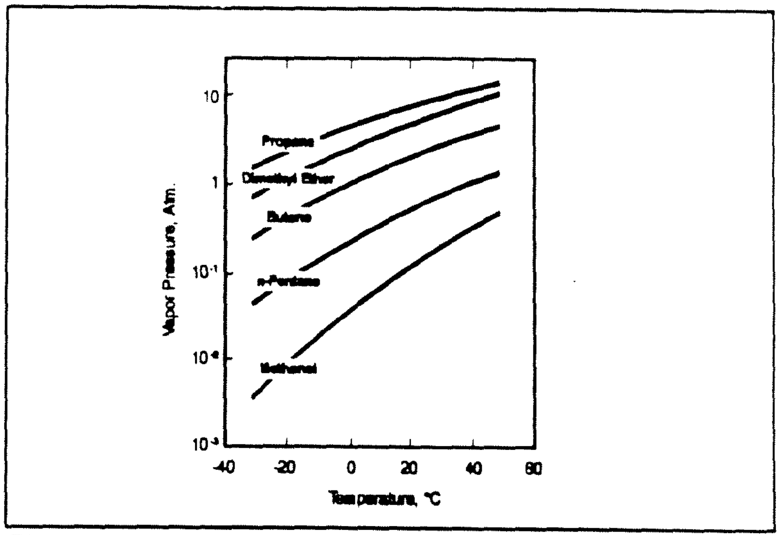

Figure 8-2., Vapor pressures of several fuels.

Conclusion

As a general rule, the fuel properties of methanol and ethanol can be significantly improved by the addition of higher alcohols. Higher alcohols offer the advantage of higher calorific value and better lubricity. In general, increasing the carbon content in the alcohol molecule improves the self-ignition properties of the higher alcohols. In addition, mixtures of methanol and higher alcohols also improve the widespread applicability of alcohol engine concepts, due to reduced wear and lube oil-related problems. Advanced methanol production processes, currently under development, may choose to produce a "fuel-grade" methanol with a lower selectivity, thus resulting in a methanol formula containing a considerable amount of higher alcohols (up to 30%, from propanol to duodecanol). [10]

ENDNOTES:

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2. Rogers, G. W., et al., "Influence of the Methanol Fuel Composition on Performance and Exhaust Emissions of Diesel-Derived Alcohol Engines." SAE Paper 881197.
3. Ibid.
4. *Oxy-Fuels News*, April 23, 1990, p. 5.
5. Urban, Charles M., et al., "Performance and Emissions of a DDC 8V-71 Engine Fueled with Cetane Improved Methanol." SAE Paper 892064.
6. Tshiteya, Rene M., et al., "The Impact of Phase Separation in Alcohol/Gasoline Blends on the Existing Fuel Distribution System." Paper accepted for publication and presentation at the 25th Intersociety Energy Conversion Engineering Conference in Reno, Nevada, August 12-17, 1990.
7. Iwai, Nobuo et al., "A Study of Cold Startability and Mixture Formation of High-Percentage Methanol Blends." SAE Paper 880044.
8. Kozole, Karl H. and James S. Wallace, "The Use of Dimethyl Ether as a Starting Aid for Methanol-Fueled SI Engines at Low Temperatures." SAE Paper 881677, 1988.
9. Karpuk, Michael E., and Scott W. Cowley, "On Board Dimethyl Ether Generation to Assist Methanol Engine Cold Starting." SAE Paper 881678, 1988.
10. Hohlein, B., et al., "Synthesis Gas Production and Synthesis of Energy Alcohol." 7th ISAFT, Paris, France, 1986.

Section 9

ETHYL TERTIARY BUTYL ETHER (ETBE)

Quick Reference Data

Oxygenate Blending Properties at 2.7 Weight % Oxygen
(Base Fuel of 87.6 AKI, 9.0 Sensitivity, and an RVP of 8.1 psi)

	MON	RON (R+M)/2	AKI	Sensitivity (R-M)	RVP (psi)
MTBE	99	113	106	167	9
ETBE	103	119	111	13.8	3
Ethanol	99	126	113	27.2	20

Requirements to Make 1 Gallon of:

	Isobutylene	Alcohol
ETBE	.68	.42
MTBE	.79	.34

Current Production Capacity

MTBE	1.1 Billion Gallons/Yr. (75 mB/d)
ETBE	None

In order to meet the Clean Air Act requirements for cities that do not attain EPA's carbon monoxide requirements, gasoline must contain 2.7% oxygen by weight. If ETBE is used as the oxygenate to satisfy this requirement, each gallon of gasoline would need to contain 17.2% ETBE by volume.

The U.S. Treasury recently approved the use of the federal alcohol fuel tax credit for ethanol used in the production of ETBE. While ETBE is not yet commercially available in large quantities, a few ETBE production facilities are now planned by industry. Given the high degree of similarity in the production processes used to make MTBE and ETBE, it is also possible that MTBE production facilities could be converted to produce or coproduce ETBE.

Useful Terms and Definitions (also see Glossary)

- **Aromatics:** high octane blending components that have a benzene ring in their molecular structure. Commonly used term for the BTX group (benzene, toluene, xylene). Aromatics are hydrocarbons.

- **Azeotrope**: a liquid mixture that is characterized by a constant minimum or maximum boiling point which is different than that of any of the components. Azeotropes distill without change in composition.

- **Distillation Curves:** the reference to plotting a line connecting the percentages of gasoline that evaporate at various temperatures. Distillation curve is used as an important control for fuel volatility (vaporization) standards.

- **Hydrocarbon**: a compound composed of carbon and hydrogen atoms.

- **Octane Number (Rating)**: a measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the greater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

- *Motor Octane:* the octane as tested in a single cylinder octane test engine at more severe operating conditions. Motor Octane Number (MON) affects high speed and part throttle knock and performance under load, passing, climbing hills, etc. Motor Octane is represented by the designation M in the (R+M)/2 equation and is the lower of the two numbers.

- *Pump Octane:* a term used to describe the octane as posted on the retail gasoline dispenser as (R+M)/2 and is the same as Antiknock Index.

- *Research Octane:* the octane as tested in a single cylinder octane test engine operated under less severe operating conditions. Research Octane Number (RON) affects low-to-medium speed knock and engine run-on. Research Octane is represented by the designation R in the (R+M)/2 equation and is the higher of the two numbers.

- **Reid Vapor Pressure (RVP)**: a method of determining vapor pressure of gasoline and other petroleum products. Widely used in the petroleum industry as an indicator of the volatility (vaporization characteristics) of gasoline.

- **Volatility**: term used to describe a gasoline's tendency to change from liquid to vapor.

