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Ethanol Fuel Modification for Highway Vehicle Use Final Report

Prepared for

U. S. Department of Energy
Assistant Secretary for
Conservation and Solar Applications
Office of Transportation Programs
Washington, D. C. 20545

July 1979
Printed January 1980

DOE
Alcohol
Fuels
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Alternative
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Ethanol Fuel Modification for Highway Vehicle Use Final Report

Prepared by
Union Oil Company of California
Science and Technology Division
Brea, CA 92621

for

U. S. Department of Energy
Assistant Secretary for
Conservation and Solar Applications
Office of Transportation Programs
Washington, DC 20545
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FORWARD

In order to commercialize any alternative fuel that might replace or extend the supply of petroleum, it is essential to achieve an extremely high degree of reliability. This requires solutions to many real and potential problems. Problems in use of alcohol fuels may be addressed by modifying the fuel composition, the mechanical system or a combination thereof. The work reported here deals with the former and addresses ethanol fuels. An earlier document, "Methanol Fuel Modification for Highway Vehicle Use", report number HCP/W3683-18, July 1978, covered methanol and is available from the National Technical Information Service (printed: \$14.00; microfiche: \$3.00).

The Department of Energy is pleased to have this highly professional addition to alcohol fuel application knowledge as reported by G. M. Nakaguchi, J. L. Keller and E. L. Wiseman.

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Alternative Fuels Utilization Branch
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ABSTRACT

A number of problems that might occur if ethanol were used as a blending stock or replacement for gasoline in present cars are identified and characterized as to the probability of occurrence. The severity of their consequences is contrasted to those found with methanol in a previous contract study. Possibilities for correcting several problems are reported. Some problems are responsive to fuel modifications but others require or are better dealt with by modification of vehicles and the bulk fuel distribution system. In general, problems with ethanol in blends with gasoline were found to be less severe than those with methanol. Phase separation on exposure to water appears to be the major problem with ethanol/gasoline blends. Another potentially serious problem with blends is the illicit recovery of ethanol for beverage usage, or bootlegging, which might be discouraged by the use of select denaturants. Ethanol blends have somewhat greater tendency to vapor lock than base gasoline but less than methanol blends. Gasoline engines would require modification to operate on fuels consisting mostly of ethanol. If such modifications were made, cold starting would still be a major problem, more difficult with ethanol than methanol. Startability can be provided by adding gasoline or light hydrocarbons. Addition of gasoline also reduces the explosibility of ethanol vapor and furthermore acts as denaturant.

ETHANOL FUEL MODIFICATION FOR
HIGHWAY VEHICLE USE

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LIST OF ACRONYMS AND ABBREVIATIONS USED

(Bibliographic reference abbreviations are provided at the beginning of the bibliography.)

ADA	air distillation apparatus (adiabatic, equilibrium)
A/F	air/fuel ratio
AISI	American Institute of Steel and Iron
ASTM	American Society for Testing and Materials
BMON	Blending Motor Octane Number
BRON	Blending Research Octane Number
BRdON	Blending Road Octane Number
BATF	Bureau of Alcohol, Tobacco and Firearms
C	Centigrade
C ₄	butane
CDA-19	completely denatured formula 19 alcohol
cm ²	square centimeter
CRC	Coordinating Research Council, Inc.
DOE	U.S. Department of Energy
EP	end point
EtOH	ethanol
FIA	fluorescent indicator adsorption
gal	gallon
g/cm ³	gram per cubic centimeter
g/l	gram per liter

g/min	gram per minute
IBP	initial boiling point.
KJ/dm ³	kilojoule per cubic decimeter
kJ/kg	kilojoule per kilogram
km	kilometer
kmph, km/hr	kilometer per hour
kPa	kilopascal
l	liter
MeOH	methanol
meq	milliequivalents
mg/cm ²	milligram per square centimeter
mg/l	milligram per liter
ml	milliliter
mm	millimeter
mm/yr	millimeter per year
MON	Motor Octane Number
RVP	Reid Vapor Pressure
RON	Research Octane Number
(R+M)/2	Research Octane Number plus Motor Octane Number divided by two
sec	second
SAE	Society of Automotive Engineers
SWAFCA	Southwest Alabama Farmers' Cooperative Association
SD-28A	Specially denatured formula 28-A alcohol
Std. Carb.	standard carburetor

