

Alcohols and Ethers

A Technical Assessment of Their Application as Fuels and Fuel Components

API PUBLICATION 4261
THIRD EDITION, JUNE 2001



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Downstream Segment

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(Based on information available through November 1999)



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FOREWORD

This publication was prepared by a task force of the Fuels Committee, a committee of the API Downstream Segment. Dr. Robert Barter and Dr. Bruce Bauman of API's Regulatory and Scientific Affairs Department assisted the work. It is based on published information and on private reports made available through November 1999 from API member companies. The assistance of these companies is gratefully acknowledged. Richard L. Courtney, Herman L. Muller, and Robert E. Reynolds served as consultants to the task force.

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Alcohols and Ethers—A Technical Assessment of Their Application as Fuels and Fuel Components

1 Introduction and Scope

1.1 GENERAL

1.1.1 In 1971 the American Petroleum Institute (API) studied the feasibility of blending ethanol with gasoline to augment domestic fuel supplies for transportation.¹ After the first Arab oil embargo in 1974, interest in using alcohols as fuels expanded to include methanol, not only as a transportation fuel, but also as a fuel for stationary power sources. In response to that expanded interest, the API published an updated technical assessment in 1976.²

1.1.2 Since 1976, many changes have occurred in the use of petroleum and non-petroleum fuels, both neat and in blends with hydrocarbon components. The earlier objective of augmenting domestic energy sources was joined by two additional objectives: a) to produce high octane gasoline without the use of lead alkyls, and b) to reduce the contribution of motor vehicles and stationary sources to air pollution. In response to the expanded use of oxygenates, API published a second updated technical assessment in 1988.³ Today, federal law requires that oxygenates be blended with gasoline in the wintertime in certain areas and be a part of reformulated gasoline in specified areas of the United States.

1.1.3 The Clean Air Act Amendments of 1977 expanded the interest in alcohols and ethers. The Clean Air Act Amendments of 1990 mandated the use of oxygenates to reduce wintertime carbon monoxide emissions in carbon monoxide nonattainment areas. It also required oxygenates in reformulated gasoline (RFG) which is mandated for use in extreme and severe ozone nonattainment areas and other ozone nonattainment areas which opt to require reformulated gasoline. Nonattainment areas are those areas not meeting the statutory federal standards for ambient carbon monoxide (carbon monoxide nonattainment areas) and ozone (ozone nonattainment areas).

1.1.4 New policy issues regarding oxygenates are expected in the future. An important objective of this publication is to provide an updated and expanded technical assessment suitable as a foundation for policy discussion.

1.1.5 The transportation fuels industry has been shaped by six important events since the issuing of the Clean Air Act Amendments of 1977: a) the increased use of alcohols as blending components, b) the appearance of marketplace concerns resulting from the misuse of alcohols as blending components, c) the implementation of federal environmental regulations covering the composition of motor fuels, d) the onset of federal regulations requiring the use of oxygenates,

e) the use of several different ethers as fuel components, and f) the ban on MTBE in California by 2002. In the future, the registration of fuels and fuel additives and the required toxicology testing may affect motor fuel composition and the use of oxygenates.

1.1.6 This technical assessment, therefore, has been expanded to include a review of the oxygenate regulations and the technical literature that has been published between 1988 and 1999. This publication summarizes information on producing and applying alcohols and ethers as fuels and fuel components. The alcohols and ethers that are considered include a) methanol, ethanol, isopropyl alcohol (IPA), tertiary-butyl alcohol (TBA), methyl tertiary-butyl ether (MTBE), tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), and diisopropyl ether (DIPE) as fuel components; b) methanol and ethanol (both neat and mixed with low levels of hydrocarbons) as transportation fuels; and c) methanol in stationary power sources. This publication assesses the technical advantages and disadvantages of alcohols and ethers with respect to hydrocarbon fuels. The analysis also addresses the following factors: a) the costs associated with producing alcohols and ethers, b) distribution, storage, and fire protection and safety concerns, and c) health and environmental concerns.

1.2 REFERENCES

1. American Petroleum Institute Committee for Air and Water Conservation, "Use of Alcohol in Motor Gasoline—A Review," API Report No. 4082, August 1971.
2. American Petroleum Institute Alcohol Fuels Task Force, "Alcohols—A Technical Assessment of Their Application as Fuels," API Report No. 4261, July 1976.
3. American Petroleum Institute Alcohol Fuels Task Force, "Alcohols and Ethers—A Technical Assessment of Their Application as Fuels and Fuel Components," API Report No. 4261, July 1988.

2 Chemical and Physical Properties of Alcohols and Ethers

2.1 GENERAL

2.1.1 The molecular formulae of several alcohols and ethers usable as gasoline blending components or as neat fuels are summarized in Table 1. Commonly accepted abbreviations will be used in the following discussions.

Table 1—Nomenclature of Oxygenates Commercially Used as, or in, Fuels

Name	Abbreviated Name	Formula
Methyl Alcohol (Methanol)	MeOH	CH ₃ OH
Ethyl Alcohol (Ethanol)	EtOH	C ₂ H ₅ OH
Isopropyl Alcohol (Isopropanol)	IPA	(CH ₃) ₂ CHOH
Tertiary-Butyl Alcohol (t-Butanol)	TBA or GTBA ^a	(CH ₃) ₃ COH
Methyl Tertiary-Butyl Ether	MTBE	(CH ₃) ₃ COCH ₃
Tertiary-Amyl Methyl Ether	TAME	(CH ₃) ₂ (C ₂ H ₅)COCH ₃
Ethyl Tertiary-Butyl Ether	ETBE	(CH ₃) ₃ COC ₂ H ₅
Diisopropyl Ether	DIPE	(CH ₃) ₂ CHOCH(CH ₃) ₂

^aGTBA (“Gasoline grade” TBA) is a mixture of TBA and solvents which lower the freeze point of TBA. Neat TBA freezes at 78.5°F.

2.1.2 Oxygenates are comprised of hydrogen, carbon, and oxygen. The properties of an oxygenate are affected by the position of the oxygen atom in the molecule and the hydrocarbon content. Molecular construction also influences interactions in blends with hydrocarbons. Characteristics of gasoline-oxygenate blends are covered in Chapter 5. Some key properties of alcohols and ethers are listed in Tables 2 and 3.

2.2 HEATING VALUE

Because molecules of alcohols and ethers carry oxygen, they require less oxygen for complete combustion than do hydrocarbons with corresponding numbers of hydrogen and carbon atoms. Table 4 shows the oxygen requirements for complete combustion of oxygenates. The oxygen content of an alcohol or ether produces no heat of combustion and, thus, a volume or weight of oxygenate produces less heat from combustion than that of a hydrocarbon. The lowest molecular weight oxygenate of interest, methanol or MeOH, produces about one-half the heat energy of gasoline, either on a weight or volume basis. Higher molecular weight oxygenates produce as much as 85 to 90% of the heat energy of gasoline.

2.3 MOLECULAR POLARITY

2.3.1 Although both alcohols and ethers contain oxygen, the location of the oxygen atom in an alcohol molecule imparts properties that are much different from those of gasoline and ethers. The molecular structures of MeOH and EtOH are compared with water, gasoline and MTBE in Figure 1. An alcohol molecule contains an OH group, or hydroxyl group, the same functional group as a molecule of water. The OH group is attached at the end of the hydrocarbon structure and is highly polar. In contrast, the oxygen atom in an ether molecule is bound within the hydrocarbon structure and creates little, if any, polarity. In the MTBE molecule, shown in

Figure 1, the oxygen atom is bound into, and surrounded by, hydrocarbon.

2.3.2 As a consequence of the OH group, an alcohol has polar characteristics similar to water. The molecular polarity is stronger for alcohols with lighter hydrocarbon structure. MeOH has the greatest polarity of all oxygenates considered as fuel.

2.3.3 The phenomenon of molecular polarity has important consequences for blends of alcohols in hydrocarbons. Occasionally, problems with vehicle driveability and fuel system water occurred with the use of gasoline-alcohol blends. The molecular polarity of alcohol was the cause of the difficulties. See Chapter 5 for further discussion.

2.4 POLAR PROPERTIES OF ALCOHOLS

2.4.1 Polar molecules have affinity for other molecules in proportion to the degree of mutual polarity. Because of the polar nature of alcohols, vapor pressure anomalies with hydrocarbon blends and water interactions can occur. The vapor pressure of alcohols, 1.8 to 4.6 psi, listed in Table 2, is much less than that of typical blended gasoline. However, as described in Chapter 5, these values are deceptive in predicting vapor pressure of gasoline-alcohol blends due to the unusual polar behavior of alcohols. At room temperature, low molecular weight substances like water or MeOH would be gases were they not collapsed into liquids by the highly cohesive molecular forces of hydrogen bonding. When molecules of MeOH are dissolved in a nonpolar hydrocarbon solvent, like gasoline, they become physically separated. This physical separation weakens molecular cohesion and MeOH behaves like a gas. This results in an otherwise anomalous increase in vapor pressure that peaks at quite low MeOH concentrations.

Table 2—Some Properties of Alcohols, Gasoline, and No. 2 Diesel Fuel^c

Property	MeOH	EtOH	IPA	GTBA ²	Gasoline ^a	No. 2 Diesel Fuel
Molecular weight	32.04	46.07	60.09	73.5	100–105	~200
Composition, weight %						
Carbon	37.5	52.2	60.0	65.0	85–88	84–87
Hydrogen	12.6	13.1	13.4	13.7	12–15	13–16
Oxygen	49.9	34.7	26.6	21.3	0	0
Relative Density, 60/60°F	0.796	0.794	0.789	0.781	0.69–0.793 ²	0.81–0.89
Density, lb/gal @60°F	6.63	6.61	6.57	6.50	5.8–6.63 ²	6.7–7.4
Lower Heating value (liquid fuel—water vapor)						
Btu/lb	8,570	11,500	13,300	14,500	18K–19K	18K–19K
Btu/gal @60°F	56,800	76,000	87,400	94,100	109K–119K	126K–131K
Boiling temperature, °F	148	173	180	176–181	80–437	370–650
Freezing point, °F	–143.8	–173.4	–126.2	78.5 (TBA)	–40	–40 to 30
Vapor pressure, psi	4.6	2.3	1.8	1.8	7–15	<0.2
Research octane number ^b	—	—	—	—	88–100	—
Motor octane number ^b	—	—	—	—	80–90	—
Cetane number ^b		0–54 ²	—	—	—	40–59
Water solubility, @70°F						
Fuel in water, volume %	100	100	100	100	Negligible	Negligible
Water in fuel, volume %	100	100	100	100	Negligible	Negligible
Viscosity, mm/s						
@68°F	0.74	1.50	3.01	5.31	0.5–0.6	2.8–5.0
@–4°F	1.345 ²	3.435 ²	11.465 ²	Solid	0.8–1.0	9.0–24.0
Flash point, closed cup, °F	52	55	53	52	–45	165
Autoignition temperature, °F	~867	~793	~750	~892	~495	600
Flammability limits, volume %						
Lower	7.3	4.3	2.0	2.4	1.4	1.0
Higher	36.0	19.0	12.0	8.0	7.6	6.0
Latent heat of vaporization						
Btu/lb @60°F	506	396	320	258	~150	~100
Btu/gal @60°F	3,340	2,378	2,100	1,700	~900	~710
Stoichiometric air/fuel, weight	6.45	9.00	10.3	11.1	14.7	14.7
Moles product/moles charge	1.06	1.07	1.07	1.07	1.06	1.06
Moles product/moles O ₂ + N ₂	1.21	1.14	1.12	1.10	1.08	1.07

Notes:

^aGasoline properties listed are representative of non-oxygenated gasoline with 100% hydrocarbon content.^bConventional laboratory engine test methods for Research octane number, Motor octane number and cetane number are not suitable for neat alcohols. See Table 15 for Octane Blending Values of alcohols in gasoline.^cSuperscripted numbers refer to references at the end of each section.

Table 3—Some Properties of Ethers and Gasoline^c

Property	MTBE	TAME	ETBE	DIPE	Gasoline ^a
Molecular weight	88.15	102.18	102.18	102.18	100–105
Composition, weight %					
Carbon	68.1	70.5	70.5	70.5	85–88
Hydrogen	13.7	13.8	13.8	13.8	12–15
Oxygen	18.2	15.7	15.7	15.7	0
Relative Density, 60/60°F	0.746	0.776	0.745	0.729	0.69–0.79
Density, lb/gal @6°F	6.21	6.46	6.20	6.07	5.75–6.58
Lower Heating value (liquid fuel—water vapor)					
Btu/lb	15,100	15,600	15,600	16,500	18,000–19,000
Btu/gal @60°F	93,500	100,600	97,000	100,000	109,000–119,000
Boiling temperature, °F	131	187	161	155	80–437
Freezing point, °F	–163		–137	–122	–40
Vapor pressure, psi	7.8	1.5	4.0	4.9	7–15
Research octane number ^b	116 ⁶	—	—	—	88–100
Motor octane number ^b	101 ⁵	—	—	—	80–90
Water solubility, @70°F					
Fuel in water, volume %	4.8	1.15	1.2	1.1	Negligible
Water in fuel, volume %	1.5	0.6	0.5	0.6	Negligible
Viscosity, mm/s					
@ 68°F	0.47 ⁷	0.44 ⁵	0.53 ⁵	0.47 ⁵	0.5–0.6
@ –4°F	0.77 ⁷	0.71 ⁵	0.89 ⁵	0.76 ⁵	0.8–1.0
Flash point, closed cup, °F	–14	11	–3	9	–45
Autoignition temperature, °F	~815	860 ⁵	580	~830	~495
Flammability limits, volume %					
Lower	1.6	1.0	1.0	1.4	1.4
Higher	8.4	7.1	6.8	7.9	7.6
Latent heat of vaporization					
Btu/lb @60°F	138	135	134	148	~150
Btu/gal @60°F	863	870	830	900	~900
Stoichiometric air/fuel, weight	11.7	12.1	12.1	12.1	14.7
Moles product/moles charge	1.07	1.07	1.07	1.07	1.06
Moles product/moles O ₂ + N ₂	1.10	1.09	1.09	1.09	1.08

Notes:

^aGasoline properties listed are representative of non-oxygenated gasoline with 100% hydrocarbon content.^bConventional laboratory engine test methods for Research octane number and Motor octane number are not suitable for neat oxygenates. See Table 15 for Octane Blending Values of ethers as gasoline blend components.^cSuperscripted numbers refer to references at the end of this section.