Key Issues and Implications

Issue # 1: ETBE is a high octane, low volatility oxygenate

Ethers (like ETBE) and heavier alcohols (such as **tertiary butyl alcohol (TBA))** are oxygenates **characterized by low volatility (low blending RVP), high octane, and provide some beneficial** cosolvency **effects that could be used by refiners to correct the blending RVP of low molecular weight alcohols.**

Implications of ETBE's High Octane Low Volatility:

- Lower VOC and evaporative emissions which will reduce smog and ozone formation.
- Lower tailpipe emissions (CO) due to presence of oxygen in the blend.
- Reduction of tailpipe HC emissions due to more complete combustion of the fuel blend.
- Reduction in toxic emissions due to substitution of ETBE for benzene and aromatics while maintaining high octane.
- Lower RVP contributes to cold start driveability problems. Tests conducted by Phillips Petroleum found that cold start driveability was not noticeably affected by as much as 23.5% by volume (equivalent of 3.7% O_2 by weight).

Detailed Information: Refer to pages 9-3 through 9-6.

Issues and Implications

Issue #2: *Compatibility with existing liquid fuels infrastructure.*

ETBE, unlike alcohols, has a relatively low solubility in water. Because of this advantage, ethers (like ETBE and MTBE) can be blended into gasoline at the refinery and shipped to the market through common carrier gasoline pipelines.

Implications of compatibility with existing infrastructure:

- ETBE can be shipped via existing product pipelines, tank trucks, etc.
- Petroleum refiners will accept ETBE just as they accept MTBE, as a blending stock for reformulated gasoline.
- ETBE is completely soluble in base gasoline (even in the presence of water) and can, therefore, be splash blended at terminals.
- Presence of ETBE in gasoline requires no engine or vehicle modifications since it has none of the corrosion or material incompatibility qualities of ethanol or methanol.

Detailed Information: Refer to pages 9-3 through 9-6.

Section 9

ETHYL TERTIARY BUTYL ETHER (ETBE)

- Introduction
- Gasoline related properties
- Performance
- Production process technology
- Supplies and commercialization
- Conclusion

Introduction

The technical feasibility and application of methanol, ethanol, tertiary butyl alcohol (TBA), and methyl tertiary butyl ether (MTBE) in motor fuels has been extensively investigated during the last two decades [1-10]. Of the possible oxygenated fuels, the two most common in use today are MTBE and ethanol. However, because of the relative scarcity of future low-priced, domestically produced methanol for MTBE and the likely trend toward lower volatility gasolines, ethyl tertiary butyl ether (ETBE) has emerged as a "best fuel" blending candidate for the future. This section discusses the blending properties, performance properties, and the process technology to produce ETBE, as compared to its two competitors: MTBE and ethanol.

Gasoline related properties

The typical properties for oxygenates are shown in Table 9-1. [11] Ethers have superior fuel blending properties when compared to the original alcohol forms. The blending RVPs (Reid Vapor Pressure) of most alcohols are much higher than their true vapor pressures, as shown in Table 9-1 and Fig. 9-1 [12]. The RVP increase is due to the unfavorable interreaction between the very polar hydroxyl group of alcohols and the non-polar hydrocarbons, leading to the formation of azeotropes. This tendency of the

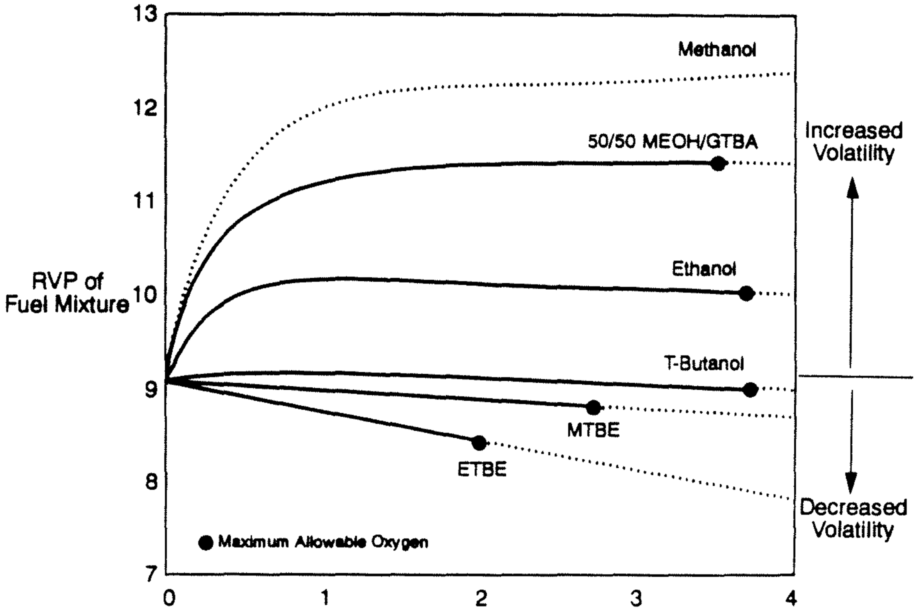
TABLE 9-1. GASOLINE RELATED PROPERTIES OF OXYGENATES

PROPERTY	ETHERS			ALCOHOLS			GASOLINE
	ETBE	MTBE	TAME	TBA	ETOH	MEOH	
Boiling Point (°F)	161	131	187	181	173	148	80-437
Freezing Point (°F)	-137.2	-164	-	78.0	-173.2	-143.5	-40.0
Vapor Pressure:							
Neat RVP (100°F)	4.0	7.8	2.5	1.7	2.3	4.6	8-15
Blending RVP	4.0	8.0	2.0	9.0	17.0	31.0*	
Octanes:							
Blending (R+M)/2	111	110	105	100	115	108*	
Water Solubility (Wt%)							
Water in Fuel	0.6	1.4	-	∞	∞	∞	Negligible
Fuel in Water	2.0	4.3	0.6	∞	∞	∞	Negligible
Density (lb/gal @ 60°F)	6.2	6.2	6.4	6.6	6.6	6.6	6.0-6.5
Energy Density (LHV)							
MBTU/Gal	96.9	93.5	100.6	94.1	76.0	56.8	109.0-119.0
MBTU/lb	15.5	15.1	15.7	14.3	11.5	8.6	18.0-19.0
Latent Heat of Vaporization (60°F):							
MBTU/Gal	0.83	0.86	0.90	1.70	2.38	3.34	~0.90
MBTU/lb	0.13	0.14	-	0.26	0.40	0.51	~0.15
Oxygen Density Vol. % @ 2.7 Wt% Oxygen	17.2	15.0	16.7	11.8	7.3	5.1	0.0
Azeotropes with Hydrocarbons	No	No	No	Yes	Yes	Yes	No

* Properties of Methanol/Cosolvent Blends

∞ Infinite

Figure 9-1
RVP Effects of Adding Oxygenates to 9 RVP Fuels



volatility of alcohol/gasoline blends to increase is common only with low molecular weight alcohols, such as methanol and ethanol.