T	temperature
TWD	Total weighted demerits (driveability rating)
V/L	vapor/liquid ratio
vol %, V %	volume percent
wt	weight
wt %, W %	weight percent
WOT	wide-open-throttle

EXECUTIVE SUMMARY

Background of Study

A study of potential problems with methanol as an automotive fuel and possible corrective fuel modifications was carried out by Union Oil for the Department of Energy and completed in early 1978. Methanol was of prime concern because earlier studies had shown it, along with liquid hydrocarbons made from oil shale or coal, to provide the most promising alternatives for highway vehicle fuel when petroleum runs short. Some observations on ethanol were also included because of known interest in the use of ethanol derived from farm products. The interest intensified rapidly, developments during 1978 including marketing of ethanol/gasoline blends on a small but commercial scale, passage of federal legislation to provide a tax advantage of 40 cents per gallon for agricultural alcohol blended at 10% concentration in gasoline, and allowance by the Environmental Protection Agency of a waiver for such blends of ethanol, known as gasohol, from prohibitions of the Clean Air Act against new fuels and additives. The Department of Energy requested Union Oil, upon completion of the methanol study, to conduct an extension of that work as applied to ethanol. Effort was to be concentrated on the technical problems attendant upon commercial distribution and utilization of ethanol, and solutions to them, as distinguished from manufacturing processes and economics.

Objectives

Although ethanol differs from gasoline less than methanol in properties relevant to its use as a fuel, a variety of problems could be expected if it were suddenly to be distributed in the present commercial fuel distribution system and used in present cars designed for gasoline. As with methanol, some problems can no doubt best be remedied by modification of engines and other equipment, and others by modifying the fuel. The objectives are essentially threefold:

1. Identify and characterize known and potential problems that might be encountered if ethanol were widely used as a fuel in the United States, either straight or blended with gasoline.
2. Evaluate possible remedies obtainable by means of fuel modification, and point out problem areas in which it appears that equipment modification would be more efficacious than fuel modification.
3. Recommend areas for investigation where further study and performance testing are needed.

Types of Ethanol-Containing Fuel

Most proposals for the use of ethanol as automotive fuel in the United States depend upon blends with unleaded gasoline, especially ones containing 10 vol % ethanol. Present federal and state tax benefits apply to blends of at least 10% ethanol, with the maximum benefit at 10%, while the EPA waiver for gasoline limits the use to 10% maximum. However, some legislative proposals call for much lower but gradually increasing concentrations, and in Brazil the objective is nation-wide

use of 16.7% blends (i.e., 20 parts ethanol to 100 parts gasoline). There is also some interest in blends containing both ethanol and methanol. Accordingly the present study covers blends of from 5 to about 20 vol % ethanol and some blends of ethanol/methanol mixtures.

At the other extreme, pure ethanol, 95% ethanol, and ethanol enriched with light hydrocarbons can all be used in vehicles with gasoline engines modified for the purpose. A growing number of vehicles, about 1000 at this writing, are said to be operating on 94-95% ethanol in Brazil. Some work has therefore been devoted to straight ethanol fuels, even though they are of less interest than blends in the United States. However the use of ethanol in diesel has been excluded, even though it is being pursued experimentally in Europe and Brazil, because the applications appear to depend primarily on engine modifications.

Problem Definition

Thirty-six potential problems are listed in Table 2 in the six areas of distribution and handling, compatibility with materials, vehicle performance, environmental effects, toxicity and safety precautions, and economic factors. The list is mostly similar to the corresponding list of potential problems with methanol fuels compiled previously. A unique problem with ethanol fuels, at least in the United States, involves possible renaturing or illicit recovery of potable alcohol (bootlegging); associated with this are the possible deleterious effects of denaturants. Eighteen potential problems from Table 2 were

selected for study to better define them and, where appropriate, to evaluate possible remedies. Others were excluded from further study in this project for various reasons: some because they are being studied elsewhere, some because they were held to be outside the scope of the present contract, and some because they were considered to be of lower priority or else not responsive to fuel modifications that might be evaluated.