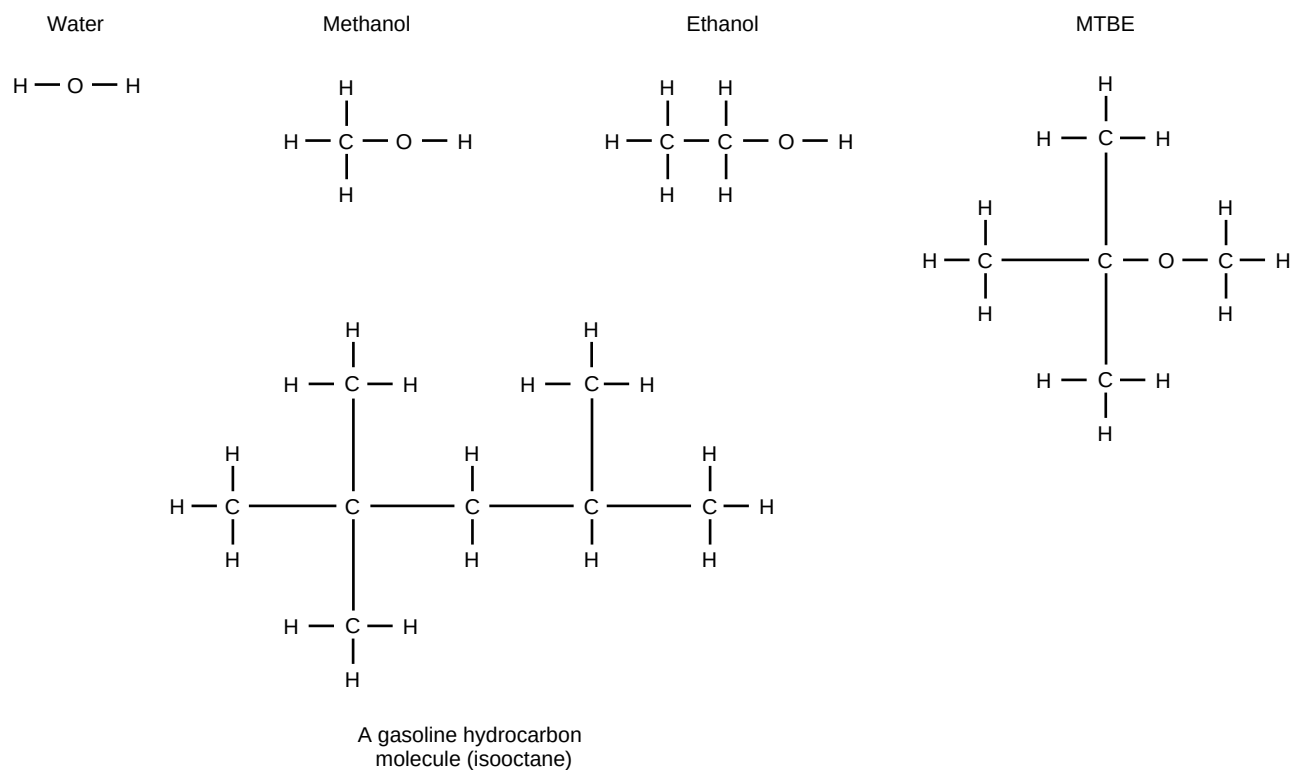


Figure 1—Molecular Structures of Water, Methanol, Ethanol, MTBE, and Gasoline

Table 4—Combustion of Alcohols, Ethers, and Hydrocarbons in Air

Fuel	Combustion Reaction Equation ^a	
Methanol	$\text{CH}_3\text{OH} + 1.5\text{O}_2 + 5.64 \text{ N}_2$	$\longrightarrow \text{CO}_2 + 2(\text{H}_2\text{O}) + 5.64 \text{ N}_2$
Ethanol	$\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 + 11.3 \text{ N}_2$	$\longrightarrow 2(\text{CO}_2) + 3(\text{H}_2\text{O}) + 11.3 \text{ N}_2$
Isopropyl Alcohol	$\text{C}_3\text{H}_7\text{OH} + 4.5\text{O}_2 + 16.93 \text{ N}_2$	$\longrightarrow 3(\text{CO}_2) + 4(\text{H}_2\text{O}) + 16.93 \text{ N}_2$
tert-Butyl Alcohol	$\text{C}_4\text{H}_9\text{OH} + 6\text{O}_2 + 22.6 \text{ N}_2$	$\longrightarrow 4(\text{CO}_2) + 5(\text{H}_2\text{O}) + 22.6 \text{ N}_2$
MTBE	$\text{C}_5\text{H}_{12}\text{O} + 7.5\text{O}_2 + 28.2 \text{ N}_2$	$\longrightarrow 5(\text{CO}_2) + 6(\text{H}_2\text{O}) + 28.2 \text{ N}_2$
TAME	$\text{C}_6\text{H}_{14}\text{O} + 9\text{O}_2 + 33.9 \text{ N}_2$	$\longrightarrow 6(\text{CO}_2) + 7(\text{H}_2\text{O}) + 33.9 \text{ N}_2$
ETBE	$\text{C}_6\text{H}_{14}\text{O} + 9\text{O}_2 + 33.9 \text{ N}_2$	$\longrightarrow 6(\text{CO}_2) + 7(\text{H}_2\text{O}) + 33.9 \text{ N}_2$
DIPE	$\text{C}_6\text{H}_{14}\text{O} + 9\text{O}_2 + 33.9 \text{ N}_2$	$\longrightarrow 6(\text{CO}_2) + 7(\text{H}_2\text{O}) + 33.9 \text{ N}_2$
Gasoline or Diesel Fuel	$\text{C}_n\text{H}_{2n} + 2 + [(3n + 1)/2] \text{ O}_2 + 3.76 [(3n + 1)/2] \text{ N}_2$	$\longrightarrow n\text{CO}_2 + (n + 1) \text{ H}_2\text{O} + 3.76 [(3n + 1)/2] \text{ N}_2$

^aBased on an air mixture of 79% nitrogen, 21% oxygen.

2.4.2 If enough water is present as a second liquid phase, as a so-called “water bottom,” the affinity of MeOH for the highly polar water molecules causes the MeOH to migrate from the gasoline blend to the water phase. These polarity effects are less pronounced for ethanol and may be insignificant for higher carbon number alcohols. Chapter 5 describes how this phenomenon of polarity affects vehicle operation with gasoline-oxygenate blends.

2.4.3 Another consequence of the strong polarity of MeOH, other alcohols and also water, is the need of high amounts of heat for vaporization. Alcohols with large hydrocarbon structures, such as TBA (or GTBA), have less polarity and have physical properties approaching those of hydrocarbons. Ethers vaporize, and have latent heats of vaporization similar to corresponding hydrocarbons in gasoline.

2.5 OTHER DIFFERENCES

2.5.1 Oxygenates differ from hydrocarbons significantly with respect to other properties: boiling point, vapor pressure, flammability, viscosity, flash point, and antiknock performance. As might be expected, the boiling temperatures are lowest for the lowest molecular weight alcohols and ethers. Being pure compounds, except for GTBA, all have constant boiling temperatures that generally categorize them in the more volatile, below 50% evaporated distillation temperature, fraction of typical gasoline.

2.5.2 Flammability limits, flash point and combustion characteristics of the alcohols, in particular, are much different than gasoline or diesel fuel. Ethers behave more like hydrocarbons in this regard. MeOH has a very rich flammability limit but also a somewhat rich lean limit for combustion. The antiknock performance of oxygenates cannot be measured using ASTM Research or Motor Methods. However, MeOH and EtOH are acknowledged as highly attractive engine fuels with superior knock resistance in engines, largely due to their high latent heats of vaporization and high combustion expansion ratios. Neat alcohols have relatively high flash point temperatures compared with hydrocarbons but, as discussed later, present certain safety concerns. The low luminosity of the flames of MeOH combustion causes concern about the use of MeOH as a neat fuel for vehicles as discussed in Chapter 6.

2.5.3 The freezing point of the ethers and the lower molecular weight alcohols is extremely low. However, the viscosities of alcohols at low temperature are much higher than those of light hydrocarbons. Because neat TBA approaches solidification at 78°F, it requires cosolvents for handling in refinery applications. Hence, the “Gasoline-Grade” version of TBA, termed GTBA, was developed.

2.5.4 Characteristics of oxygenates in blends with gasoline are covered in Chapter 5 and, as neat fuels for gasoline and diesel engines, in Chapter 6.

2.6 REFERENCES

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3 Oxygenates Production Technology, Capacity, and Costs

3.1 METHANOL

3.1.1 Worldwide methanol capacity in 1998 was about 37 million metric tons, or about 12.3 billion gallons per year (802 thousand barrels per calendar day). North American capacity was about 8.3 million metric tons, or about 2.7 billion gallons per year (176 thousand barrels per calendar day).¹ Major North American producers include Methanex, Hoechst-Celanese, Borden, Lyondell, Beaumont Methanol, Edmonton Methanol, Quantum, Clear Lake Methanol, Fortier Methanol, Georgia Gulf, and Ashland.^{1,2} For perspective, U.S. consumption of gasoline in 1998 was 127 billion gallons (8,253 thousand barrels per calendar day)³ and California consumption was about 14 billion gallons (918 thousand barrels per calendar day).⁴

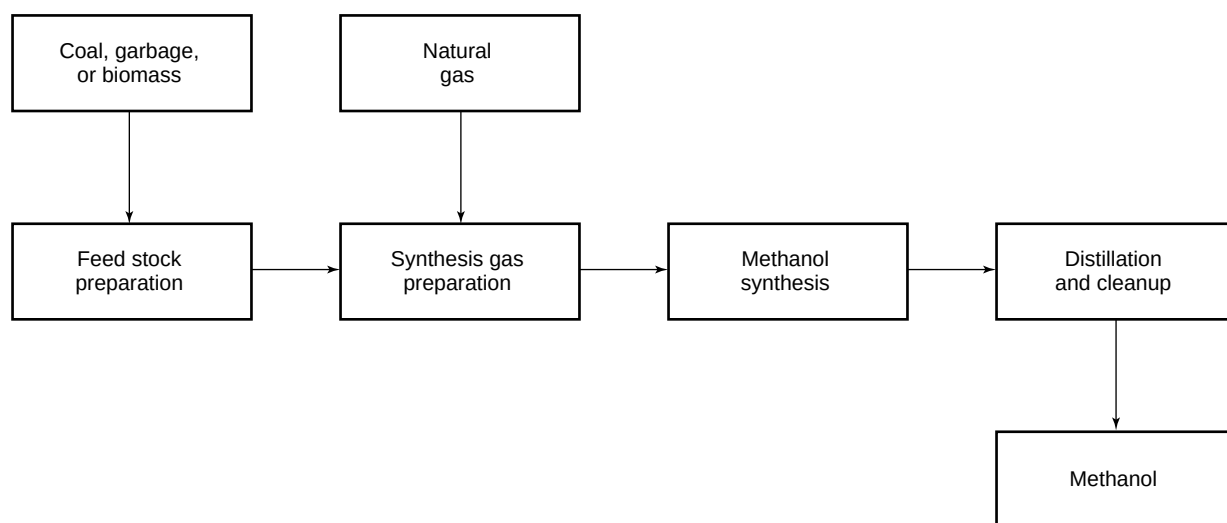


Figure 2—Methanol Production Process—Simplified Diagram

3.1.2 Essentially all methanol world wide is produced from natural gas. Technology also exists to manufacture methanol from coal, cellulosic refuse, or most types of biomass.⁵ In methanol production the feedstock is used to prepare a synthesis gas, either through reforming or catalytic partial oxidation.

3.1.3 Natural gas requires little preparation for producing the synthesis gas. Other feedstocks, including coal, have to be sorted, screened and pulverized before the synthesis gas step. Feedstocks other than natural gas may also contain sulfur that has to be removed from the synthesis gas. Since natural gas often contains little sulfur, there may be no need for sulfur removal when natural gas is used as the feedstock. Figure 2 is a simplified diagram of the methanol production process.

3.1.4 Most methanol industry analysts believe that a massive methanol plant production program would be required to support supply of fuels designed to operate on 85 – 100 percent methanol,⁶ i.e., the existing worldwide methanol manufacturing capacity and near term expansion will be able to supply tradition chemical markets (including formaldehyde and acetic acid) and to supply the requirements for the manufacture of MTBE for use in gasoline.

3.1.5 Estimates of methanol operating and plant capital costs depend strongly on a number of factors.^{6,7,8,9} These factors include technology employed, plant size and location, infrastructure needed, return on investment required, and cost of feedstock. In every case, the capital charge is a major part of the total cost of methanol. For example, Wagner and Tatterson in 1987 estimated capital costs to build a new methanol plant that uses natural gas feedstock to be \$250 – \$260 million for a 300 million gallon per year plant on the Gulf Coast or in the Middle East producing methanol with state-of-the-art technology.⁸ Wagner and Tatterson also estimated capital to fund a new methanol plant that uses coal as feedstock to be about

\$900 million. The coal plant incurs extra cost because of the additional facilities required for handling and preparing the feedstock and cleaning up the synthesis gas. Beyaert in 1988 estimated capital costs of \$416 – 650 million for new plants of 292 million gallons per year capacity in remote locations producing methanol using natural gas feedstock.⁶ In 1992, Hahn estimated capital costs of \$339 million 1988 dollars for a 2,500 metric ton per day, or about 300 million gallon per year, methanol plant on the Texas Gulf Coast, to \$418 and \$590 million for similar plants in Saudi Arabia and Australia, respectively.⁹ For larger plants of 10,000 metric tons per day, or about 1.2 billion gallons per year, Hahn estimated capital costs of \$883 million to \$1,088 million and \$1,537 million for plant locations similar to those of the smaller plants.

3.1.6 Feedstock costs are also major and can be highly variable. Estimated costs for natural gas feedstock used by Wagner and Tatterson as well as by Beyaert ranged from less than \$1.00 per million Btu for undeveloped remote locations (where the price of flared gas is very dependent on local factors and markets) to a market price of \$2.00 per million British thermal units (MMBtu) for U.S. natural gas on the Gulf Coast. The current price is about \$2.35 per MMBtu. Hahn also recognized huge uncertainties in predicting natural gas prices, and estimated natural gas prices from \$0.85 to \$3.08 per MMBtu for a short term scenario (2000) to \$1.21 – 3.79 for medium or long term projections (2005 and beyond). In addition, Hahn estimated that an increase in natural gas prices of \$1.00 results in an increase of \$0.10 per gallon of methanol.

3.1.7 The return on investment (ROI) required also affects methanol production cost significantly, and most studies have assumed about 10 – 15 percent. Some methanol producers might be willing to build plants yielding lower ROI, however, others might expect at least 15 percent, depending upon the

availability of alternative investments, perception of risks, and government incentives.

3.1.8 Estimates by Beyear of long-term methanol costs delivered to the U.S. West Coast from new plants in the Middle East and Australia range from 50 cents to 97 cents per gallon.⁶ Capital costs in this study were based on reported and estimated costs to build methanol plants at various locations around the world from 1981 – 1987. The costs include factors for building in developed (Middle East) and undeveloped (Australia) remote locations and assume an after tax ROI of 15 percent above inflation.

3.1.9 Wagner and Tatterson estimated future costs to produce fuel grade methanol from natural gas in plants on the U.S. Gulf Coast and a developed site in the Middle East that employ advances in steam reforming and catalytic partial oxidation technology.⁸ The authors assumed a 15 percent after tax ROI (10 percent ROI above 5 percent inflation), and estimated the cost of methanol delivered to the U.S. Gulf Coast at 43 cents per gallon. Methanol costs for a coal plant were estimated at 97 cents per gallon.

Table 5—Estimated Methanol Production Costs at the Plant Gate

	Port Arthur, Texas, USA	Point Lisas, Trinidad	Jubail, Saudi Arabia	Dampier, Australia	Edmonton, Canada	Prudhoe Bay, Alaska, USA
Capital Investment	339	378	418	590	355	575
Short Term						
Investment	17	24	29	30	18	30
Depreciation	–3	–4	–4	–5	–3	–5
Non-gas oper.	10	11	13	16	10	17
Natural gas	30	15	11	11	25	8
Tax	8	11	13	14	8	13
Sum	63	58	62	66	58	63
Medium Term						
Investment	15	21	25	26	15	25
Depreciation	–3	–3	–4	–5	–3	–5
Non-gas oper.	10	11	13	16	10	17
Natural Gas	37	19	14	15	31	12
Tax	6	10	11	11	7	11
Sum	66	57	59	63	60	60
Capital Investment	883	985	1,088	1,537	925	1,498
Long Term						
Investment	10	14	16	18	10	16
Depreciation	–2	–2	–2	–3	–2	–3
Non-gas oper.	6	6	7	9	5	10
Natural gas	37	19	14	15	31	12
Tax	4	6	7	8	4	7
Sum	55	43	42	46	49	42

Notes:

1. Capital investment in million 1988 U.S. dollars.
2. Other costs in cents per gallon of methanol in 1988 U.S. dollars.
3. A 2,500 metric ton per day plant is used in the short term and medium term.
4. A 10,000 metric ton per day plant is used in the long term.
5. Cost of capital is 11 percent in the short term and 9 percent in the medium and long term for low-risk countries.
6. An additional 3 percent is added to the cost of capital for high risk countries (Trinidad and Saudi Arabia).
7. Depreciation results in a tax benefit, and thus has a negative sign.
8. Numbers may not add up due to rounding.