Policy Issue #1

> Ethers (like ETBE) and heavier alcohols (such as tertiary butyl alcohol (TBA)) are oxygenates characterized by low volatility (low blending RVP), high octane, and provide some beneficial cosolvency effects that could be used by refiners to correct the blending RVP of low-molecular weight alcohols.

This is illustrated in Fig. 9-1, by the suppression of methanol's RVP increase when it is mixed with GTBA (gasoline grade tertiary butyl alcohol).

Table 9-1 and Fig. 9-1 also show that ETBE has a vapor pressure advantage over ethanol or even MTBE. At the 2.0 weight percent oxygen level, ETBE has 1.5 psi lower RVP than ethanol and 0.5 psi lower RVP than MTBE. This advantage increases as the oxygen level increases. At the 3.0 level, ETBE has a 1.8 psi lower RVP than ethanol and a 0.8 psi lower RVP than MTBE. When used in gasoline, this allows the use of more butane and other desirable low-cost blend stocks, without RVP penalty. [13]

Low-molecular weight alcohols are infinitely soluble in water. This property is a major drawback to the development of methanol and ethanol as gasoline components because of their phase separation in the presence of water.

Policy Issue #2

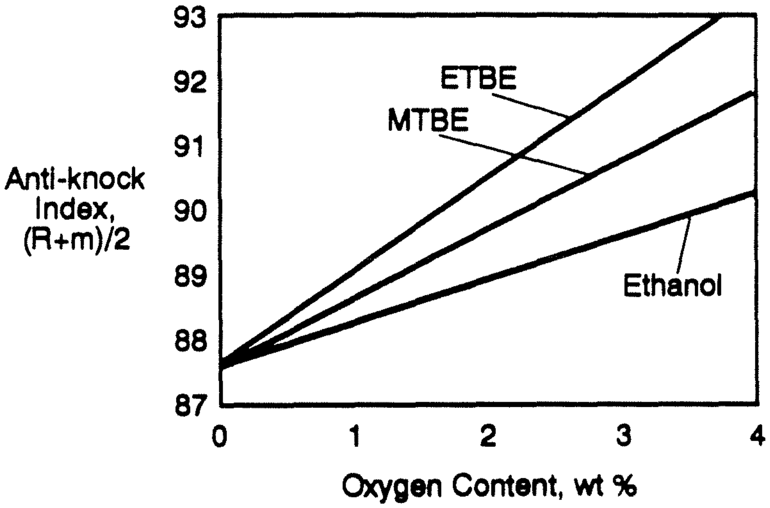
> ETBE, unlike alcohols, has a relatively low solubility in water. Because of this major advantage, ethers (like ETBE) can be blended to gasoline at the refinery and shipped to the market through common carrier gasoline pipelines.

Ether/gasoline blends do not experience the problem of phase separation. Ethers are even used to improve the water tolerance of alcohol/gasoline blends.

Performance

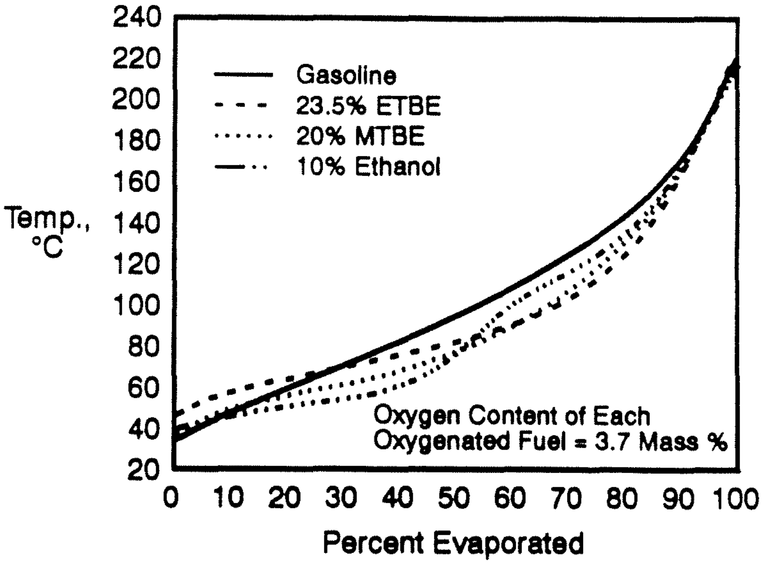
ETBE has a significantly higher Motor Octane Number (MON) Boost, or anti-knock ratio, than either of ethanol or MTBE. This is expected to enhance vehicle performance since most of today's smaller, higher performance engines operate at higher engine speeds which is more closely represented by the operating conditions of the ASTM Motor Octane Method. Figure 9-2 [14] shows the effect of the oxygenates on anti-knock index as a function of oxygen content.

Figure 9-2
Oxygenate Effect on Anti-knock Index



Alcohols form azeotropes with hydrocarbons, ethers do not. The azeotrope reduces the boiling points in some regions of the gasoline distillation curve, as shown in Figure 9-3. [15] Which part of the curve is affected depends on the boiling point and the type of oxygenate used. The lighter alcohols such as methanol and ethanol form minimum boiling point azeotropes with hydrocarbons and produce a substantial increase in the front-end volatility of the distillation.

Figure 9-3
Effects of ETBE, MTBE, and Ethanol at Equal Oxygen Content, on the Distillation Characteristics of Gasoline