Problems vs Remedies

As with methanol, most of the non-economic problems identified can be attributed to fundamental differences between ethanol and gasoline in physical and chemical characteristics such as heat of vaporization, heat of combustion, combustion stoichiometry, boiling range, solvent characteristics, etc. The methods available for changing these properties to correct problems are (1) to convert ethanol to other compounds with more favorable properties, and (2) to modify fuel composition by adding or removing other components. The principal examples of the first are the same as with methanol: conversion to hydrocarbons, ethers or higher alcohols. Conversion of ethanol to gasoline-range hydrocarbons by the Mobil process is assumed to solve technical problems in utilization of the alcohol, but would have no advantage over conversion of methanol, a lower cost feedstock. Ethanol can, like methanol, add to tertiary olefins to give tertiary alkyl ethers, but there are several negative factors: (1) as for methanol, the supply of proper olefins is limited,

(2) ethanol is a more costly reactant than methanol, and (3) ethyl tertiary alkyl ethers, unlike their methyl counterparts, contain alpha hydrogen atoms that are susceptible to peroxidation. The conversion of ethanol partially to higher alcohols or, more strictly, the production from coal-based synthesis gas of mixed alcohols consisting mostly of ethanol and higher alcohols, is an attractive possibility; recent catalyst developments suggest that it may be more feasible than previously thought. As with methanol again, the second route of modifying fuel composition by addition or removal of other components offers many options. Among them are the use of additives, change in gasoline composition, and inclusion of cosolvents.

Problems with Straight Ethanol

Lack of driveability is without question the most serious technical problem with straight ethanol in unmodified gasoline engines; conversion of the alcohol to hydrocarbons is the only fuel modification known to be effective. Engine modifications to give the correct air/fuel ratio and uniform cylinder-to-cylinder distribution can provide driveability with straight ethanol; other problems are therefore evaluated as if engines had been so modified. Cold starting is more difficult with ethanol than with methanol, the pure alcohol requiring even higher temperatures. The addition of light hydrocarbons or gasoline improves startability, though more is required than with methanol; 10% pentane was effective at -10°C and 20% gasoline at 3°C in a bench simulation test. Brazil does not permit such additives, and cold starting must be provided there by engine modification.

Explosibility of the saturated vapor at common temperatures is a hazard with ethanol as with methanol; the addition of hydrocarbons for cold starting corrects this by making the vapor too rich to ignite. Ethanol burns with a somewhat luminous flame so that it would not present the same difficulty for fire-fighting that the near-invisible flame of methanol does. Compared to methanol, ethanol is far less toxic to humans or other mammals. It appears, however, to be more toxic to much marine life.

Problems with Straight and Blended Ethanol

The likelihood of bootlegging efforts, i.e., the recovery and diversion of ethanol to beverage use without paying the federal tax of \$5.55 per liter (at 200 proof), is a threat to tax collections with either straight or blended ethanol. Some authorized denaturants are undesirable as fuel components, and it has been shown that recovery of tolerably potable alcohol from gasoline blends containing otherwise suitable denaturants is not difficult. Some possibly improved denaturants for fuel alcohol are suggested.

It is common experience, when vehicles and service station tanks are first changed from gasoline to ethanol blends, for fuel filters to become plugged with sediment apparently removed from tank and pipeline surfaces by cleaning action of the new fuel. The fuel filters in this situation have not failed, but served their intended function of protecting the engine. Laboratory tests confirmed the dirt-loosening ability of both ethanol

blends and straight ethanol. The storage stability of gasoline was not reduced by blending with ethanol, and ethanol-rich fuels were quite storage-stable.

Ethanol-containing fuels can damage automotive paints and some non-metallic fuel system materials that are satisfactory with gasoline, though it appears to be less deleterious than methanol fuels. Corrosion of metals appears to be more serious with ethanol than with methanol fuels in some situations and less in others. Six metals and twelve non-metallic fuel system materials were tested by immersion in ethanol fuels for extended periods, the metals at two temperatures and the non-metals at one or two; four automotive paints were exposed briefly at room temperature.

In unseparated blends and wet alcohol-rich fuels, ethanol corroded magnesium and possibly zinc more than methanol; however the zinc tests are suspect and inconclusive. In phase-separated blends, ethanol fuels were more corrosive to magnesium, steel,terne alloy and possibly zinc; methanol fuels were more corrosive to aluminum. In dry alcohol-rich fuels, methanol was more corrosive to magnesium and terne alloy. Of the non-metallic materials, cork, polyester-bonded fiberglass and polyurethane deteriorated in the ethanol-containing fuels at 48°C. At room temperature the fiberglass softened in a blend containing both ethanol and methanol but was not affected by other ethanol-containing fuels. These results are indicative but the serviceability of materials should not be judged solely from such limited immersion tests because materials of the same

type may differ between different formulations, and actual applications may be more or less severe than immersion tests.