Source: Reference 9

3.1.10 Hahn's estimates for the cost of a gallon of methanol at the plant gates are shown in Table 5. They range from a low of 42 cents per gallon for the long term case to a high of 66 cents for the short and medium term cases. The author used an ROI of 11 percent for short term and 9 percent for the medium and long term cases for low risk locations (U.S., Canada, and Australia) and added 3 percent for high risk locations (Trinidad and Saudi Arabia). This study also reported estimated costs per gallon of methanol delivered to Dallas, Los Angeles and New York, as shown in Table 6.

3.1.11 Whereas Beyear and Wagner/Tatterson limited their studies to methanol delivered to the U.S. Gulf and or West Coast, Hahn went considerably further. His primary source for methanol production costs was a Bechtel study for the State of California¹⁰ and included four cases, near term, short term,

medium term, and long term, corresponding roughly to 1995, 2000, 2005, and post 2005, respectively. (Because 1995 is history, the data presented in this report will not include the near term case.) The work was based on production costs, transportation costs, distribution and marketing costs, and the incremental costs of a flexible fuel vehicle (FFV). In addition to plant gate and delivered costs, costs and prices were developed for Dallas, Los Angeles, and New York. For these cities the estimated price of M85 and the estimated "full cost," of M85 which includes the incremental costs of an FFV were compared to estimated gasoline costs. Also, instead of the 1.8 gasoline equivalency factor for 100 percent methanol (see Chapter 6), Hahn used a factor of 1.68 for M85 which includes efficiency improvements for FFVs and the gasoline portion of the fuel.

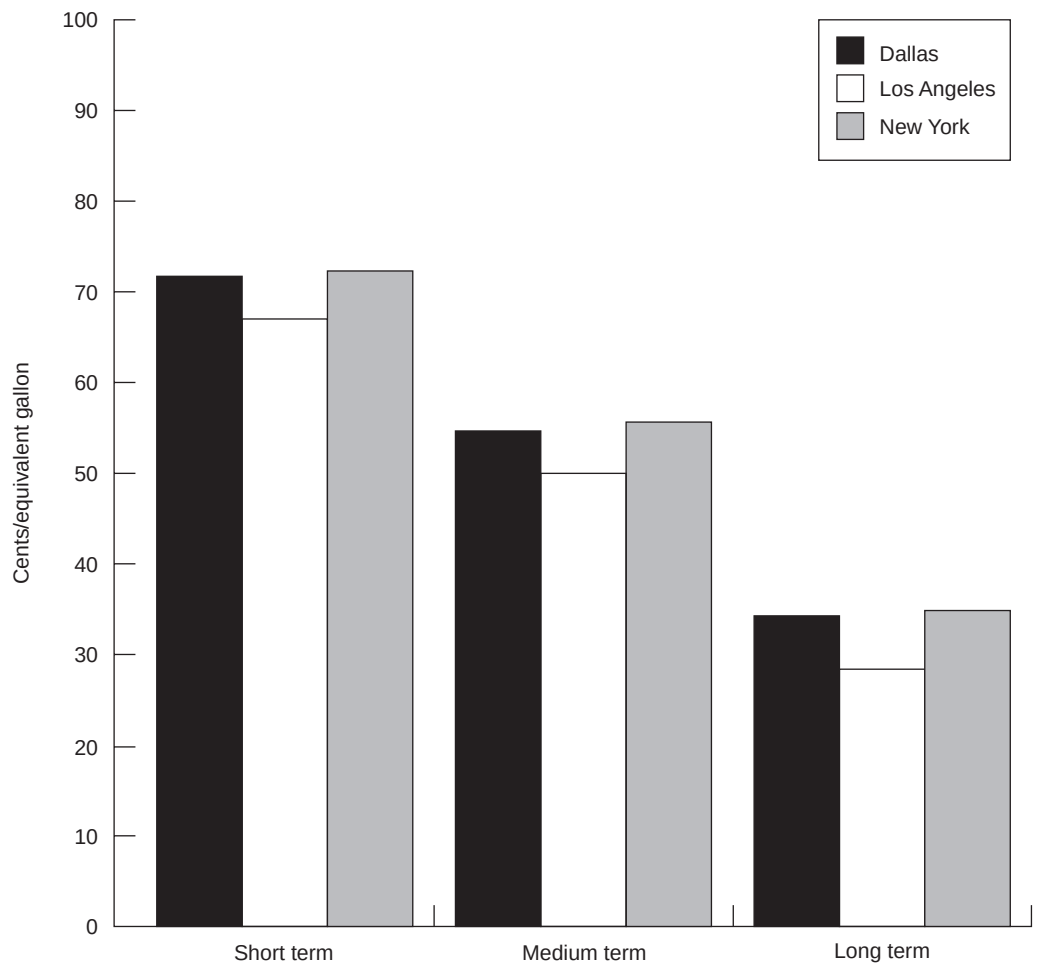
Table 6—Estimates of Delivered Methanol Costs

	Port Arthur, Texas, USA	Point Lisas, Trinidad	Jubail, Saudi Arabia	Dampier, Australia	Edmonton, Canada	Prudhoe Bay, Alaska, USA
Transport Costs						
Dallas	3	5	8	9	16	64
Los Angeles	8	5	5	4	9	52
New York	4	2	5	6	14	62
Delivered Cost						
Short Term						
Dallas	65	63	70	75	74	127
Los Angeles	71	63	67	70	66	115
New York	66	60	67	72	72	125
Medium Term						
Dallas	68	62	67	72	76	124
Los Angeles	74	62	64	67	69	113
New York	69	59	64	70	74	122
Long Term						
Dallas	58	47	50	55	65	106
Los Angeles	63	47	47	50	57	94
New York	58	45	47	52	63	104

Notes:

1. Costs in cents per gallon of 1988 U.S. dollars.
2. Total delivered cost is the sum of plant gate costs and transportation costs.
3. Numbers may not add up due to rounding.

Sources: Reference 9, also Reference 10 for transportation costs.



Source: Reference 9

Figure 3—City Comparison: Full Cost M85 Minus Gasoline Price, Base Case

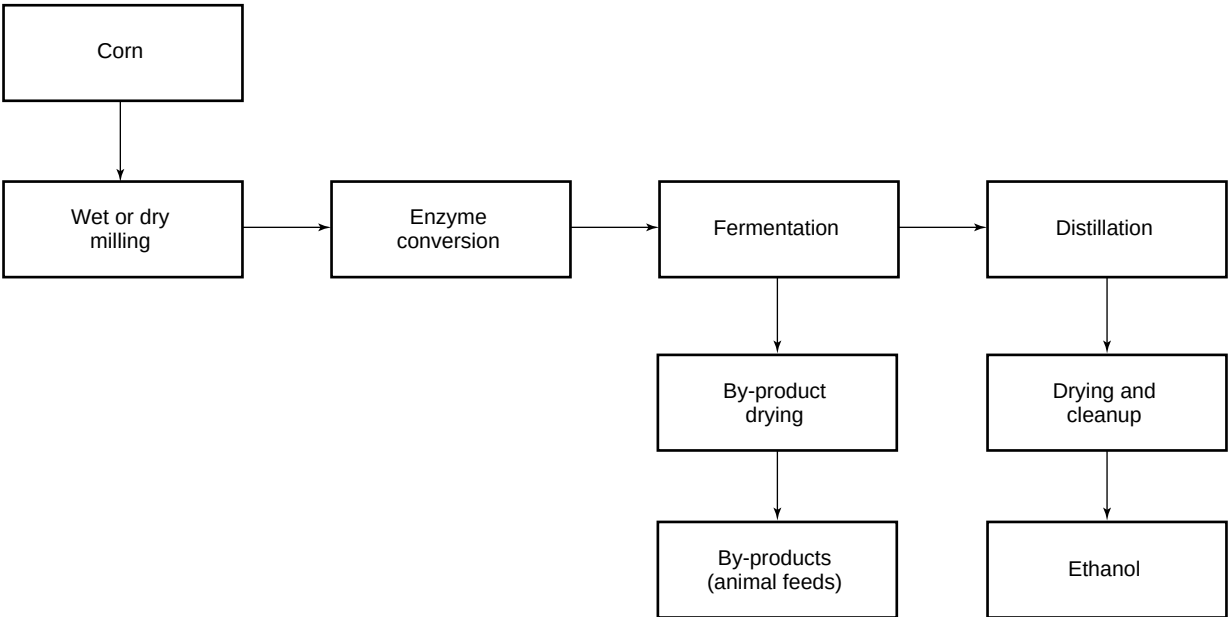


Figure 4—Ethanol Production Process—Simplified Design

3.1.12 Because of the many uncertainties associated with the costs of future motor fuels, Hahn performed sensitivity studies varying the capital charges, the real after-tax cost of capital (ROI), natural gas costs, and the FFV costs. Figure 3 is a graphic representation of Hahn's base case. It shows how the gap between the full cost of M85 and gasoline narrows substantially with time but still remains in favor of gasoline in the long term. The sensitivity studies also show that the combination of all the factors in favor of lower M85 costs still resulted in about a 45 cents higher cost for the methanol fuel per equivalent gallon of gasoline for the short term, which narrowed to about 10 cents per gallon for the long term case.

3.1.13 The energy balance for the production of methanol is shown in Table 7. In methanol manufacture, natural gas serves as both feedstock and the source of process energy; therefore, the energy balance is simple. The methanol produced contains about 65 percent of the energy contained in the natural gas consumed by the plant. The 35 percent loss of energy can be viewed as the penalty for liquefying the gas to methanol.

3.1.14 The primary economic consideration in the use of methanol is the cost. Based on the above estimates, the cost of methanol or M85 produced from natural gas that is equivalent to one gallon of gasoline remains above the price needed to be competitive with gasoline for the foreseeable future. Accordingly, unless crude prices increase significantly, or government subsidies are granted, or major advances in production technology are developed, the assessment that was made almost 10 years ago that methanol cannot compete with gasoline¹¹ is still valid today.

3.1.15 With today's technology, methanol from plants using cellulosic refuse of biomass for feedstocks is at least as expensive as methanol produced from coal.¹² Costs for collection and transportation of the raw materials are high and very site specific.

3.2 ETHANOL

3.2.1 U.S. Fuel Ethanol capacity in 1995 was about 7 billion gallons per year, or 111 thousand barrels per calendar day.² Actual production in 1998 was 1.45 billion gallons per

year, or 95 thousand barrels per calendar day.³ The major U.S. producer is Archer Daniels Midland with a capacity of about 750 million gallons per year (49 thousand barrels per calendar day). Other significant U.S. producers, but all with 110 millions per year or less capacity, are Minnesota Corn Processors, New Energy Company of Indiana, Cargill, High Plains Corporation, A. E. Staley, Midwest Grain Products, AGP, Chief Ethanol Fuels, and Nebraska Energy.²

3.2.2 Essentially all of the fuel ethanol in the United States is produced from corn. A bushel of corn yields about 2.5 gallons of ethanol. The remainder is produced from other grains, such as barley and waste sugars.

3.2.3 In the United States ethanol is produced by either dry milling or wet milling processes.¹³ In the wet milling process water is added to the grinding step. The choice between the two processes depends largely on the ability of manufacturers to market by-products. The major by-product of the dry milling process is distillers dried grain and solubles (DDGS), which is sold in competition with soybean meal as animal feed. By-products of the wet milling process include corn gluten feed, corn gluten meal, and corn oil. Corn gluten feed is sold as livestock feed, corn gluten meal is used to make poultry feed. By-products from both processes also include carbon dioxide (CO₂).

3.2.4 After milling, starches from the corn are converted by enzymes to fermentable sugars. The sugars are then fermented with yeasts, and the by-products are separated and dried. The low-proof beer from fermentation is distilled to yield 190-proof ethanol, which is further dried and purified to yield essentially 200-proof ethanol. Figure 4 is a simplified diagram of the ethanol production process.

3.2.5 Capital employed and especially feedstock costs have a significant impact on the production costs of ethanol. Costs of ethanol from new wet and dry milling plants using an average of 1997 – 1998 corn prices of \$2.25 per bushel are estimated to be \$1.09 and \$1.24 per gallon, respectively.¹⁴ The production costs are summarized in Table 8 and apply to new, undepreciated plants. Without depreciation, i.e., without capital recovery from large, fully depreciated plants, ethanol costs are much lower. With favorable corn prices and by-product markets, variable costs to produce ethanol have been reported well under \$1.00 per gallon, some as low as \$0.50. For the past 10 years almost one half of the increase in ethanol capacity in the United States has been achieved by expanding large wet milling facilities, and these plants may carry only a small part of the initial capital charges, or may now be fully depreciated. However, even the fully depreciated plants are significantly affected by feedstock prices; a change in the price of corn of \$1.00/bushel affects the variable costs of ethanol by 30 – 40 cents per gallon.

Table 7—Energy Balance for Production of Methanol

	MBTU per Gallon of Methanol
Feedstock and process energy (natural gas)	88
Energy in product	57
Overall efficiency, percent	65

Source: Reference 6

Table 8—Ethanol Production Costs in New Facilities
(1998 Dollars)

	Wet Milling	Dry Milling
Capacity, million gallons per year	100	40
Capital Investment, \$ million	245	98
	Dollars per gallon of ethanol	
Corn at \$2.25 ^a per bushel	0.90	0.90
By-product Credit	0.60 ^b	(0.45)
Operating Costs	0.37 ^c	0.37
Capital Recovery	0.42 ^d	0.42
Total	1.09	1.24

Note: Capital recovery is based on a 10 percent real return after taxes which equates to an annual capital charge of 17.1 percent.

^a Average of 1997 and 1998 prices.

^b Average of 1997 and 1998 by-product credits.

^c ERS AG Info. Bulletin No. 663, January 1993.

^d Based on the assumptions at bottom of Table 8.

Source: Reference 14.

3.2.6 The energy balance in ethanol manufacture is complicated because of the way feedstock energy is evaluated and because the plant uses different sources for process energy. The plant also generates by-products. The corn feed stock has calorific energy. However, since the corn is not burned directly for fuel, the plant should not be charged for the energy content of the corn as received but for the energy needed to grow the corn, i.e., the energy for fertilizer and herbicide manufacture, for cultivation and transportation, and for corn drying. Also, good land requires less energy to produce corn than land that must be irrigated (i.e., requiring additional energy to supply the water). Most large plants use coal for process fuel, but smaller plants generally use natural gas, distillate fuel or residual fuel. Finally, a credit is given for the by-products that equals the energy needed (or the replacement value) to produce the same amount of animal feed using the most efficient alternative method, which is growing soybeans. No credit is given for refinery energy savings because essentially all ethanol is added to gasoline downstream, usually at terminals. These considerations were used by Muller and Ho in 1986 with information available at that time to calculate an energy efficiency of ethanol of 95 percent.¹⁵

3.2.7 A more recent energy study of the production of ethanol in 1995 by Shapouri, Duffield and Graboski for the U. S. Department of Agriculture (USDA) concluded that the net energy value of corn ethanol has become positive in recent years due to technological advances in ethanol production and increased efficiency in farm production.¹⁶ Also, corn

Table 9—Net Energy Value of Corn Ethanol,
Btu per Gallon

Production Phase	Milling Process		Weighted Average
	Dry	Wet	
Corn Production	21,225	22,074	21,793
Corn Transport	1,212	1,260	1,244
Ethanol Conversion	47,425	53,273	51,343
Ethanol Distribution	3,173	3,173	3,173
Energy Losses	<u>5,046</u>	<u>5,380</u>	<u>5,271</u>
Total Energy Used	78,081	85,160	82,824
By-Product Credits	13,410	15,500	15,056
Net Energy Value ^a	19,290	14,301	16,193
Energy Ratio	1.30	1.21	1.24

^a A gallon of ethanol contains 83,961 Btu on a high heat value basis.