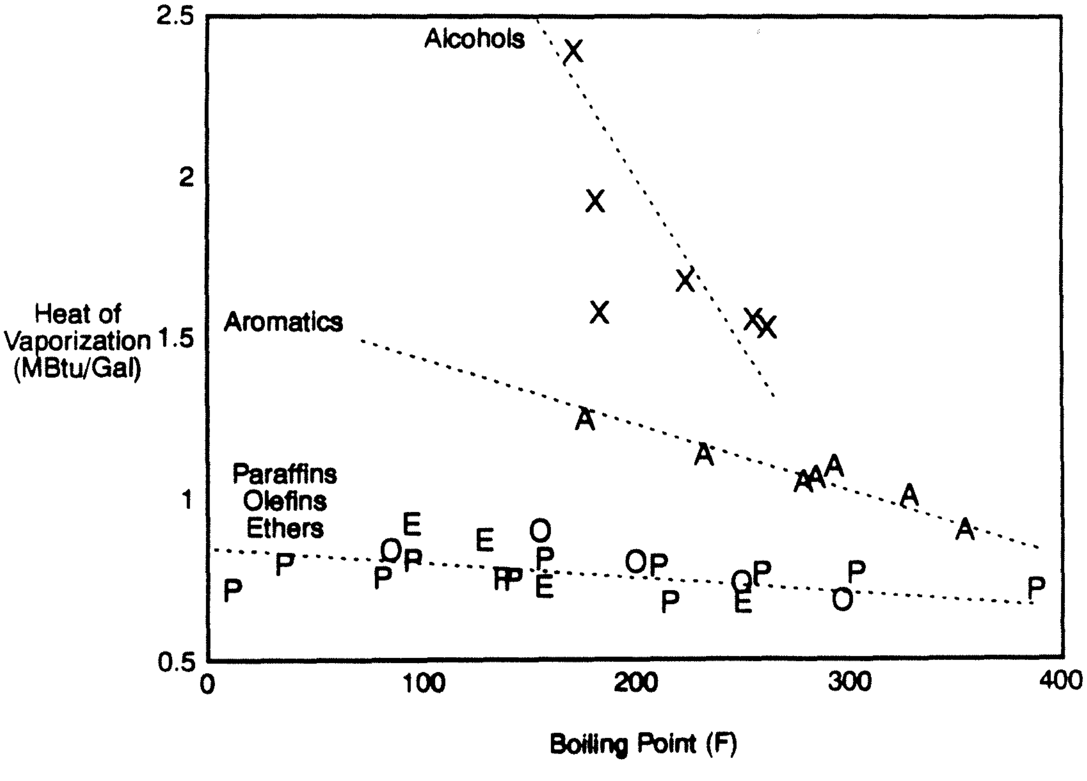


Since ethers do not form azeotropes with hydrocarbons, ETBE produces a more favorable increase in the mid-range volatility of the gasoline. This helps improve the "cold driveability" index of gasoline by lowering the 50% point of gasoline, as illustrated in Fig. 9-3.

Both alcohols and aromatics have a significantly higher heat of vaporization (Hv) requirement, but alcohols have the advantage of a lower boiling point. Ethers have a low Hv, independent of their boiling points, as shown in Figure 9-4. [16] During cold engine operation, the fuel vaporization process super-cools the air since there is no other source to draw heat from. Fuels with both a high Hv and a high boiling point, such as aromatics (xylene, toluene, benzene), will be the most difficult to vaporize because they super-cool the air. A poor vaporization leads to poor fuel/air mixing which contributes to incomplete combustion (higher HC emissions). To avoid this problem, General Motors (GM) has suggested reducing the 90% point temperature of the gasoline distillation curve by removing the back end (high boiling portion) of the fuel and increasing the mid-range volatility of the fuel. This can be accomplished by the blending of ETBE with gasoline. [17] Previous studies by others have also shown that increasing mid-range volatility will reduce HC emissions from the tailpipe. [18] These results confirm the expected beneficial effect of ETBE on the gasoline distillation curve.

ETBE's low boiling point also has the added benefit of putting more of the octane into the front end of the distillation curve. This produces a better octane distribution through the full boiling range of the gasoline and provides added performance during high RPM engine operation.

Figure 9-4
Heat of Vaporization of Oxygenates and Hydrocarbons



Although the use of ETBE in gasoline is currently limited to 12.7 volume percent (2.0 weight percent oxygen) by the EPA's "gasoline substantially similar rule," studies were performed with levels of ETBE ranging from 0.0 to 23.5 volume percent (3.7 weight percent oxygen) in gasoline. The obtained results show that cold start driveability was not found to be noticeably affected by as much as 23.5 percent ETBE. No considerable detrimental effects were observed due to corrosion of typical materials found in fuel systems. The swelling of polymeric and elastomeric parts of the fuel systems was shown to be no greater than with typical fuels in current use.

Production process technology

Figure 9-5 [19] shows the simplified flow chart for the production of ETBE and MTBE, by a catalytic reaction between isobutylene and ethanol or methanol, respectively. A mixture of C_4 feedstock from fluid catalytic cracking unit (FCCU), is combined with ethanol or methanol in a controlled optimized ratio to isobutylene. The resulting mixture is fed to the liquid-phase, fixed-bed ETBE or MTBE reactor, containing an ion exchange resin catalyst. The typical composition of the C_4 stream from FCCU is shown in Table 9-2, while the composition of the product stream is illustrated in Table 9-3. [20] The C_4 feedstock can also be obtained from the by-product isobutylene from olefin plants and from isobutane dehydrogenation plants.

Figure 9-5
Flow Chart of MTBE/ETBE Process

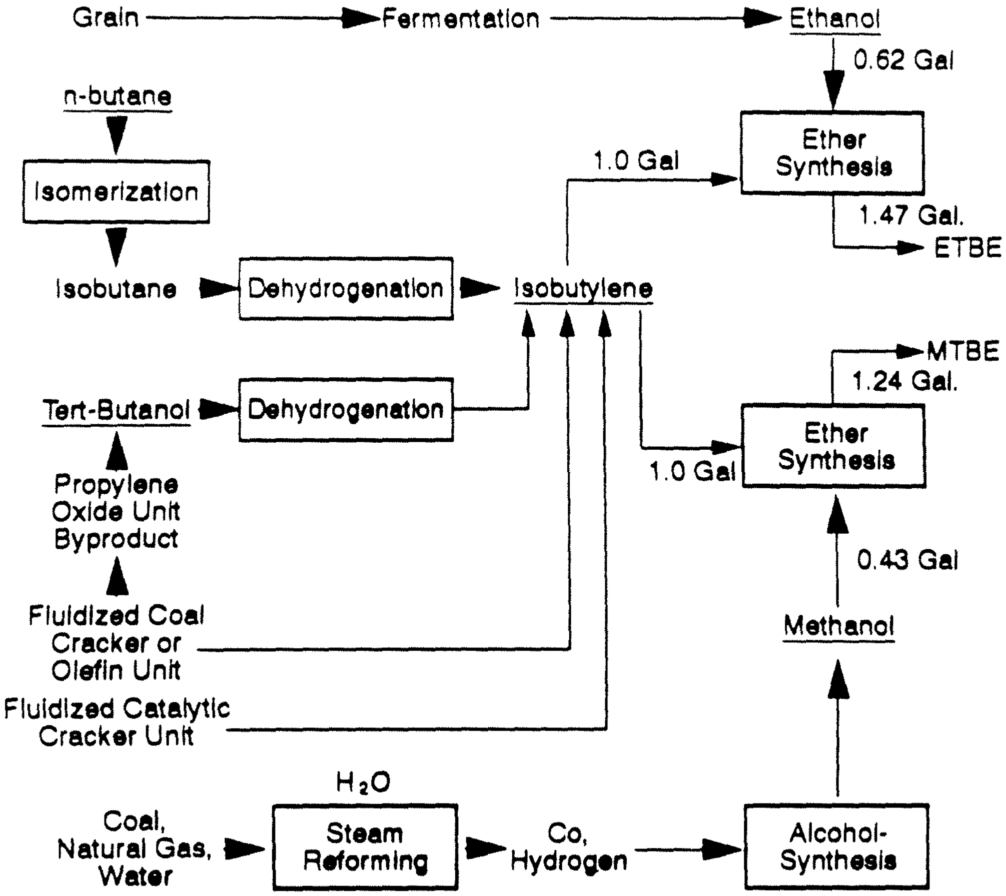


TABLE 9-2. CHARGE STOCK COMPOSITION

FCCU C_4 STREAM

Component	BPSD
Isobutane	2,296
Isobutylene	959
Butene-1	905
Normal Butane	931
TR-Butene-2	1,102
CIS-Butene-2	676
Pentanes	89
	6,958