In a laboratory simulation of wear in Bosch roller-vane fuel injection pumps, rapid wear occurred with ethanol blends but not with straight ethanol. This was the reverse of the finding with methanol, where the straight alcohol increased wear but blends did not. The antiwear additive that controlled wear with methanol was also effective with the ethanol blends.

Based on vapor lock simulation tests, enrichment of ethanol with light hydrocarbons or gasoline sufficient to provide cold startability does not increase the susceptibility to vapor lock seriously. Addition of ethanol to gasoline does increase the vapor locking tendency but much less than an equal volume of either methanol or butane. The modest increase in vapor lock with blends could be controlled by withholding some butane, with much less loss than gain in fuel volume or energy. Vapor locking is increased appreciably in blends containing both ethanol and methanol.

Problems with Ethanol Blends

Phase separation in the presence of water is probably the most serious technical problem with ethanol as well as methanol blends. However, the water tolerance of ethanol blends is several times greater than methanol blends. Phase separation should therefore be more easily prevented, and the separated aqueous phase is less corrosive to aluminum, though more so to some other fuel system metals. The water tolerance is

relatively less dependent on gasoline aromatic content and more dependent on alcohol concentration. Cosolvents, though effective, do not appear to be needed with ethanol blends, at least at 10% or higher concentrations and at moderate temperatures. However blends would still have to be protected from adventitious water or excessive exposure to humid air to prevent phase separation; all the blends tested outdoors for storage stability, though protected from rain, separated within 13 weeks. When phase separation does occur, the aqueous phase of blends with 10 vol % or more alcohol contain more hydrocarbon and less alcohol than the aqueous phase for methanol blends. Aromatic hydrocarbons are extracted preferentially in the aqueous phase.

Because the water tolerance of ethanol blends decreases rapidly with decreasing alcohol concentration, blends with low ethanol content are more susceptible to phase separation than those of higher content, and are preferably avoided. Mixing of ethanol blends with unblended gasoline, as with methanol blends, generally reduces the water tolerance more than in proportion to the alcohol content. Mixing of a nearly water-saturated blend with gasoline can therefore cause immediate phase separation and should also be avoided.

The literature and in-house data both show Road as well as Research and Motor blending octane values to be approximately the same for ethanol and methanol. However Road blending values on both alcohols in a fleet of recent model California cars were considerably lower than those determined elsewhere. This suggests that the octane value in practice with the latest model cars may be less than previously expected.

The volume expansion on blending ethanol with gasoline was found to be somewhat less than with methanol at 10 vol % concentration, 0.08 vs 0.15%; but about the same at higher concentrations, approximately 0.2%, for about 20 to 60 vol % alcohol.

Ethanol at 10 vol % concentration caused only little and uncertain degradation in warm-up driveability in two carburetted cars, but at 22 vol % the degradation was pronounced and statistically significant. Modification of carburetors to give approximately the same equivalence ratio with the 22% blend as standard carburetors gave with gasoline improved driveability markedly in one car and only slightly in the other. Surprisingly, a 1979 model carbureted car with 3-way catalyst and an exhaust oxygen sensor to control the air/fuel ratio showed a severe loss in driveability with both blends. The air/fuel control system that was expected to correct for the leaning effect of alcohol is not operative until the engine warms up and was therefore ineffective for warm-up driveability.

Evaporative emission measurements made in several laboratories in connection with the 1978 waiver request to EPA for Gasohol showed that evaporative emissions increase approximately 50% with 10 vol % of ethanol in a blend, even when the Reid Vapor Pressure of gasoline and blend were equalized. The increase appears to be caused more by the increase of low boiling fractions in the blend than to reduction in charcoal canister adsorption capacity for blend vapors. Methanol blends are therefore expected to cause even greater evaporative emissions than ethanol blends.

Several recent studies of fuel economy in DOE and EPA laboratories have shown an average increase in fuel consumption of 3% for 10 vol % ethanol blends and 5% for 10 vol % methanol blends, both compared to base gasoline in the same cars and driving pattern. These results are in line with the heats of combustion of the fuels and disagree with increases in fuel economy that have been claimed for alcohol blends in uncontrolled road tests, sometimes with different groups of cars on blend and base fuel.