Source: Reference 16

yields have been trending higher in recent years, and the production of agricultural chemicals has become more efficient. In addition, modern ethanol production facilities conserve energy by utilizing cogeneration facilities that produce steam and electricity simultaneously. Table 9 is a summary of the USDA study on the energy efficiency of ethanol production for both the dry and wet milling processes and a weighted average taking into account that wet milling represents two-thirds of U.S. ethanol production and dry milling one-third. The calculations are also based on high heating values. The authors note that using either low or high heating values is valid for the energy balance calculations as long as the basis is consistently applied. By-product credits were based on the replacement value, and no credit was given for CO₂. The USDA study concludes that corn ethanol production is energy efficient by a ratio of 1.24 for modern facilities.

3.2.8 The primary consideration for fuel ethanol is also the cost. With the cost of ethanol produced from corn at over \$1.00 per gallon in a new plant, and third quarter 1999 gasoline Gulf Coast spot prices of about \$0.65 per gallon, fuel ethanol manufacture in new plants will continue to depend on subsidies. In the absence of such, only ethanol produced in fully or partially depreciated plants that primarily support variable costs may compete with gasoline or with other oxygenates.

3.2.9 Ethanol can also be produced from cellulose or biomass such as wood, corn stover, and municipal solid wastes, but the processes that use these resources have serious tech-

nical and economical problems. For example, cellulose is difficult to dissolve and hydrolyze, and the sugars produced are not fermentable with normal yeasts. Also, because of the low value density of the raw materials, supply and front-end processing must be done on a major scale. This means that processing plants must be very large and therefore would require large capital investments. Furthermore, lignin, which is partially polymerized phenolic resin, is a major by-product of ethanol from cellulose (wood), and there is no ready market for this material. Activities in this area have been limited to work in university and government facilities.^{17,18} Full scale commercial production is not expected in the foreseeable future unless valuable uses for lignin and other by-products are found or there are major advances in technology.

3.3 TERTIARY-BUTYL ALCOHOL (TBA)

Worldwide capacity of TBA is estimated at 60 thousand barrels per calendar day (920 million gallons per year).³¹ U.S. capacity is about 38 thousand barrels per calendar day (580 million gallons per year). Of this, Arco Chemicals (now Lyondell Petrochemical) and Texaco Chemical produce about 33 thousand barrels per calendar day and 12 thousand barrels per calendar day, respectively, as a co-product of propylene oxide production.¹⁹ TBA can also be produced by the direct hydration of isobutylene. In the United States there is currently no market for TBA to be used as a gasoline component by itself, and all TBA available for fuel use is being converted to isobutylene for MTBE production.

3.4 OTHER ALCOHOLS

Other alcohols that could be used in gasoline include isopropyl alcohol (IPA) and butyl alcohols other than TBA. Essentially all these alcohols produced in North America are used as chemical feedstocks or as solvents. They are usually too expensive for use as a gasoline blending component; however, IPA has been used in gasoline at 2 percent or less to prevent carburetor icing.^{20,21}

3.5 METHYL TERTIARY-BUTYL ETHER (MTBE)

3.5.1 Current worldwide MTBE capacity is about 523 thousand barrels per calendar day (8.0 billion gallons per year). North American capacity is estimated at 248 thousand barrels per calendar day (3.8 billion gallons per year).²² Actual U.S. consumption is 250 thousand barrels per calendar day (about 3.8 billion gallons per year), more than 80 thousand barrels per calendar day (about 1.2 billion gallons per year) were imported.

3.5.2 Major producers of merchant MTBE in North America are Arco Chemical (now Lyondell Petrochemical), Texaco Chemical, Huntsman Corporation, Texas Petrochemical, EGP Fuels (Enron), Valero, Alberta Envirofuels, Belvieu Environmental Fuels (Enterprise/Sun/Mitchell), and Global

Octane.^{2,22} MTBE production has expanded explosively in recent years to meet RFG requirements, but future MTBE demand is predicted to grow slowly. World MTBE capacity appears more than adequate to cover demand through the year 2000.

3.5.3 MTBE is produced by reacting isobutylene with methanol over an ion-exchange catalyst.²² Major sources of the isobutylene feedstock are derived from catalytic cracking and ethylene cracking; isobutylene is a refining by-product of these processes, and its supply is therefore generally limited to use in the refinery where it is produced. Merchant MTBE is manufactured from isobutylene that is produced by dehydrating tertiary butyl alcohol (TBA), or by isomerizing butane to isobutane followed by dehydrogenation.

3.5.4 Costs of MTBE produced from butanes in world scale plants have been estimated by DeWitt & Company, and are shown in Table 10. The assumptions for these costs are based on 1996 conditions and the study revealed full MTBE costs ranging from \$1.07 per gallon produced in a plant on the U.S. Gulf Coast to about \$1.12 for MTBE from a plant in Saudi Arabia and delivered to the U.S. The DeWitt study concluded that overall, the data indicate that these two world scale plants would be reasonable investments provided U.S. MTBE prices are at average or better levels.

3.6 TERTIARY-AMYL METHYL ETHER (TAME)

3.6.1 TAME is produced via the MTBE process using a feedstock that contains isoamylenes. Plants that produce TAME are limited to refineries for in-house use, i.e., there is currently no merchant TAME available.

3.6.2 Current U.S. TAME capacity is about 23 thousand barrels per calendar day (about 353 million gallons per year).² Current worldwide TAME capacity is estimated to be 47 thousand barrels per calendar day (about 721 million gallons per year).

3.7 DIISOPROPYL ETHER (DIPE)

3.7.1 Diisopropyl ether (DIPE), or isopropyl ether (IPE) has recently been under consideration as a gasoline blending component, and both Mobil²⁵ and UOP,²⁶ each with their own catalyst technology, have announced low cost processes to produce this ether. DIPE is produced from propylene and water, and in either process the propylene is hydrated to isopropyl alcohol (IPA) and further reacted to maximize DIPE and minimize IPA yields. Both processes are refinery based and do not depend on external sources of alcohol for etherification. Mobil showed costs of 78 cents per gallon of DIPE, excluding catalyst and licensing fees. The addition of an additive to the Fluid Bed Catalytic Cracker Unit (FCC) to maximize propylene yield reduced costs to 74 cents per gallon. These costs compared

Table 10—Cost of Producing MTBE

Capital Costs, \$ million	500,000 metric tons/year (1.6 billion gallons) from butanes			
	U.S. Gulf Coast		Saudi Arabia	
	285		410	
	\$/ton	\$/gal	\$/ton	\$/gal
Feedstocks				
Butane	134.87	0.38	108.49	0.31
Methanol	91.54	0.26	50.92	0.14
Total Feeds	226.40	0.64	159.41	0.45
Variable Costs (Electricity, Fuel Gas, Cooling Water, Catalyst Replacement)	39.26	0.11	14.42	0.04
Fixed Costs (Labor/Overhead, Maintenance, Insurance)	30.13	0.08	44.20	0.12
Cash Costs	295.80	0.735 ^a	218.02	0.61
ROI, 15% before Taxes	85.50	0.24	126.00	0.35
Full Cost	381.30	1.07	344.02	0.96

Note: Numbers may not add up due to rounding.

^aMTBE/Oxygenates Clean Fuels, Dewitt & Co., Inc. Issue 686, August 5, 1999.

Source: Reference 22.

favorably with the costs of producing MTBE from world-scale size plants.

3.7.2 Actual use of DIPE in fuel has been limited to oil companies that are affiliated with chemical companies that produce isopropyl alcohol.²⁷ Special procedures are used to handle and store neat DIPE.²⁸

3.8 ETHYL TERTIARY-BUTYL ETHER (ETBE)

ETBE has been proposed as a means for expanding the range of available oxygenates which have favorable octane and volatility blending characteristics, as well as the advantage of pipeline fungibility. ETBE can be made by reacting isobutylene with ethanol over a catalyst, similar to the MTBE process. Although ETBE has very good blending properties, economics currently favor MTBE production. Ethanol cost, even applying the 54 cent per gallon tax subsidy, is still considerably higher than the price of methanol.²⁹ However, if feedstock costs should favor ethanol, a number of MTBE plants in North America are being or have been modified for production of ETBE in addition to MTBE. It is estimated that about 53 thousand barrels per day of ETBE capacity, or about 812 million gallons per year, could be readily available,³⁰ if the economics turn favorable.

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4 Regulation of Alcohols and Ethers

4.1 HISTORY

4.1.1 Prior to the passing of the Clean Air Act Amendments of 1977, there were no federal or state regulations controlling the use or properties of fuels containing alcohols or ethers. Gasoline-alcohol blends were marketed in the 1930s and 1940s in Nebraska and surrounding states as Agrol, Alcoline, and Alky-Gas.^{1,2} Low levels of alcohols, such as isopropyl alcohol, have been used since 1950 as carburetor antiicing additives. Beginning in 1969, Atlantic-Richfield Company (ARCO) used gasoline-grade tertiary-butyl alcohol in blends with gasoline in a number of marketing areas for about 10 years. From 1974 through 1977, a blend of 10 percent by volume ethanol and 90 percent by volume gasoline, known as gasohol, was tested in Nebraska. In 1978 the Nebraska Gasohol Commission commercially introduced gasohol, which was the beginning of widespread use of ethanol as a fuel component.¹

4.1.2 Neat alcohols also were of interest as fuels. Henry Ford was an early proponent of neat alcohol fuels and in the 1880s he designed one of his early automobiles to run on eth-

anol.² General Motors Research investigated the use of ethanol as a fuel in the 1920s.³ Methanol has been the fuel used to power Indianapolis 500 race cars since the 1950s.

4.2 CLEAN AIR ACT REQUIREMENTS

4.2.1 General

4.2.1.1 Attempts to achieve national goals for improved air quality and energy self-sufficiency often give rise to conflicting solutions. The Department of Energy (DOE) considers alcohols to be viable extenders of the U.S. gasoline supply and methanol as an automotive fuel for the future.⁴ The EPA mandated the phasedown of lead antiknock compounds in gasoline beginning in 1980. The EPA implemented restrictions on gasoline vapor pressure beginning in 1989, which limited the use of butane, a component of high octane blending value. The implementation in 1995 of the toxics reduction requirement of the Clean Air Act Amendments of 1990 in many cases will reduce the aromatics content of gasoline, in part by dilution with oxygenates. Further, the Clean Air Act Amendments of 1990 required the use of oxygenates. The combination of these EPA regulations forces refiners and marketers of gasoline to consider new ways to restore the lost octane. One approach is to blend oxygenates into gasoline, but this is subject to certain legal and practical limitations.

4.2.1.2 The EPA is empowered to regulate fuel volatility and any other fuel property which, if uncontrolled, could contribute either directly or indirectly to air pollution. Under Section 211(f) of the Clean Air Act, as amended in 1977, unleaded gasoline marketed for use in vehicles manufactured after 1974 must be substantially similar to those fuels used during the federal emissions certification testing procedures. The EPA was concerned that oxygenated blends could adversely affect exhaust and evaporative emissions control systems. After recognizing the ad hoc commercialization of ethanol blends in 1978, the EPA began to impose restrictions.

4.2.1.3 The first potential restriction considered by the EPA eventually became a non-restriction. It dealt with gasohol, a blend of one part agriculturally-derived ethanol with nine parts finished gasoline. After the first Arab oil embargo in 1974, gasohol marketing was stimulated by a variety of tax incentives. When the “substantially similar” rule was written into the Clean Air Act Amendments of 1977, the EPA faced a dilemma. Gasohol was a politically popular fuel that could not technically be construed to be substantially similar to certification gasoline because it contained up to 3.7 percent by weight oxygen. However, the Clean Air Act Amendments of 1977 provided that the EPA could grant a waiver of Section 211(f) requirements if the applicant demonstrated that the fuel in question did not significantly deteriorate, or contribute to the deterioration of the performance of any motor vehicle emissions control system.

4.2.1.4 In 1978, gasohol interests applied to the EPA for a waiver. However, the EPA failed to render a determination of the application within the 180-day period provided for by law, and a waiver was thereby automatically granted for gasohol by operation of the Act. By permitting this automatic waiver, the EPA allowed gasohol blending but reserved its right to enforce Section 211 provisions in the future. The only restriction was the fuel consisted of 90 percent by volume unleaded gasoline and 10 percent by volume ethanol.

4.2.1.5 In 1981, the EPA ruled that unleaded fuels blended with oxygenates at concentrations of 2.0 percent by weight or less oxygen provided by aliphatic ethers and alcohols (other than methanol) qualified as being substantially similar.⁵ All finished blends were required to meet at least one of the seasonal and geographical [ASTM D 439](#) volatility class limits.⁶ Some of the test procedures within the [ASTM D 439](#) specification are considered unsuitable for use with oxygenated fuel blends. In 1991, EPA revised the “substantially similar” rule to allow fuels containing aliphatic ethers and/or alcohols (excluding methanol) to contain no more than 2.7 percent oxygen by weight. Also, the requirement involving [ASTM D 439](#) was changed to the new specification for automotive spark-ignition engine fuel, [D 4814-88](#).⁶

4.2.1.6 The “substantially similar” rule allowed oxygenates, such as ethanol, propyl alcohols, butyl alcohols, higher molecular weight alcohols, and ethers to be used at volume concentrations proportionate to their respective oxygen contents. Thus, compounds containing less oxygen that were more similar to hydrocarbons in chemical and physical characteristics than methanol could be used at higher volume concentrations. For example, the “substantially similar” rule nominally allows about 12 percent by volume butyl alcohol or 15 percent by volume MTBE in a typical gasoline (see Table 11). Methanol blends were excluded from the “substantially similar” rule at concentrations above 0.3 percent by volume because of questions concerning the effects of gasoline-methanol mixtures on fuel system components, water separation, and evaporative emissions.⁷ Methanol was allowed at a maximum of 0.3 percent by volume, a level consistent with long-standing commercial applications as a fuel system deicer and as a cosolvent for other permitted fuel additives.