ETHANOL STREAM

COMPONENT	BPSD
Ethanol	485
Water	32
	511*

* CH_3CH_2OH-H_2O Solutions have a negative mixing volume.

TABLE 9-3. PRODUCT STREAM COMPOSITION

C. STREAM RETURNED TO REFINERY FOR ALKYLATION CHARGE OR OTHER

Component	BPSD
Isobutane	2,296
Isobutylene	35
Butene-1	905
Normal Butane	931
TR-Butene-2	1,102
CIS-Butene-2	676
Pentanes	89
Diethyl Ether	2
	6,036

TBA PRODUCT

COMPONENT	BPSD
ETBE	10
TBA	133
Other C-8's	79
Water	1
	233

ETBE PRODUCT

COMPONENT	BPSD
Diethyl Ether	2
ETBE	997
TBA	1
	1,000

The chemical reactions that occur and the volumetric yield equations are shown in Table 9-4. [21] In addition to the main reaction producing MTBE and ETBE, side reactions occur that produce, in addition to tertiary butyl alcohol (TBA) and diisobutylene (DIB), a small amount of diethyl ether (DEE).

TABLE 9-4. ETBE AND MTBE REACTIONS

Main Reaction

$$CH_2C(CH_3)_2 + CH_3CH_2OH \longrightarrow (CH_3)_3COCH_2CH_3$$

ethanol ETBE

$$CH_2C(CH_3)_2 + CH_3OH \longrightarrow (CH_3)_3COCH_3$$

methanol MTBE

Side Reactions	**Typical Concentrations**
1. $2iC_4^= \longrightarrow DIB$	<.1%
2. $iC_4^= + H_2O \longrightarrow TBA$	2.0%
3. $2\ CH_3\text{-}CH_2OH \longrightarrow CH_3\text{-}CH_2\text{-}O\text{-}CH_2CH_3 + H_2O$ Diethyl Ether	<.02%

Volume Yield Equation

$1.0iC_4^= + 0.62\ ETOH = 1.46\ ETBE$

$1.0iC_4^= + 0.43\ MeOH = 1.27\ MTBE$

An isobutylene conversion level of as high as 96% for ETBE or MTBE is achieved. However, significant amounts of alcohol are found in the bottoms product (ETBE/MTBE). Because of both the azeotropic properties of alcohols and the distribution problems due to their phase separation, an ethanol/methanol recovery system is included in the design in order to produce high purity ETBE/MTBE suitable for the merchant market and pipeline distribution systems. The ether/alcohol mixture is fractionated in an alcohol extractor where the alcohol is contacted counter currently by a circulating wash water stream leaving this extractor containing less than 100 ppm of ethanol. The circulating wash water with absorbed ethanol flows from the bottom of the extractor to the ethanol stripper where the ethanol is recovered as an overhead product and recycled to the ETBE reactors. Although the water content of this ethanol stream poses no problem to the reaction catalyst, an additional amount of TBA is produced.

The catalyst used in the process is sensitive to poisoning by organic and inorganic bases, nitrogen compounds and trace metals, all present in the feedstocks. The catalyst activity decays at a rate proportionate to the level of feedstock impurities. The catalyst life can be extended to two years or more, depending on the type of design and technology involved. Conversion in a well-run operation can be maintained for a 2-year period. [22]

Supplies and commercialization

As mentioned earlier, the two oxygenated fuels most used today are MTBE and ethanol. ARCO Chemical Company, which completed the construction of its first MTBE plant in December of 1979, is the largest producer in the world with a total capacity for MTBE of over 2.5 million metric tons per year.

It has been suggested that the main constraint to future use of ethers in the gasoline pool will be the availability of isobutylene to react with ethanol or methanol. If this is the case, ETBE will enjoy an added advantage over MTBE in that less isobutylene is required to react with ethanol on a per gallon basis, i.e., 0.68 gallons isobutylene for 1 gallon of ETBE vs. 0.79 gallons of isobutylene for 1 gallon of MTBE. On the other side of the equation, more ethanol than methanol is required to make equivalent amounts of ETBE and MTBE, respectively. This presents no problems since ethanol is and will be an abundant, domestically produced fuel or feedstock. This is very important in light of national security concerns, especially when estimates of future methanol supplies predict that the majority of sources will be from either the Middle East or the USSR.

The economics for ETBE have not been completed yet and until the process is completely proven, current economics favor the production of MTBE. However, the technology exists to produce ETBE at such time as conditions warrants. Now that the U.S. Treasury has approved the use of the federal alcohol fuel tax credit for ethanol used in the production of ETBE, this opens an economical route for ethanol to go into gasoline in the form of a hydrocarbon-like ether.

Conclusions

ETBE is a potentially valuable blending stock for gasoline. Because it can be produced from isobutylene and agriculturally (grain or biomass) based ethanol, tax incentives have been created to increase its economic viability. Experimental studies at concentrations of up to 23.5 volume percent did not show any "fatal flaw." Based on overall properties and performance, ETBE, a new blending component in gasoline and useful octane enhancer, was evaluated comparable or even better to those of the base gasoline, ethanol and MTBE. [23]

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Section 10

HEALTH AND SAFETY ISSUES

Quick Reference Data

Toxicity

	Toxic Dosage (for 70 kg adult human) mls
Gasoline	115-470
Diesel Fuel	63
Methanol	60-240
Ethanol	

Dispersal in Water-Borne Spills

Gasoline	slow - by evaporation and water action
Diesel fuel	slow - by evaporation and water action
Methanol	rapid - 100% soluble in water
Ethanol	rapid - 100% soluble in water

Useful Terms and Definitions (also see Glossary)

- **Butanethiol:** a substance with a strong, offensive and unique odor, used as a fuel malodorant to provoke instant recognition by the public as methanol.