4.2.1.7 The 1978 waiver (effective December 16, 1978, but actually issued in 1979) for gasohol specified 10 percent by volume ethanol, and the original “substantially similar” rule permitted between 0 and 5.4 percent by volume of ethanol. Blends with more than 5.4 percent by volume and less than 10 percent by volume were not covered by exact language until 1982 when the EPA clarified the waiver and permitted concentrations of ethanol up to and including 10 percent by volume. The EPA does not mandate that blends containing up to 10 percent by volume ethanol must meet [ASTM D 439](#) or [D 4814](#) requirements. Thus, the direct addition of up to 10

Table 11—Some Oxygenated Compounds Approved by EPA for Use in Unleaded Gasoline

Compound ^a	Broadest EPA Waiver	Date	Maximum Oxygen, Weight %	Maximum Oxygenate, Volume %
Methanol	Substantially similar	July '81	—	0.3
Propyl Alcohols	Substantially similar	July '81	2.7	(9.6) ^d
Butyl Alcohols	Substantially similar	July '81	2.7	(11.5) ^d
Methyl tertiary-butyl ether (MTBE)	Substantially similar	July '81	2.7	(14.9) ^d
Tertiary-amyl methyl ether (TAME)	Substantially similar	July '81	2.7	(16.6) ^d
Isopropyl ether	Substantially similar	July '81	2.7	(17.3) ^d
Methanol and butyl alcohol or higher molecular weight alcohols in equal volumes	Substantially similar	July '81	2.7	7.4
Ethanol	Gasohol ^b	1979, 1982	(3.5) ^{d,e}	10.0
Gasoline grade tertiary-butyl alcohol (GTBA)	ARCO	1981	3.5	(15.7) ^d
Methanol + GTBA (1:1 maximum ratio)	ARCO (OXINOL [®])	1981	3.5	(9.4) ^d
Methanol @ 5 volume % maximum + 2.5 volume % minimum cosolvent ^f	DuPont	1985	3.7	c
Methanol @ 5 volume % maximum + 2.5 volume % minimum cosolvent ^g	Texas Methanol (OCTAMIX)	1988	3.7	c

Notes:

^aAll blends of these oxygenated compounds are subject to [ASTM D 439](#) volatility limits except ethanol. Contact the EPA for current waivers and detailed requirements, U.S. Environmental Protection Agency, Field Operations and Support Division (EN-397F), 401 M Street, S.W., Washington, D.C. 20460.

^bSee Chapter 4, Clean Air Act Requirements.

^cVaries with type of cosolvent.

^dCalculated equivalent for average specific gravity gasoline (0.737 specific gravity @60°F, *NIPER Gasoline Report*). Calculated equivalent depends on the specific gravity of the gasoline.

^eValue shown is for denatured ethanol. Neat ethanol blended at 10.0 volume % produces 3.7 weight % oxygen.

^fThe cosolvents are any one, or a mixture of, ethanol, propyl alcohols, and butyl alcohols. Corrosion inhibitor is also required.

^gThe cosolvents are a mixture of ethanol, propyl, butyl, and higher alcohols up to octyl alcohol. Corrosion inhibitor is also required.

percent by volume of ethanol to unleaded gasoline can be made at distribution terminals or at other points in the distribution network. EPA allows up to 2 percent by volume of MTBE in the unleaded gasoline to which ethanol is added, if the MTBE is present only as a result of commingling in transport and storage and not purposely added as an additional component. Blending in such a manner, without regard for meeting [ASTM D 4814](#) specifications for volatility, is commonly referred to as “splash blending.”

4.2.1.8 The first waiver dealing with methanol concentrations above 0.3 percent by volume was granted to Sun Oil Company in 1979. It allowed the use of 2.75 percent by volume methanol with an equal volume of TBA up to a blend oxygen total of 2 percent by weight oxygen. Sun Oil Company demonstrated that cosolvents, namely higher molecular weight alcohols, reduced some of the adverse effects of methanol on volatility and water tolerance in blends. ARCO also received a waiver in 1979 to use up to 7 percent by volume TBA, which ARCO had marketed since 1969. These waivers were superseded by the “substantially similar” definition in 1981.

4.2.1.9 At the request of ARCO, the EPA granted a waiver in 1981 for the use of the following blends containing a maximum of 3.5 percent by weight oxygen: a) gasoline-grade

TBA (GTBA), and b) OXINOL[®], up to 1:1 volume ratio methanol in GTBA. At the maximum permitted level, methanol concentration in the finished gasoline blend could be as high as 4.8 percent by volume in typical gasoline. The highest allowable content of an oxygenate listed is 15.7 percent by volume GTBA. Figure 5 shows the relation between percent by weight oxygen and percent by volume oxygenate for a number of oxygenates.

4.2.1.10 The EPA granted a waiver request submitted by DuPont in 1985 for a maximum of 5.0 percent by volume methanol with at least 2.5 percent by volume cosolvent of ethanol, propyl, or butyl alcohols in the finished blend, up to a limit of 3.7 percent by weight oxygen, accompanied by specific corrosion inhibitors. In addition, the waiver incorporated a water tolerance or phase separation requirement.⁸

4.2.1.11 The EPA's concern in granting this waiver as DuPont requested was the potential effects of the combination of methanol and ethanol on evaporative emissions. Even though previous EPA waivers specified volatility limits according to [ASTM D 439](#) for finished blends, EPA initially required that a special volatility restriction called Evaporative Index (EI) also be imposed before granting the waiver to DuPont in January 1985.⁸ Upon petition, the EPA subse-

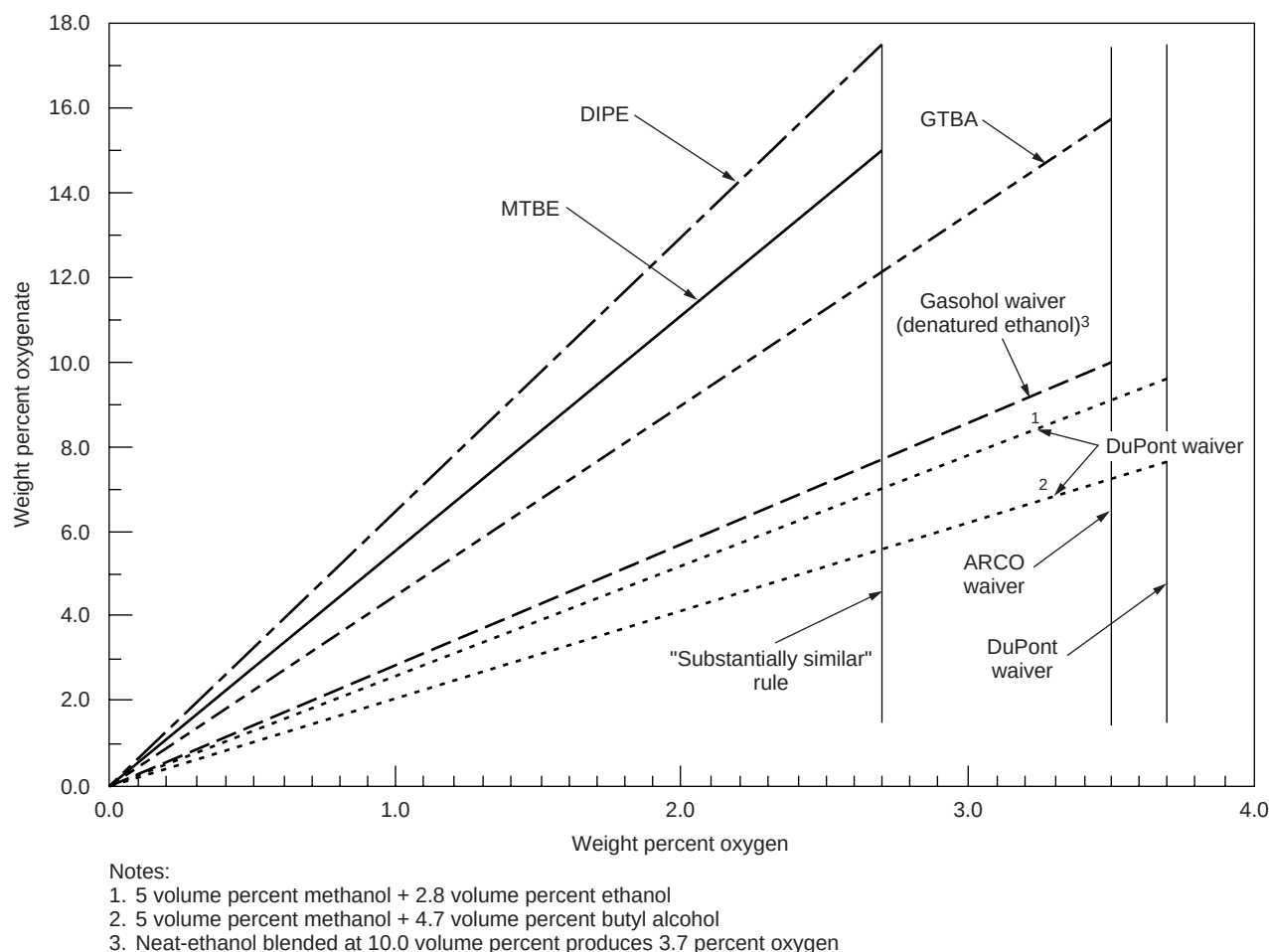


Figure 5—Relationship Between Volume Percent Oxygenate and Weight Percent Oxygen in 0.748 Relative Density Gasoline

quently reconsidered and withdrew the EI requirement but emphasized that the ASTM standards be followed rigidly.⁹

4.2.1.12 Other waivers granted for oxygenates by EPA are summarized in Table 11.

4.2.2 Clean Air Act Amendments of 1990

4.2.2.1 The Clean Air Act Amendments of 1990 required states with carbon monoxide nonattainment areas to revise their state implementation plan (SIP) to require the use of oxygenated gasoline in the wintertime. The oxygenated gasoline programs are state administered programs and they began on November 1992 for 39 designated carbon monoxide nonattainment areas. Since then about a dozen areas have submitted requests to EPA seeking redesignation as being in attainment. Some states also are removing their requirements for oxygenated gasolines. For the current status of the oxygenated gasoline program, EPA and state officials should be

contacted. EPA proposed guidelines for the program which stated the control period should be for at least four high carbon monoxide months (shorter periods would be accepted if the state can show no air quality impact). If the state chose an averaging control system, the minimum average oxygen content would be 2.7 percent by weight with a minimum oxygen content for each gallon of 2.0 percent by weight. Without averaging, each gallon must contain 2.7 percent by weight oxygen. The maximum oxygen content was 2.9 percent by weight for substantially similar oxygenates and 3.7 percent by weight for ethanol or methanol-cosolvent blends. Lower oxygen contents are allowed if a state can demonstrate that the higher oxygen levels of the EPA guidelines adversely affect air quality for pollutants other than carbon monoxide.

4.2.2.2 The Clean Air Act Amendments of 1990 also address fuel requirements for ozone nonattainment areas. The EPA classifies the ozone nonattainment areas into extreme, severe, serious, moderate, marginal, transitional, and incom-

plete categories. The law required reformulated gasoline (RFG) in the nine worst nonattainment areas (extreme and severe) effective January 1, 1995.

4.2.2.3 The law also allows other ozone nonattainment areas the option of choosing to have the RFG requirements apply to their areas (opt in) upon petition by the governor of their state. About 30 areas chose to opt in and of those about half have subsequently asked to opt out of the program. EPA issued a final rule on July 8, 1996, permitting opt-in areas (not required areas) to opt out of the RFG program under specified conditions. For the current status of the program, EPA should be contacted.

4.2.2.4 The final RFG rule was issued in 1994.¹⁰ It consisted of two phases. Phase I, which became effective January 1, 1995, required a 15 to 17% reduction in both ozone forming VOC emissions during the summer and air toxics emissions throughout the year from vehicles. It specified the use of the “simple model” for 1995 through 1997, but permitted the “complex model” to be used earlier. The “complex model” had to be used after January 1, 1998. Phase II, which became effective January 1, 2000, requires a 25 to 29% reduction in ozone forming VOCs and a 20 to 22% reduction in air toxics from vehicles. It also specifies a 5 to 7% reduction in oxides of nitrogen emissions from vehicles during the summer.

4.2.2.5 Both the “simple model” and “complex model” reformulated gasoline are as of this writing required to have a minimum oxygen content. The requirement may be met on either a per gallon or average basis. The per gallon minimum is 2.0 percent oxygen by weight, which means that each and every gallon must contain at least 2.0 percent by weight. If averaging, the average minimum limit is 2.1 percent oxygen by weight and each gallon must contain at least 1.5 percent oxygen by weight. Higher limits for both per gallon and average apply to RFG areas that have been ratcheted by the EPA. The maximum allowed oxygen content for summer reformulated gasoline was originally 2.7 percent by weight with an option of 3.5 percent by weight on notice by states under specified circumstances. This was changed in 1996 to 2.7 percent by weight maximum oxygen for “substantially similar” oxygenates and to the maximum limit allowed under waivers (e.g., 10 percent by volume for ethanol). On notification by states, the maximum limit can be set at 3.2 percent oxygen by weight if the higher (waiver) level will interfere with attainment or maintenance of air quality standards.¹¹ The EPA still allows 10 percent by volume ethanol to be added to gasoline containing up to 2.0 percent by volume MTBE that is not purposely added, except the total oxygen content cannot exceed 4.0 percent by weight. The 4.0 percent by weight is the upper oxygen limit where “simple model” and “complex model” are applicable.

4.2.2.6 The oxygen requirements for federal RFG and for California Phase 2 RFG are summarized in Table 12. It

Table 12—Oxygen Requirements for Reformulated Gasoline

Basis	Federal RFG	California Phase 2 RFG
Per Gallon, mass %		
Min.	2.0	1.8 ^d
Max.	2.7 ^b Substantially Similar 4.0 ^c Ethanol	3.5
Average, mass %		
Min.	2.1	N/A
Cap for Average or Model ^a , mass %		
Min.	1.5	0 ^{d,e}
Max.	2.7 ^b Substantially Similar 4.0 ^c Ethanol	2.7

Notes:

^aApplies to federal “simple” and “complex” models and California Predictive Model.

^bWintertime oxygenated RFG program for carbon monoxide nonattainment areas maximum is 2.9 mass %.

^cDepends on relative density of base gasoline, actual maximum limit is 10 vol % ethanol. On notification of a state, the maximum limit can be set at 3.2 mass % if the higher level will interfere with attainment or maintenance of air quality standards. The 4.0 mass % is the upper oxygen limit where the “simple” and “complex” models are applicable.

^dFederal 2.0 mass % minimum limit takes precedence in federal RFG areas.

^eCalifornia 1.8 mass % minimum limit applies in wintertime only in specified areas.

should be noted that federal requirements take precedent over California requirements for designated federal ozone nonattainment areas.

4.2.3 Fuel and Fuel Additive Registration Regulations

4.2.3.1 Since 1975, under Section 211 (b) of the Clean Air Act, it has been unlawful to introduce into commerce any gasoline or diesel fuel and their respective additives unless they are registered with EPA. Any fuel or fuel additive, which was registered as of May 27, 1994, had to have a supplemental registration with additional data by November 27, 1994, in order to continue marketing the product. The registered products are then subject to a three-tier toxicological testing program. Tier 1 requires manufacturers to provide emissions characteristics, exposure analyses, and a literature search. If insufficient data exist, then manufacturers are required under Tier 2 to conduct a 90-day subchronic toxicity test on rodents with additional health effects testing for carcinogenicity/mutagenicity, teratogenicity, reproductive toxicity, and neurotoxicity. All Tier 1 requirements had to be submitted by May 27, 1997. Tier 2 requirements must be met by January 2004.



Documents

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Tier 3 testing may be required at EPA's discretion after reviewing the Tier 1 and Tier 2 submission. A fuel or fuel additive which has not been previously registered, but is compositionally similar to a registered material can be registered as a registrable fuel or fuel additive and marketed. A new fuel or additive, which was not registered as of May 27, 1994, will not be registered until all Tier 1 and Tier 2 information is available.

4.2.3.2 To develop the information, a consortium of about 150 companies was formed. API is the agent for contracting the testing for the consortium. The oxygenates to be tested are ethanol, TBA, MTBE, ETBE, TAME, and DIPE. None of the waived oxygenates containing methanol have undergone a supplemental registration. However, any of the previously registered waived gasoline-methanol-cosolvent blends can be used after a supplemental registration is made and the required additional information submitted. The Tier 1 and Tier 2 requirements still must be submitted by May 27, 1997.