- **Nigrosine:** a dye, to be added in small amount (up to 15% volume) to methanol to enhance the luminosity of methanol flame.

- **Toxicity:** the quality, state, or relative degree of being poisonous.

Key Issues and Implications

Issue #1: *Toxicity*

Methanol is highly toxic if ingested, and, in relatively small quantities can cause blindness or death. Poisoning can also occur by inhalation of methanol vapors or by prolonged skin exposure. There is a high potential for unintentional ingestion of methanol since it is odorless, colorless, and tasteless. In contrast, the toxicity of ethanol is quite low, being only toxic if ingested in very large quantities.

Implications of Toxicity:

- Special handling procedures will be needed for all phases of methanol production, shipping, blending, and retail sales to prevent inadvertent poisoning or unnecessary exposure.

Proposed Solutions:

- Additives need to be developed for neat methanol fuels that will provide a distinct/unique odor and unpleasant taste to methanol, as well as a distinguishable flame color for safety.
- Mechanical systems will have to be installed on methanol fuel tanks and refueling points to prevent syphoning or accidental ingestion.

Detailed Information: Refer to page 10-1 through 10-5.

Issue #2: Water Contamination

Alcohol leaks and spills on surface and subsurface water can harm animal and plant ecosystems.

Implications of Water Contamination:

- Ethanol disperses quickly and is highly biodegradable in the environment; ethanol is also less toxic to marine life and less costly to clean up than petroleum-based fuel spills. As a result, ethanol spills will represent a much less severe hazard than gasoline, diesel fuel, or methanol spills.
- Methanol is more toxic than ethanol, but also disperses quickly in the environment. Its rapid dispersion will result in less severe environmental impacts than spills of petroleum-based fuels.

Detailed Information: Refer to page 10-4 through 10-5.

Issue #3: *Land Contamination*

Alcohol leaks and spills on land can poison terrestrial animal and plant life.

Implications of Land-Based Spills:

- Methanol, like gasoline and diesel, is very toxic to terrestrial plant and animal life but its effects are much shorter lived than those of petroleum-based fuels. Ethanol is not highly toxic and the effects of ethanol spills on land are not anticipated to be serious since ethanol dissipates quickly in the environment.

Proposed Solutions:

- Precautions in shipping and handling that are currently used for crude oil and gasoline will be sufficient for transporting methanol and ethanol.

Detailed Information: Refer to page 10-5.

Issue #4: *Flammability and Leak Detection*

Like gasoline and diesel, both ethanol and methanol are flammable liquids, and thus pose safety hazards. Moreover, leaks of methanol are difficult to detect, as is the fuel while burning.

- Methanol is odorless and lacks flame luminance under daylight conditions, making leaks difficult to detect and flames difficult to see.
- Due to higher points of ignition, both ethanol and methanol are much less flammable than gasoline or diesel. Thus, increased substitution of alcohols for gasoline/diesel will contribute to reducing the number of highway fires.

Proposed Solutions:

- The addition of additives such as nigrosine and gasoline would increase flame visibility.
- A distinctive agent to provide an odor to methanol needs to be identified and universally adopted, just as has been done for natural gas.

Detailed Information: Refer to page 10-5 through 10-6.

Section 10
HEALTH AND SAFETY ISSUES

- Toxicity
- Leaks and Spills in Water
- Leaks and Spills on Land
- Safety

Introduction

Modern society has become adept at producing, transporting, storing and dispensing a variety of transportation fuels. The key motor transportation fuels -- gasoline and diesel fuel -- have a number of serious drawbacks which require careful handling to prevent accidental poisoning and widespread ecological damage in the event of a transportation accident or leaking storage facility. Standard procedures have been developed to limit these risks to socially acceptable levels.

Concerns have been raised that the introduction of alcohol fuels (particularly methanol) into widespread use for transportation fuels will create new safety and health concerns. These concerns are of three types: toxicity; environmental damage in the event of a major water or land-based spill; and flammability.

Toxicity

A person may come into contact with a liquid motor fuel either through inhalation, ingestion, or dermal contact. Ingestion or swallowing is the most likely cause of serious acute poisoning. All of the existing motor liquid fuels, including ethanol, pose a toxic threat if sufficient amounts are ingested.

Diesel Fuel

Diesel fuel is highly toxic. [1] Its ingestion may cause nausea, vomiting, cramping, liver and kidney damage, lung irritation, and central nervous system depression ranging from a mild headache to coma, and death. Death would result from ingestion of just 63 ml (1/4 cup) for the average adult male. However, since diesel fuel will often cause regurgitation, large quantities of ingested fuel will often not stay in the stomach, thus avoiding the acute toxicity discussed above. Unfortunately, when regurgitation occurs, aspiration into the lungs of even small amounts of diesel fuel may result in severe irritation with coughing, gagging, difficulty breathing, chest pain, chemical pneumonitis and bronchopneumonia.

Gasoline

According to the American Association of Poison Control Centers (AAPCC), about 35,000 incidences of gasoline ingestion are reported annually in the United States. Most of them are a result of attempted siphoning from gasoline tanks. Gasoline is toxic if ingested in moderate quantities. Ingestion of even small amounts (5 to 10 ml) of gasoline may cause a burning sensation in the mouth, throat, and chest, and intense irritation and burning in the gastrointestinal tract with nausea, vomiting, diarrhea, and abdominal pain. Ingestion of 27 - 40 ml of gasoline will result in more serious symptoms including central nervous system depression, headache, dizziness, drowsiness, fever, and transient liver damage. Severe intoxication may cause unconsciousness and comma or convulsions with seizures. Fatal dose estimate for the average adult range from 115-180 ml to 470 ml, but death has been reported at a dose as low as 13 ml. The fatal dose for children is 13 to 20 ml. Gasoline is even more hazardous if aspirated into the lungs following regurgitation or belching. Once in the lungs, even small amounts may cause severe chemical pneumonitis, and death from lung insufficiency. Gasoline vapor is considered by the U.S. Environmental Protection Agency (EPA) to be a human carcinogen (with 68 incidences in 1986), and is suspected of causing various other chronic effects. [2] In addition, gasoline vapor contains benzene, a group of human carcinogens which was estimated to cause 155 cancer incidences in 1986. [3] Gasoline's threshold limit value (TLV) of 300 ppm and short term exposure limit (STEL) of 500 ppm were set by EPA at least in part to protect against the cumulative toxic effects of benzene.

Methanol

Policy Issue #1

> Methanol is highly toxic. Ingestion of small quantities of methanol can cause blindness; large quantities cause death. Methanol poisoning can also occur by inhalation of the vapors or by prolonged exposure of the skin. Since methanol has no color, taste or odor, it has the potential to be ingested unintentionally more readily than the other liquid motor fuels.

The use of additives to provide a distinctive taste, color and odor to methanol would be beneficial. Various hydrocarbons in small amounts are successfully used as additives, such as in M85 (85% methanol, 15% gasoline).

Symptoms of overexposure to methanol result from methanol's metabolism in the body. Methanol is slowly metabolized to formate, which is in turn oxidized to form CO_2 which is then exhaled. Thus, in severe or long methanol exposure, the body's ability to metabolize the formate is overwhelmed, causing formate buildup and acidosis of the blood. The minimum lethal dose of methanol exposure in the absence of medical treatment generally ranges between 300 and 1000 mg/kg.

Ingestion is the most common form of methanol poisoning in humans. For the average adult male weighing 70 kg, toxic effects can begin with ingestion of as little as 18 ml (approximately 3 to 4 teaspoons), and as little as 26 to 70 ml can be fatal. However, there are cases described where as little as 6 ml proved fatal while in other cases 500 ml has not resulted in any permanent damage.

The normally fatal dose for methanol ingestion ranges from 60 to 240 ml. Since the toxic effects of methanol occur 10 to 48 hours after ingestion, there is sufficient time to seek medical attention. [4]

Ethanol

Ethanol is medically referred to as a hypnotic or depressant. It depresses activity in the upper brain and is also toxic if ingested in sufficiently large quantities, but it is much less toxic than methanol or gasoline. Generally, intoxication will bring sleep or unconsciousness before a toxic amount can be ingested. In rats, the lethal dose of ethanol is 13.7 g/kg of body weight [5] or 10-40 times greater than that for methanol. Abuse of ethanol is a major drug problem in most countries. U.S. federal law requires that some highly pure (generally 95-100%) ethanol used for scientific and industrial purposes be adulterated or "denatured" to discourage people from drinking it. Various denaturants are used, including methanol and gasoline.

Leaks and Spills in Water

Since methanol is infinitely soluble in water, a spill in open water disperses rapidly. In addition to its rapid dispersion, complete elimination from the environment occurs as a result of methanol's rapid biodegradation (decomposition of methanol as a result of natural processes). A wide variety of marine and terrestrial microbes metabolize methanol. [6] As a result, recolonization of methanol spill sites is very rapid (a matter of months) with no long-term effects, while the effects of petroleum spills may require years to disappear. Cleanup of methanol spills on water requires less effort and cost than petroleum fuel, and is generally more effective. For small spills, one only needs to monitor and isolate the area for several days, allowing natural biodegradation to complete the task. [7]

Policy Issue #2

In general, methanol is less toxic to marine life than petroleum fuels, and many of its poisoning effects are temporary and reversible.

Ethanol, like methanol, is biodegradable and infinitely soluble in water. Thus a spill in open water disperses rapidly. Ethanol is much less toxic than methanol and gasoline and its poisoning effects are handled much more easily.

Leaks and Spills on Land

Gasoline and diesel fuel are very toxic to terrestrial plant and animal life. [8,9] In this characteristic, it is similar to methanol. [10,11]

Policy Issue #3

Methanol, like the petroleum fuels, is very toxic to plant and animal life. However, the toxic effects of methanol spills are much shorter-lived than petroleum fuel spills, as discussed earlier.

Safety

Policy Issue #4

> The use of neat methanol and ethanol raises concerns about their lack of odor and lack of flame luminance. Concern over methanol (and to a lesser extent, ethanol) flame luminosity stems from the fact that methanol burns with a near invisible flame under daylight conditions.

An investigation into flame luminosity would consist of quantifying the flame luminance of methanol over the entire burn period. This would provide basic data to help in selecting a potential additive.

Nigrosine has been identified as a potential methanol luminosity enhancer. [12] The addition of 15 vol. % unleaded gasoline (M85) has also been suggested as a methanol fuel standard to increase flame visibility for safety reasons.

Because methanol, like natural gas, has no offensive odor which alerts users of a leak or spill, an agent must be introduced to provide a smell as an early warning. A fuel malodourant must be offensive enough to provoke instant recognition. Furthermore, the odor should be unique so that it will not be mistaken for other substances. **Butanethiol** has been identified as a promising malodourant, offering a relatively strong odor at a low concentration. [13]

Both the U.S. Department of Transportation and the National Fire Prevention Association (NFPA) classify methanol and ethanol as flammable liquids. Therefore, the federal codes and NFPA standards governing fire protection for transport, storage, and handling of flammable liquids are directly applicable to neat alcohol and blend fuels. [14]

Ethanol burns at a temperature of 13°C (55°F), and methanol at a temperature of 11°C (52°F). This is considerably higher than that of gasoline, which has a flame temperature of -43°C (-45°F).

Therefore, both ethanol and methanol are much less flammable than gasoline, and their use as liquid transportation fuels will contribute to reducing the number of fires caused by gasoline on U.S. highways every year.

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GLOSSARY

Adiabatic: occurring without loss or gain of heat.

Alcohol: a hydrocarbon in which one atom of hydrogen has been substituted by a hydroxyl group (e.g., methane, a hydrocarbon, is CH_4 while methanol, an alcohol is CH_3OH; the "OH" being the hydroxyl group).

Aromatics: high octane blending components that have a benzene ring in their molecular structure. Commonly used term for the BTX group (benzene, toluene, xylene). Aromatics are hydrocarbons.

Azeotrope: a liquid mixture that is characterized by a constant minimum or maximum boiling point which is different than that of any of the components. Azeotropes distill without change in composition.

Benzene Ring: structural arrangement of atoms believed to exist in benzene and other aromatic compounds showing six carbon atoms in symmetrical hexagonal fashion.

Btu: British thermal unit, i.e., the amount of heat required to raise the temperature of 1 lb. of water 1°F under one stated condition of pressure (1 atm) and temperature (from 60° to 61°F).

Butanethiol: a substance with a strong, offensive and unique odor, used as a fuel malodorant to provoke instant recognition by the public as methanol.

Calorie (cal): the energy required to heat 1 gram of water 1°C (from 14.5° to 15.5°C, 1 atm.). One kilocalorie (1 k cal) = 1000 cal. One calorie is also defined as equal to 4.184 joules.

Celsius (Centigrade): a temperature scale commonly used in the sciences; at sea level, water freezes at 0°C and boils at 100°C. $°C=5/9\ (°F-32)$.

Cetane Number (Rating): measure of a fuel's ease of self-ignition; the higher the number the better the fuel for a diesel engine (i.e., the percentage by volume of the hydrocarbon cetane ($C_{16}H_{34}$) in a mixture of cetane and 1-methylnaphthalene that gives the same ignition lag as the fuel oil being tested).

Combustion: an exothermic chemical reaction of a fuel with oxygen, often intended for the direct production of heat.