4.3 LEADED GASOLINE

Although the EPA established mandatory compositional limits for unleaded fuel blends, it does not regulate the use of oxygenates in leaded gasolines. A considerable range of formulations of leaded gasolines may have existed at retail outlets. However, effective January 1, 1996, the Clean Air Act Amendments of 1990 banned the use of any fuel produced with the use of lead additives in motor vehicles operating on a street or highway.

4.4 PUMP LABELING

During the wintertime oxygenated gasoline period in carbon monoxide nonattainment areas, federal law requires dispensing pumps to be labeled, "The gasoline dispensed from this pump is oxygenated and will reduce carbon monoxide pollution from motor vehicles." In addition there are state laws concerning dispensing pump labeling of gasoline-oxygenate blends. The labeling laws are not uniform. At least 29 states require labeling of the presence and type of alcohol in the fuel at the pump as a consumer protection measure. An additional 13 states require labeling for alcohols or ethers. One state requires labeling for oxygen.¹² In an attempt toward uniformity, the National Conference on Weights and Measures has issued the "Uniform Regulation For Fuels, Petroleum Products, and Automotive Lubricants" which provides model wording for states to adopt (last amended in 1991). Because of the introduction of several ethers and their variable usage, a new model labeling regulation has been developed so dispensing pump labels would not have to be changed after each fuel delivery. The new regulation changes the labeling trigger from 1.0 percent by volume of alcohols or ethers to 1.5 percent by weight oxygen. Further, the predominant type of oxygenate would be labeled (e.g., "contains etha-

mol" or "with MTBE"). Where mixtures of ethers are present, the label would read "contains MTBE or other ethers."

4.5 NEAT AND NEAR-NEAT ALCOHOLS FUELS

There are no federal regulations controlling the use of alcohols as fuels where the alcohol is the primary constituent of the fuel. However, under the Energy Policy Act of 1992 (EPACT), methanol, denatured ethanol, and other alcohols cannot be defined as an alternative fuel unless the alcohol concentration is 85 percent by volume or more and it is blended with gasoline or other fuels. The Secretary of DOE can allow alcohol concentrations as low as 70 percent by volume to provide for cold starting, safety, or other vehicle functions.

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5 Alcohols and Ethers Blended with Gasoline

5.1 GENERAL

5.1.1 Oxygenates provide several significant engine performance benefits particularly for older, non-computer controlled cars when used as supplements to gasolines. Major incentives for their use are reduced exhaust emissions, improved octane ratings and extension of petroleum supplies. As discussed in Chapter 2, the presence of the oxygen atom in the alcohol or ether molecule imparts properties that are quite different from those of hydrocarbons. In turn, a gasoline-oxygenate blend may have physical and chemical characteristics that are very different from either the oxygenate or the base gasoline. Many blend properties are linearly proportional to the amount of each component and are predictable.

5.1.2 Other properties of gasoline-oxygenate blends must be determined empirically. Volatility characteristics of gasoline-alcohol blends can be especially anomalous to those of neat gasoline. In turn, vehicle response to volatility properties of gasoline-alcohol blends often is different from operation on neat gasoline. Because of the strong molecular polarity of MeOH, gasoline-MeOH blends had characteristics of volatility, water tolerance and materials compatibility, which were dissimilar to those of gasoline. In an effort to offset vehicle problems posed by MeOH, mixtures of cosolvents and corrosion inhibitors with MeOH were used commercially in gasoline blends during the 1980s.^{1,2,3} As indicated in Chapter 4, currently, no supplemental registration exists for a waiver to allow the use of MeOH in gasoline. As neat motor fuel, however, MeOH has distinct advantages for vehicles specifically tailored for its use. (Alcohols as neat or near-neat fuels are covered in Chapter 6.)

5.1.3 Besides oxygen content, other properties of blends that primarily affect vehicle operation are energy content, volatility and resistance to spark knock. Water tolerance characteristics also are of concern because of the effects of water on driveability should phase separation occur. Chemical compatibility of vehicle fuel system materials and blends is critical to vehicle durability.

5.2 HEATING VALUE EFFECTS

The heating value of oxygenates is less than that of gasoline. Except for MeOH, EtOH has the lowest energy content of all oxygenated hydrocarbons, one-third less than typical gasoline on a volumetric basis and 37 percent less on a mass basis. At the upper concentration of EtOH allowed by the EPA, the maximum heating value deficiency of a gasoline-EtOH blend, compared to gasoline, is 3.4 percent. Table 13 lists maximum decreases for individual oxygenates. Losses range from 2.0 percent for TAME to 3.4 percent for EtOH. Lower heating value of oxygenated blends is reflected in vehicle fuel economy, which will be discussed later in this chapter.

5.3 EFFECTS ON BLEND VOLATILITY

Volatility characteristics considered important to vehicle operation and emissions are distillation, vapor pressure, and vapor-liquid ratio (V/L). Alcohols have been found to influence volatility parameters of a gasoline blend to a greater degree than ether compounds.

5.3.1 Distillation

5.3.1.1 Oxygenates, except for GTBA, have constant boiling points ranging from 131°F for MTBE to 187°F for TAME. When blended with gasoline, which generally boils over a range of 80°F to 437°F temperature, oxygenates usually are located in the initial 50 percent evaporated fraction of the blend.

5.3.1.2 Adding alcohols to hydrocarbons or gasoline depresses the boiling temperature of individual hydrocarbons. The effect of alcohol addition on the shape of a distillation curve is shown in Figure 6.^{4,6} Addition of 10 volume percent significantly reduces T_{50} , the temperature for the first 50 percent of the fuel to evaporate. Alcohols depress the boiling point slightly less for aromatic hydrocarbons than for aliphatic hydrocarbons. Higher molecular alcohols such as GTBA have lesser effects on boiling point depression. Ethers, such as MTBE, have the same effect on distillation as the addition of a hydrocarbon of the same volatility. Fifteen volume percent MTBE significantly lowers the distillation temperature curve of gasoline between 15 percent and 50 percent evaporated.

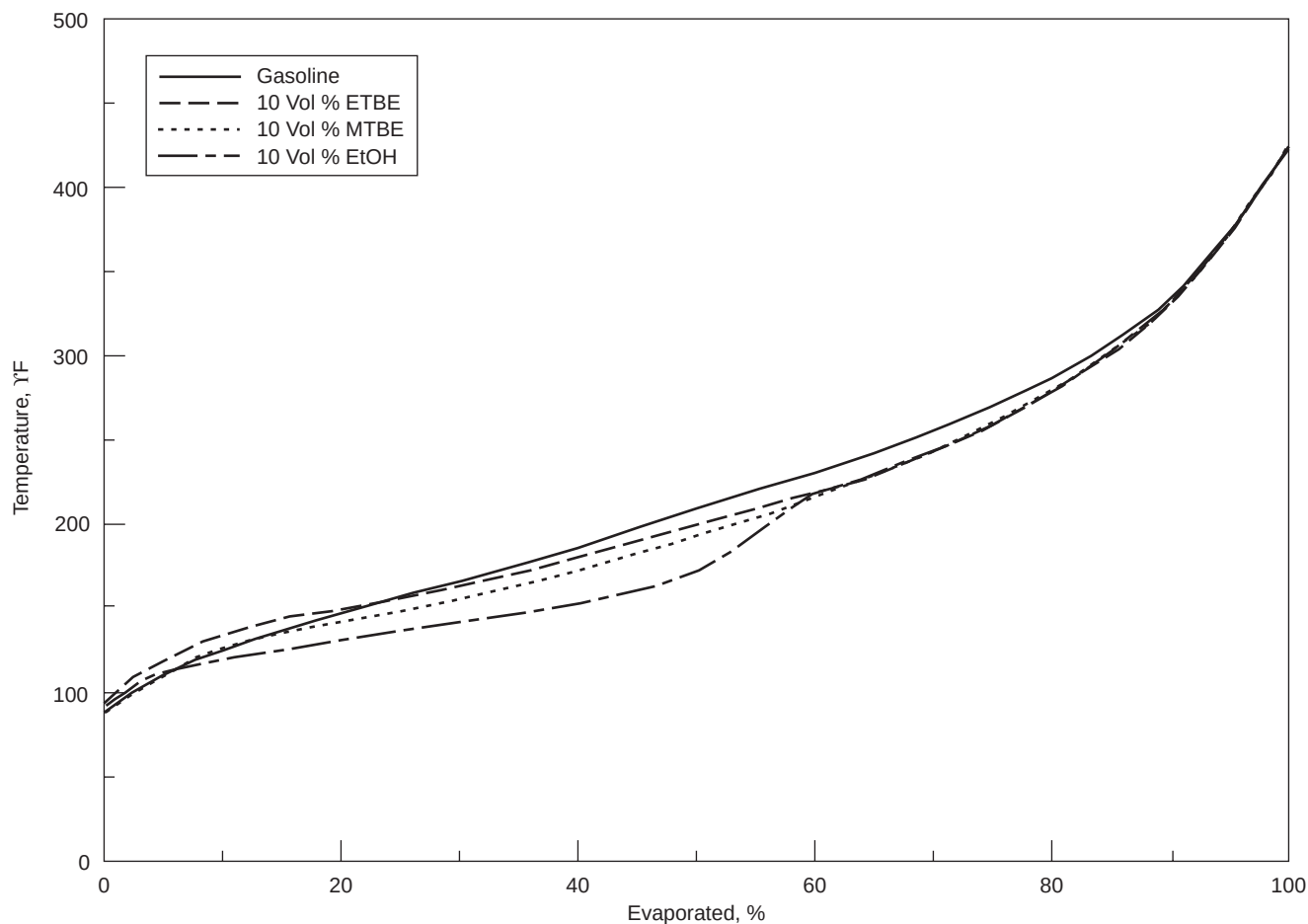
5.3.1.3 The depression of the mid section of a gasoline distillation curve caused by the addition of lower boiling point alcohols and ethers raised questions about the necessity for blends to match historical specifications for gasoline distillation characteristics and vapor pressure.^{4,5} Traditionally, specifications for volatility of automotive gasolines have been based upon technical evidence of vehicle requirements and environmental applications. Studies of volatility effects of gasoline-oxygenate blends on vehicle driveability will be covered later in this chapter.



Table 13—Heating Value of Gasoline-Oxygenate Blends

Oxygenate	Max Permitted Concentration ^a (gals/gal blend)	Lower Heating Value ^b		
		For max Conc. Oxygenate, Btu	Gasoline-Oxygenate Blend (Btu/gal @ 60°F)	% Decrease
None	—	0	114,500 ^c	0
Methanol	0.003	170	114,330	0.1
Ethanol	0.100	7,600	110,650	3.4
IPA	0.096 ^b	8,390	111,900	2.3
TBA	0.157 ^b	14,770	111,300	2.8
MTBE	0.149 ^b	13,930	111,370	2.7
TAME	0.166 ^b	16,700	112,190	2.0
ETBE	0.173 ^b	16,780	111,470	2.6
DIPE	0.177 ^b	17,700	111,930	2.2

Notes:

^aSee Chapter 4 for oxygenate concentrations permitted by EPA.^bConcentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.^cFor average non-oxygenated gasoline with 0.748 relative density @60°F.

Source: Reference 4.6

Figure 6—Effect of Oxygenates on Distillation

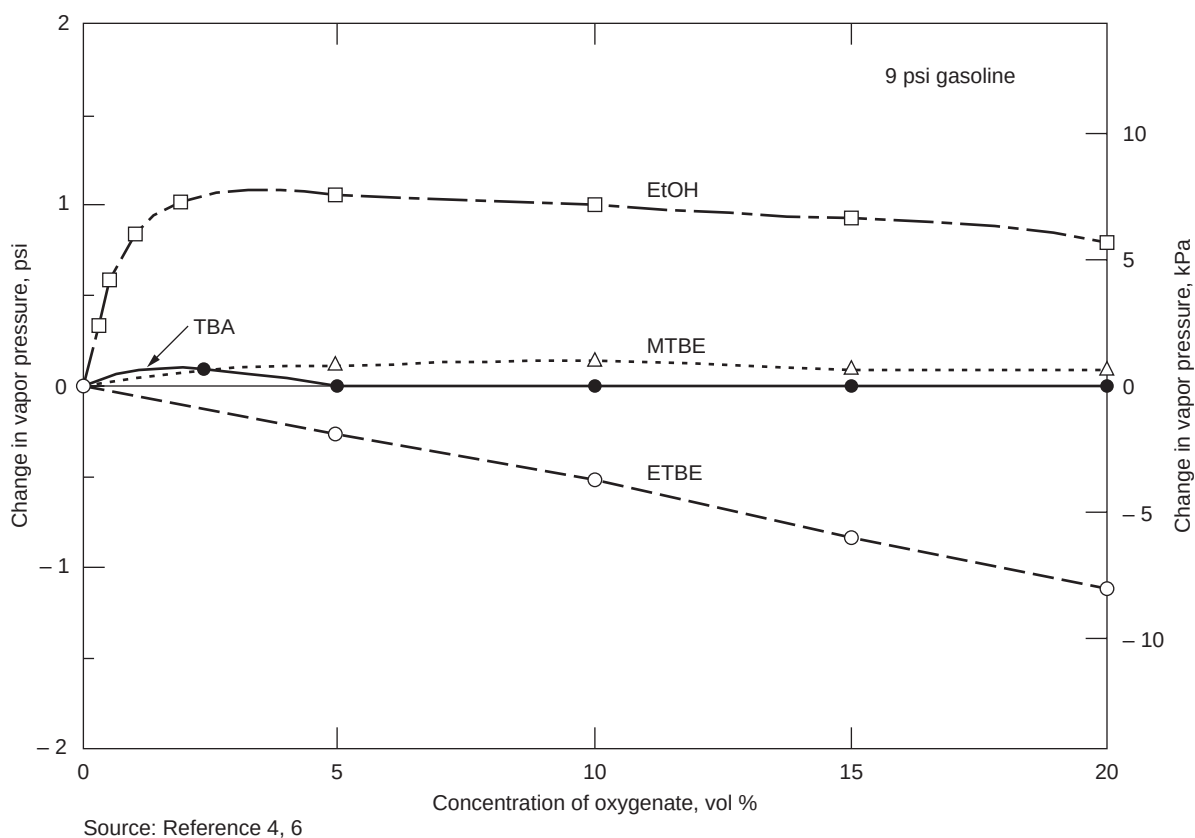


Figure 7—Effect of Oxygenates on Vapor Pressure

5.3.2 Vapor Pressure

5.3.2.1 Vapor pressure is another important volatility parameter of gasoline affected by addition of oxygenates, particularly alcohols. Aliphatic ethers have blending characteristics similar to hydrocarbons and change blend vapor pressure in linear relationship with the vapor pressure of the ether and its concentration. Ethers affect gasoline blend vapor pressure much the same as hydrocarbons of equivalent vapor pressure.^{4,6} Figure 7 shows that MTBE, with a vapor pressure of 8 psi, changed the vapor pressure of 9 psi base gasoline very slightly. ETBE, with 4 psi vapor pressure, reduced the vapor pressure from that of the base gasoline in linear fashion, similar to the effect of a hydrocarbon component.

5.3.2.2 Alcohols, in contrast to ethers, always increase hydrocarbon blend vapor pressure, although not in proportion to alcohol vapor pressure or concentration. The physical phenomenon of molecular polarity is responsible for this behavior. Polar molecules have affinity for other molecules in proportion to the degree of mutual polarity. At room temperature, low molecular weight substances such as water or light alcohol such as MeOH, would be gases were they not

collapsed into liquids by the highly cohesive molecular forces of hydrogen bonding. However, when MeOH is dissolved in a non-polar solvent like gasoline, its molecules become physically separated. The physical separation weakens molecular cohesion, and MeOH behaves like a gas. The release of alcohol molecules as gas causes an anomalous increase in vapor pressure that peaks at quite low concentrations of MeOH. The gaseous molecular release of EtOH from gasoline is much less pronounced, and is insignificant for higher carbon number alcohols.