Combustion Air: the air fed to a fire to provide oxygen for combustion of fuel. Air is essentially 79% nitrogen and 21% oxygen by volume. Combustion air may be preheated before injection into a engine.

Combustion Efficiency: the efficiency computed by dividing the actual heat produced in the engine by the total heat potential of the fuel consumed.

Compression Ratio (CR): the maximum cylinder volume divided by the minimum cylinder volume.

Corrosion: a gradual wearing away or alteration by a chemical or electrochemical.

Denaturant: a substance added to ethanol to make it unfit for human consumption so that it is not subject to alcohol beverage taxes.

Denature: the process of adding a substance to ethanol to make it unfit for human consumption; the denaturing agent may be gasoline or other substances specified by the Bureau of Alcohol, Tobacco and, Firearms.

Distillation Curves: the reference to plotting a line connecting the percentages of gasoline that evaporate at various temperatures. Distillation curve is used as an important control for fuel volatility (vaporization) standards.

Enthalpy Requirement: the additional heat input required by the engine's fuel induction system to achieve the required degree of fuel vaporization for smooth operation.

Equivalence Ratio: measure of the actual fuel/air mixture to the stoichiometric fuel/air ratio.

Exhaust Gas Recirculation (EGR): the recirculation of exhaust gases to the combustion chamber to reduce the peak combustion temperature for the reduction of NO_x emissions.

Exothermic: chemical change accompanied by a liberation of heat.

Fahrenheit Scale: a temperature scale in which the boiling point of water is 212 and its freezing point 32°; at sea level °F = 9/5°C+32.

Formic Acid: a colorless, pungent liquid acid (HCOOH) that is made by acidification of sodium formate. Formerly obtained from ants, spiders, etc. Synthetically, it is formed in the combustion chamber during the combustion of methanol or water-contaminated ethanol. Also known as methanoic acid.

High Molecular Weight/Long Chain Alcohols: with respect to transportation liquid fuels, these are alcohols that have more than 4 carbon atoms (i.e., C_5 and above) in their molecular structure and their main use may be as additives and cosolvents in methanol to prevent phase separation and as corrosion preventives. They include n-decanol, n-hexanol, and n-octanol.

Hydrocarbon: a compound composed of carbon and hydrogen atoms.

Hydrogen Bond: a bond between the hydrogen atom of one molecule and a pair of unshared electrons on the electronegative atom of another molecule.

Hydroxyl: the chemical group or ion OH that consists of one atom of hydrogen and one of oxygen, is neutral or positively charged and is characteristic especially in alcohols, oxygen acids, glycols, phenols, and hemiacetals.

Joule (J): the amount of energy produced by 1 W in 1 second. This is equivalent to one newton of force over a distance of 1 m. One joule = 0.239 cal.

Latent Heat of Vaporization: the amount of heat required to vaporize a unit quantity of a fuel, generally measured at one atmosphere of pressure and at the boiling point of that liquid.

Low Molecular Weight/Short Chain Alcohols: with respect to transportation liquid fuels, these are alcohols that have from 1 to 4 carbon atoms (i.e., C_1 - C_4) in their molecular structure and include methanol, ethanol, propanol and butanol.

Maximum Brake Torque (MBT): the timing associated with a particular fuel for a particular combustion chamber; aside from the fuel/air mixture, the moment of ignition has the greatest influence on pollutant emissions.

Mole (symbol "mol"): the quantity of a chemical substance that has a weight in mass units numerically equal to the molecular weight. In chemistry, moles are used as the standard unit of measure and for the comparison of compounds. The mass units must be specified, i.e., atoms, electrons, kilograms, etc.

Nigrosine: a dye, to be added in small amount (up to 15% volume) to methanol to enhance the luminosity of methanol flame.

Octane Number (Rating): a measurement term used to identify the ability of a fuel to resist spontaneous combustion; the lower the octane rating the greater the tendency for a fuel to prematurely ignite due to heat and compression inside the cylinder and cause engine "knock."

- *Motor Octane:* the octane as tested in a single cylinder octane test engine at more severe operating conditions. Motor Octane Number affects high speed and part throttle knock and performance under load, passing, climbing hills, etc. Motor Octane is represented by the designation M in the (R+M)/2 equation and is the lower of the two numbers.

- *Pump Octane:* a term used to describe the octane as posted on the retail gasoline dispenser as (R+M)/2 and is the same as Antiknock Index.

- *Research Octane:* the octane as tested in a single cylinder octane test engine operated under less severe operating conditions. Research Octane Number affects low-to-medium speed knock and engine run-on. Research Octane is represented by the designation R in the (R+M)/2 equation and is the higher of the two numbers.

Olefins: a gasoline component resulting from several refining processes. Examples are ethylene, propylene, butylene. Olefins often contribute to the formation of gum and engine deposits.

Phase Separation: the formation of layers due to the presence of water within a low level alcohol-gasoline blend, with most of the hydrocarbons in the upper layer and water, alcohol, and some aromatic hydrocarbons in the lower level. This condition can lead to driveability problems.

Reid Vapor Pressure (RVP): a method of determining vapor pressure of gasoline and other petroleum products. Widely used in the petroleum industry as an indicator of the volatility (vaporization characteristics) of gasoline.

Solubility: the amount of a substance that will dissolve in a given amount of another substance and is typically expressed as the number of parts by weight dissolved by 100 parts of solvent at a specified temperature and pressure or as percent by weight or by volume.

Spark Advance: the optimal spark setting, an operating parameter dependent on the rate of flame development and propagation within the combustion chamber.

Stoichiometric: characterized by, or being a proportion of, substances or energy exactly right for a specific chemical reaction with no excess of any reactant or product, i.e., chemically correct.

Stoichiometry (of fuel/air): the proportion required between fuel and air for a specific fuel to allow complete combustion of the chemical reactions to occur (i.e., the proportions that are exactly right).

TAME (Tertiary Amyl Methyl Ether): an ether formed by the reaction of methanol and either isoamylene or isopentalene.

Terne Metal: sheet iron or steel coated with an alloy of about 4 parts lead to 1 part tin.

Toxicity: the quality, state, or relative degree of being poisonous.

Vapor/Liquid (V/L) Ratio: a test to determine a fuel's tendency to vapor lock (i.e., the temperature required to create a V/L ratio of 20).

Vapor Lock: the inability of a fuel system to supply the required quantity of fuel to the engine because of the formation of excessive vapor in the system.

Volatility: term used to describe a gasoline's tendency to change from liquid to vapor.

Watt (W): the common base unit of power in the metric system. One kilowatt (1 kW) = 100 W; one kilowatt hour (1 kWh) = the amount of power equivalent to 1 kW and consumed for one hour.

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