5.3.2.3 As listed in Table 14, the vapor pressures of EtOH, IPA and GTBA, 2.3 to 1.8 psi, are much lower than that of gasoline, seven to 15 psi. As explained above, low molecular weight alcohol in gasoline forms a nonideal solution that does not follow linear blending relationships and causes increased blend vapor pressure. Figure 7 illustrates that, in 9 psi gasoline, 2 percent EtOH with 2.3 psi vapor pressure, increased blend vapor pressure about 1.0 psi. Additional amounts of EtOH did not further increase vapor pressure. Considering the phenomenon of molecular polarity, the plateau shape of the curve suggests that EtOH vapors exist in disproportion to alcohol concentration of the blend. Therefore, the effect of EtOH is greater in gasolines with lower vapor pressure.

Table 14—Vapor Pressure Blending Values of Oxygenates

Oxygenate	Vapor Pressure, psi	Concentration Permitted, ^b Volume %	Blending Value Vapor Pressure, psi	Maximum Vapor Pressure Change, ^d psi
MeOH	4.6	0.3	40	—
EtOH	2.3	10.0	18	+0.9
IPA	1.8	9.6 ^c	14	+0.5
GTBA	1.8	15.7 ^c	9	0.0
MTBE	7.8	14.9 ^c	8	−0.2
TAME	1.5	16.6 ^c	2	−1.2
ETBE	4.0	17.3 ^c	4	−0.9
DIPE	4.9	17.7 ^c	0.7	−1.5
Gasoline ^a	7 – 15		7 – 15	

Notes:

^aGasoline without oxygenate.^bSee Chapter 4 for oxygenate concentrations permitted by EPA.^cConcentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.^dChange for a 9.0 psi vapor pressure gasoline without oxygenate.

5.3.2.4 Figure 8 shows that the vapor pressure effect of EtOH is less in gasolines of higher vapor pressure.⁶ The explanation for this result is that the partial pressure fraction generated by the alcohol mole fraction is constant for a given temperature, regardless of how much partial pressure is contributed by the gasoline. To compensate for the vapor pressure contribution of alcohol addition, gasoline-alcohol blends require special tailoring of the hydrocarbon content.

5.3.2.5 Table 14 compares blending values for vapor pressure of oxygenates that can be used for calculations of the vapor pressure for gasoline-oxygenate blends containing oxygenate near the maximum permitted concentration. EtOH has a blending value of 18 psi, approximately eight times that of its neat state. The vapor pressure of a gasoline-EtOH blend can be adjusted by removal of all of the butanes and reducing the pentanes. However, this action would produce a distillation curve with a prominent flat segment that could adversely affect vehicle driveability characteristics during cold start and drive away. Because of the impracticality of hydrocarbon adjustment of the vapor pressure of gasoline-alcohol blends containing 9 – 10 volume percent EtOH, the U.S. EPA issued Phase II volatility regulations for conventional gasoline in 1992 which permitted gasoline-EtOH blends to exceed ASTM specifications for vapor pressure by 1.0 psi during the summer. Gasoline-alcohol blends containing IPA and/or

GTBA, with blending values of 14 and 9 psi, are not allowed the exemption of 1.0 psi that was granted gasoline-EtOH blends. For these blends, vapor pressure must be adjusted by means of hydrocarbon compounding.

5.3.2.6 When gasoline-alcohol blends are commingled with gasoline, as they might be in routine product handling or refueling, the effects of alcohol in the blend are the same as those described. Figure 9 shows that a mix of a gasoline-EtOH blend with gasoline of the same vapor pressure, in this case 9 psi, resulted in significantly increased vapor pressure.⁷ The vapor pressure peaked to 9.8 psi for a mixture containing 20 percent gasoline-EtOH blend and 80 percent gasoline. The increase of 0.8 psi was about the anticipated amount from an addition of 2 percent EtOH (20 percent of 10 percent = 2 percent).

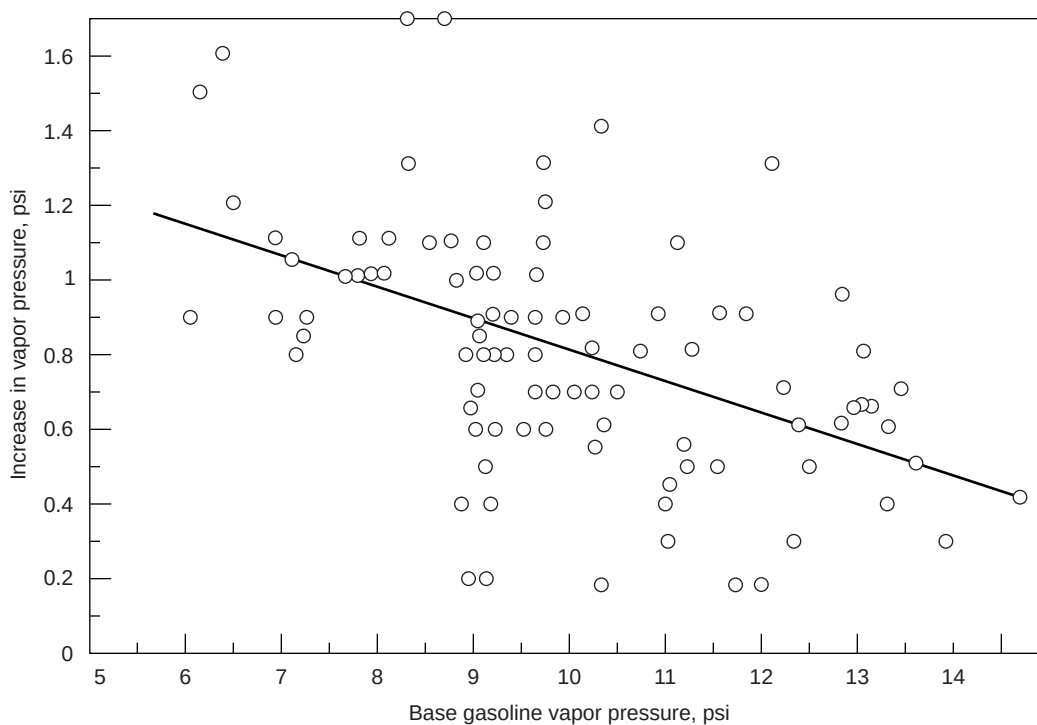
5.3.2.7 Measurement of vapor pressure of gasoline-alcohol blends requires techniques that eliminate the possibility of water contamination during heating because of the alcohol's affinity for water. New ASTM procedures^{8,9,10} have been developed for use with oxygenated blends and replaces the time-honored Reid Vapor Pressure test.

5.3.3 Vapor to Liquid Ratio

5.3.3.1 At elevated operating temperatures, highly volatile fuel can cause vehicle vapor lock and increased evaporative emissions. Vehicle vapor lock is caused by excessive vapor that displaces liquid in the fuel system and results in fuel starvation and power loss. A gasoline volatility parameter, Vapor-Liquid Ratio or V/L , is a useful predictor of gasoline performance in a fuel system at high temperature. The temperature for a specific V/L either can be measured or calculated for gasoline by using a combination of distillation values and vapor pressure. Automotive engineering experience has determined that a $V/L=20$ correlates best with vapor lock protection with most cars. Temperatures for $V/L=20$ for various geographical areas and seasons are specified by ASTM and SAE.^{11,12}

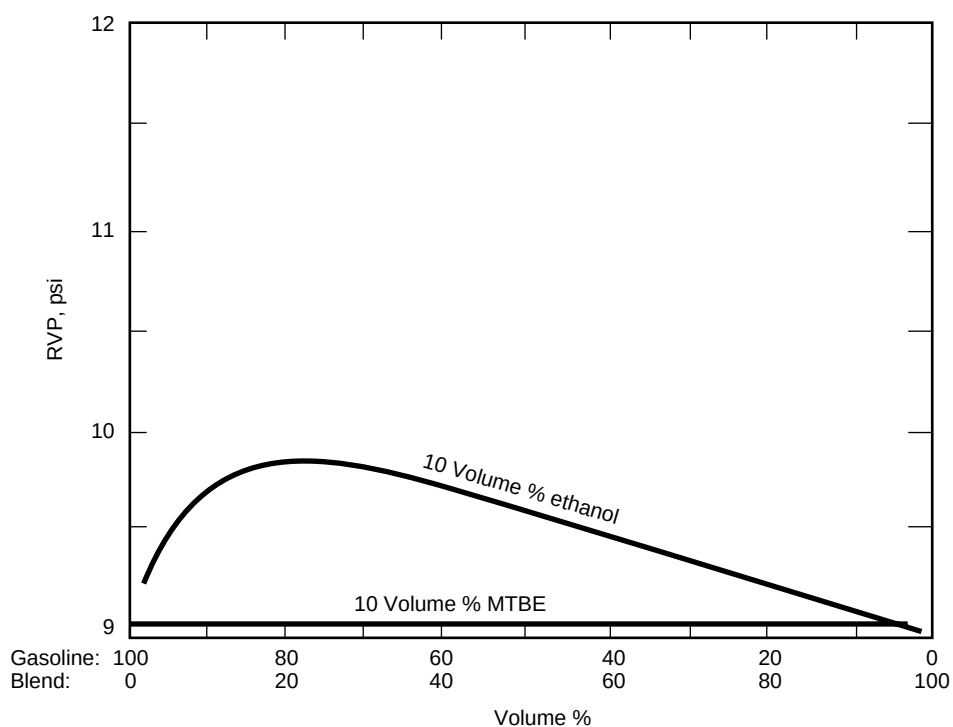
5.3.3.2 [ASTM D 4814](#), Standard Specification for Automotive Spark-Ignition Engine Fuel, includes volatility requirements for gasolines according to geographical areas of the U.S. and seasonal periods. The schedule applies specifications for both volatility, in terms of vapor pressure and distillation, as well as for temperature for $V/L=20$. [ASTM D 4814](#) specifications apply to all conventional gasolines and gasoline-oxygenate blends.¹¹ Because EtOH is splash blended, volatility requirements may not always apply. Specifications for federal and California reformulated gasolines are not included in [ASTM D 4814](#).

5.3.3.3 Calculations of temperatures for specific V/L of gasoline-alcohol blends using ASTM procedures do not predict measured values. Figure 10 shows that the correlation of calculated versus measured temperatures for a $V/L=20$ for gasoline



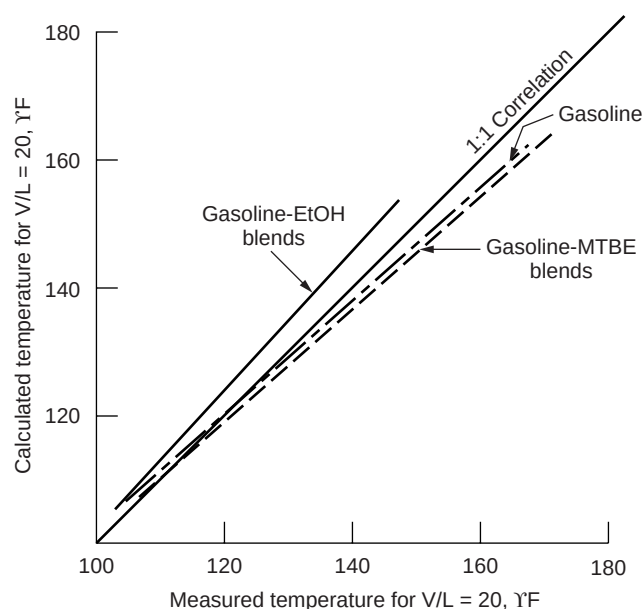
Source: Reference 6

Figure 8—Effect of EtOH Addition on Vapor Pressure of Base Gasoline



Source: Reference 7

Figure 9—Effect of Commingling a Gasoline and a Gasoline-EtOH Blend of the Same RVP



Source: Reference 13, 14

Figure 10—Calculated Versus Measured Temperature for $V/L = 20$

and for gasoline with MTBE are quite good.^{13,14} The equations predicted slightly lower temperature values for gasoline-MTBE blends, and higher than measured temperature values for gasoline-EtOH blends. Obviously a higher than measured temperature predicts better vapor lock protection than can be delivered. ASTM recommends against calculations to determine temperature for V/L for all gasoline-oxygenate blends.

5.3.3.4 Figure 11 shows how the addition of butane and alcohols changed the temperatures at which various V/L s occurred.¹⁵ Higher temperatures for a given V/L indicate better vehicle fuel handling at high temperature. For example, the reference gasoline reached a $V/L=20$, $T_{V/L=20}$, at a temperature of 160°F. Adding five-volume percent butane to the reference gasoline reduced the $T_{V/L=20}$ to 138°F, which, coincidentally, is the same temperature produced by the addition of 10 volume percent EtOH. The SAE and ASTM specification for $T_{V/L=20}$ for the highest temperature service in the United States is 140°F.

5.4 LABORATORY OCTANE EFFECTS

5.4.1 Oxygenates are attractive as gasoline blending components to increase antiknock performance or octane quality. Adding small percentages of oxygenates to gasoline can produce large gains in laboratory octane ratings. Each volume percent of an oxygenate added to a typical unleaded gasoline, with 87 (R + M)/2 octane, increases blend octane between 0.1 and 0.3 numbers. In higher-octane gasoline, incremental

octane gains are less. Blending octane values, expressed as (R + M)/2, of oxygenates are shown in Table 15.

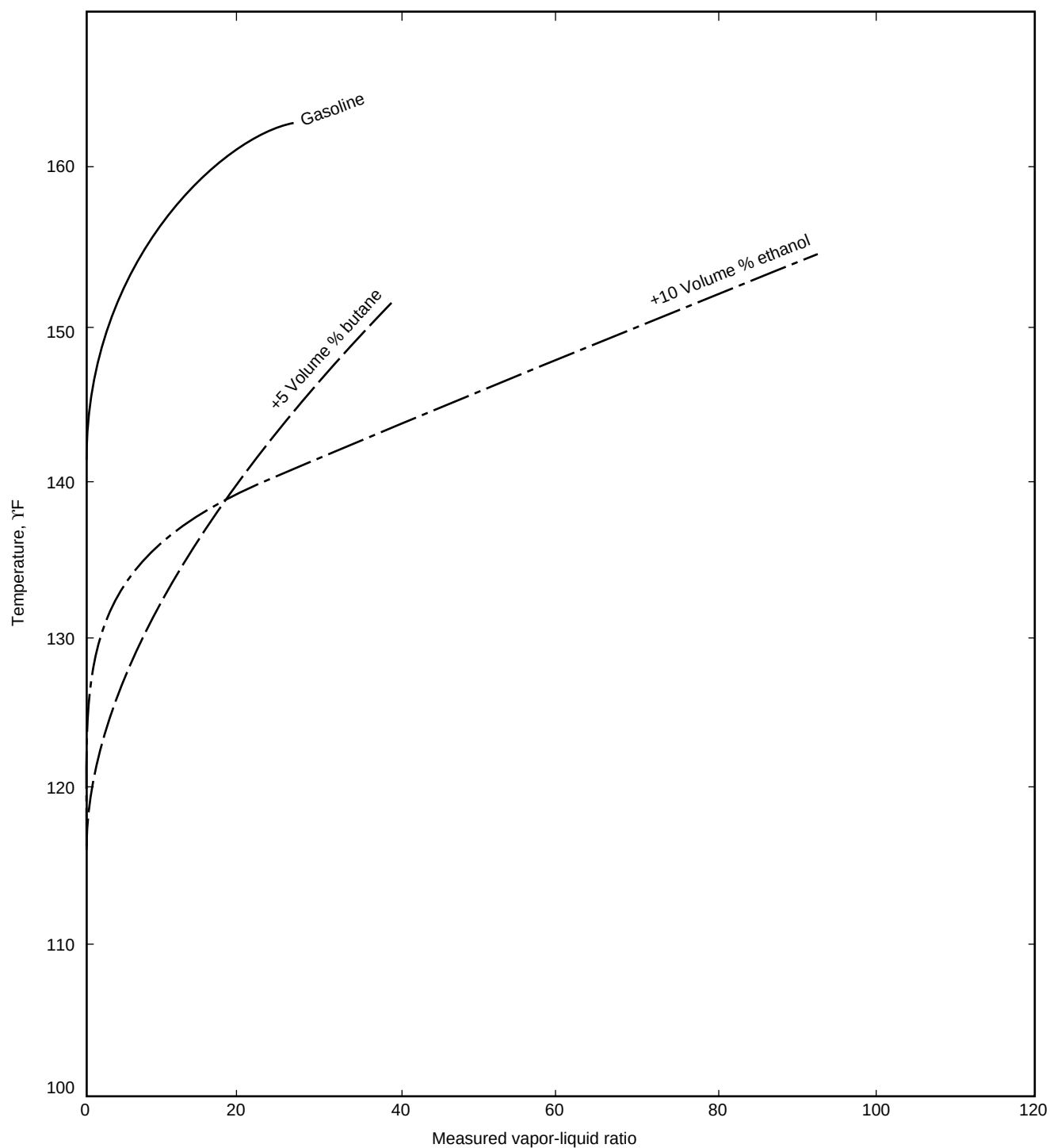
5.4.2 Of these oxygenates, MeOH has the highest octane blending value, 119 (R + M)/2, but, as discussed previously, is not currently used in blends. EtOH also offers superior blending octane value. At its permitted limit, it provides a boost of almost three numbers. Higher molecular weight alcohols have lower blending values but, nevertheless, are very attractive as octane improvers. Antiknock performance improvement from alcohol results mainly from charge cooling within the engine. The high latent heat of vaporization of alcohol reduces charge temperature well into the process of combustion and promotes cooling of the end gas.¹⁶ A gasoline-alcohol blend with 10 volume percent EtOH has about 20 percent greater latent heat of vaporization than gasoline producing the same net combustion energy. As discussed later, however, charge cooling benefits of gasoline-alcohol blends have not been found to importantly reduce vehicle exhaust emissions of NO_x .

5.4.3 Laboratory octane improvement from ethers at maximum allowable concentration is typically three or more octane numbers. The superior antiknock performance of ethers results from combustion characteristics rather than vaporization differences. Vaporization properties of ethers are similar to those of hydrocarbons and do not appear to be responsible for antiknock benefits.

5.5 WATER SENSITIVITY AND TOLERANCE

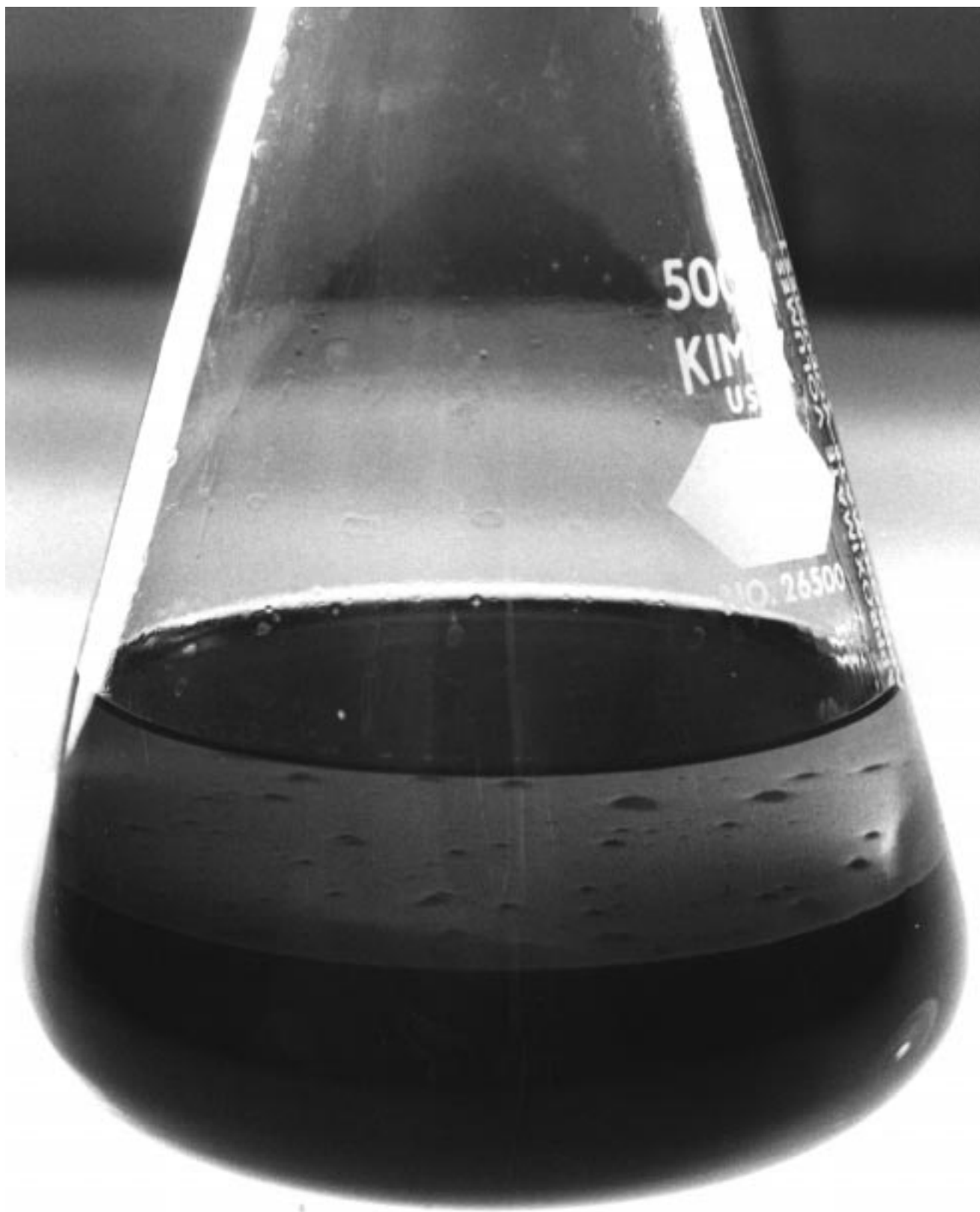
5.5.1 The solubility characteristics of alcohol in gasoline depend upon the relative influence of the hydrocarbon and the hydroxyl group of the molecule. The hydroxyl groups attached to short hydrocarbon chains, such as MeOH and EtOH, exerts more affinity for water and less for a hydrocarbon. Alcohols with longer hydrocarbon chains are more soluble in gasoline. When small amounts of water are present in a gasoline-EtOH blend, hydrogen bonds form between water and EtOH molecules and result in the separation of the water-alcohol phase from the gasoline. Higher order alcohols, such as IPA and GTBA, are more soluble in gasoline than EtOH and have less problems with water separation. Ethers also have little affinity for water and do not separate.

5.5.2 Figure 12 is a photograph showing phase separation.¹⁷ Paraffinic hydrocarbons predominate in the upper phase, while the lower phase consists primarily of alcohol, water, and small amounts of aromatic hydrocarbons.¹⁸ Because alcohol is less soluble in gasoline at low temperature, phase separation tendency increases as temperature decreases, as shown in Figure 13. For 10 volume percent EtOH in a blend with a gasoline containing 25 volume percent aromatics, phase separation began at 70°F with the presence of 0.7 volume percent water. At -20°F, phase separation occurred with about 0.4 volume percent water in the blend. A gasoline with a lower aromatic



Source: Reference 15

Figure 11—Effect of EtOH and Butane on Vapor-Liquid Ratio



Source: Reference 17

Figure 12—Photograph of Gasoline-Alcohol Phase Separation



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Table 15—Octane Boost with Selected Oxygenates

Oxygenate	Concentration Permitted ^a (Volume Percent)	Typical Blending Value ^b (R + M)/2	Boost at Concentration Permitted ^c (R + M)/2
Methanol	0.3	119	0.1
Ethanol	10.0	115	2.8
IPA	9.6 ^d	106	1.8
TBA	15.7 ^d	97	1.6
MTBE	14.9 ^d	110	3.4
TAME	16.6 ^d	105	3.0
ETBE	17.3 ^d	111	4.2
DIPE	17.7 ^d	107	3.5

Notes:

^aSee Chapter 4 for oxygenate concentrations permitted by EPA.^bOctane blending values vary with oxygenate concentration, base fuel octane, and composition. See Glossary, Appendix A, Blending Value.^cOctane boost is calculated for 87 octane (R + M)/2 unleaded gasoline.^dConcentrations vary with density of the base fuel. This value was calculated for gasoline with 0.748 relative density at 60/60°F.

content exhibited lower water tolerance. Once separation begins, additional water will add to the water phase.

5.6 VOLUME EXPANSION OF GASOLINE-ETOH BLENDS

A small volume expansion occurs when EtOH is added to gasoline. At 10 volume percent EtOH, about a 0.1 percent increase in volume was measured in a blend with gasoline of 0.794 relative gravity. The expansion effect increased at higher EtOH concentrations, peaking at about 20 volume percent EtOH.¹⁵ Another study reported as much as 0.6 percent increase due to 12.5 volume percent EtOH.¹⁹ The expansion effect is greatest in gasolines of high density. In this document, no attempt has been made to adjust any values or results for possible expansion effects of EtOH in blends.

5.7 VEHICLE PERFORMANCE OF GASOLINE-OXYGENATE BLENDS

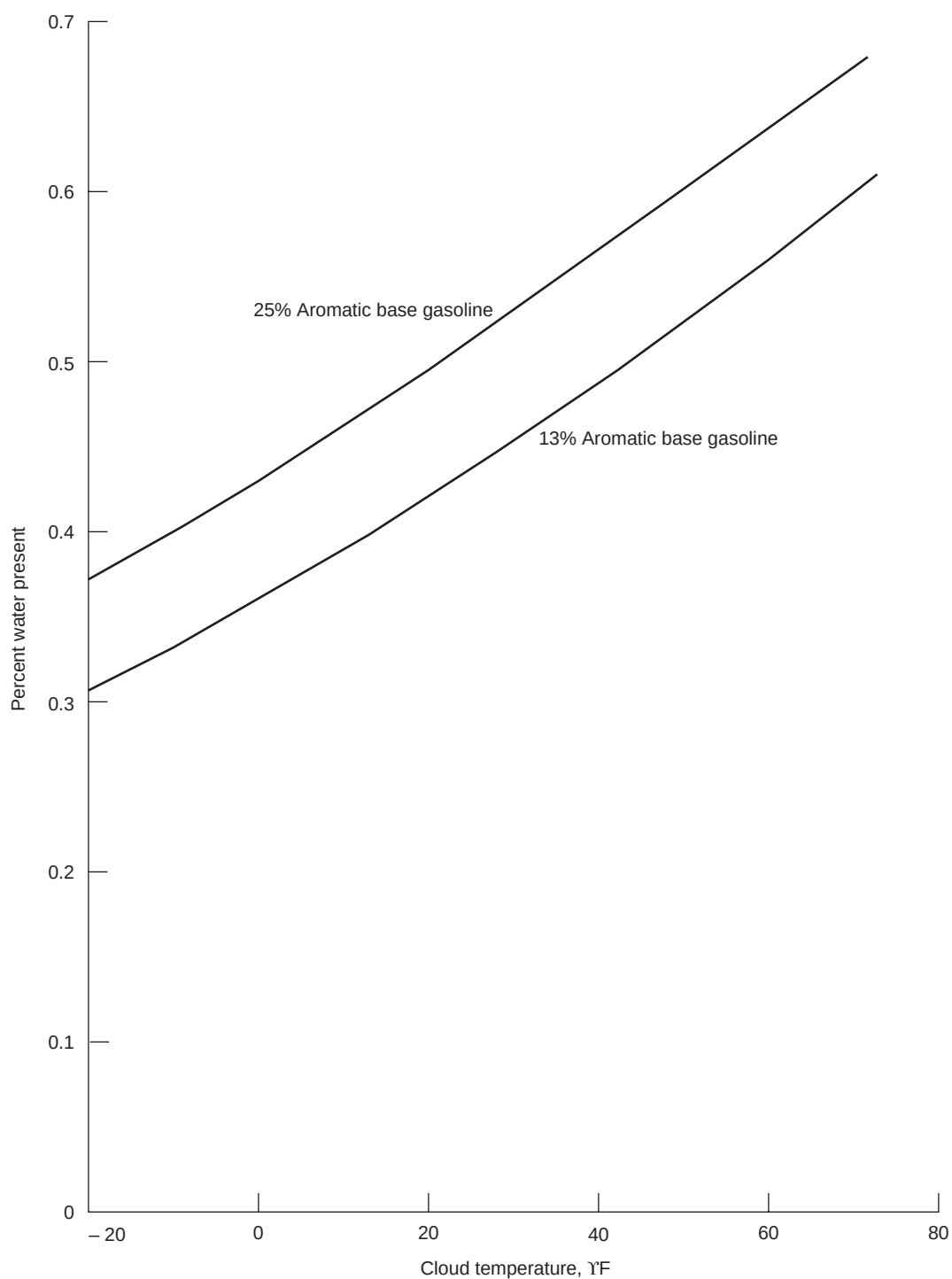
5.7.1 Acceptance of oxygenated gasolines was hindered in the 1980s by the wide variety of vehicle technology in use that had been designed to operate on gasoline. Since the 1960s, vehicle technology had been pursued as the key to eliminate automotive air pollution. During the 1970s and 1980s, in its effort to reduce national fuel consumption, the U.S. government mandated the auto industry to increase vehicle fuel economy and encouraged gasoline suppliers to use alcohol as a gasoline extender. Concurrently, Federal and California timetables for reduced vehicle emissions

pressured the auto industry to expedite new technology to the marketplace. Many vehicles that were engineered to run on gasoline simply were not suitable for operation on gasolines blended with alcohol.

5.7.2 Gasoline blends containing either MeOH or EtOH were found to have caused swelling of certain fuel system elastomers.^{20,21,22,23} Phase separation problems with gasoline-ethanol blends were reported to have caused corrosion of vehicle fuel tanks and supply lines.^{20,24} Engines of older vehicles without computer controls encountered fuel mixture enrichment with gasoline-oxygenate blends, and often had problems of misfiring, surging and stalling. As late as 1987, most auto manufacturers remained cautious about possible side effects of oxygenated gasolines on driveability and fuel system durability. Nine of ten auto manufacturers surveyed by EPA in 1987 cautioned new car customers that, if driveability problems occurred with the use of gasoline containing 10 percent EtOH, gasoline should be used.²⁵ The tenth manufacturer specifically recommended against the use of any oxygenated gasoline.

5.8 VEHICLE TECHNOLOGY FACTORS

5.8.1 Table 16 summarizes the variety of vehicle emission control devices generally found on vehicles of several model years. Closed crankcase ventilation, initiated in 1960 models and employed currently to control emissions of blow-by gases, ranks as the most cost-effective control for hydrocarbon emissions. Control of evaporative hydrocarbon emis-



Source: Reference 18

Figure 13—Water Tolerance of Gasoline—10% EtOH Blend



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