In summary, most of the technical problems with ethanol blends are directionally similar but less severe than those with methanol blends. Water tolerance is several times as great, so the risk of phase separation is less and cosolvents do not appear to be needed, but the ethanol must be initially anhydrous and blends must be stored and shipped dry, the same as methanol blends. Volatility is increased less than with methanol, and vapor lock is much less affected, but evaporative emissions are still increased over those from gasoline. The effects of ethanol on fuel economy and driveability appear to be moderately less than those of methanol, in line with the lesser effects on heat of combustion and air/fuel mixture leaning. Straight ethanol, like methanol, can also be used in cars designed for it. Cold startability is more difficult with ethanol, requiring greater enrichment with light hydrocarbons if mechanical starting aids are not used. Problems associated with toxicity and compatibility with materials would be less serious with ethanol. A unique problem with ethanol, either straight or blended, in the

United States is the potential for bootlegging and the consequent need for denaturants and abiding by Bureau of Alcohol, Tobacco and Firearms regulations.

The following areas, limited to the use of ethanol in blends, are suggested as most needing further investigation:

- The production of ethanol and higher alcohols from coal.
- The economics of ethanol as a fuel versus the economics of other alternative fuels.
- Compatibility with fuel system materials and system durability, both in vehicles and in commercial fuel distribution.
- Denaturants that are inexpensive, harmless to fuel, and resistant enough to renaturing to qualify for a completely denatured formula.
- Water tolerance of blends at low alcohol concentration.
- Evaporative emissions and methods of control.
- Accurate fuel economy comparisons under realistic conditions.

I. INTRODUCTION

A. Purpose and Scope of the Study

As reported in the previous methanol contract study*, petroleum production in the United States is declining and dependence on imported oil, now near 50%, continues to grow. World petroleum production has been projected to peak about the year 2000. Coal-derived methanol has been identified by the U.S. Department of Energy (DOE) as one of the logical candidate alternative automotive fuels for use in the mid-term 1985-2000 period. The other alternative fuels are liquid hydrocarbons from coal and shale. Therefore work was done in the previous contract to appraise known and potential problems associated with the use of methanol in present type automotive engines and to assess potentially practical solutions achievable by modification of the fuel. Some observations on ethanol were included in that work.

Before gasohol, a blend of 10 vol % ethanol in gasoline, attracted wide attention in 1978, the methanol contract work was extended to assess potential problems with the use of ethanol as an automotive fuel. Although methanol has been studied rather thoroughly, ethanol has had more actual use as a motor fuel. However, the potential problems associated with its use in modern cars had not been widely studied in the laboratory. Experiments similar to those used in the methanol project were carried out to show the relationships of ethanol, methanol

* Methanol Fuel Modification from Highway Vehicle Use - Final Report, J. L. Keller, G. M. Nakaguchi and J. C. Ware, Report HCP/W3683-13 for U.S. Department of Energy, July 1978.

and gasoline to one another. Because of the growing use of ethanol and the better potential availability and economics of methanol, the combination of both alcohols in gasoline blends was studied.

The economics of ethanol production was considered to be outside the scope of this study.

This report includes: a preliminary appraisal of problems and possible fuel modifications based on existing information, the experimental and computational work undertaken, a discussion of the results, the conclusions drawn and recommendations for further DOE investigations.

B. Properties of Ethanol

Ethanol and methanol, unlike gasoline, are single chemical compounds with sharply defined boiling points. The chemical composition and behavior of both ethanol and methanol are in some ways more similar to water than to gasoline. Gasoline consists of a mixture of hundreds of different compounds, which are predominantly hydrocarbons with from 4 to 12 carbon atoms each. The properties of ethanol and methanol are contrasted with gasoline in Table 1. The differences in boiling temperature, flash point, heating value, heat of vaporization, stoichiometric air/fuel ratio for combustion and water solubility are responsible for most of the problems encountered on mixing or replacing gasoline with alcohols. Most of the properties of ethanol are intermediate to those of gasoline and methanol. These differences as well as experience reported in the literature indicate that potential problems with the use of ethanol would be less severe than those encountered with methanol.

Table 1.

Properties of Ethanol, Methanol and Gasoline^a

	<u>Ethanol</u>	<u>Methanol</u>	<u>Gasoline</u>
Chemical Formula	CH ₃ CH ₂ OH	CH ₃ OH	Mixture of C ₄ -C ₁₂
Molecular Weight	46.07	32.04	100-105 (Avg.)
Composition, wt %			
Carbon	52.2	37.5	85-88
Hydrogen	13.1	12.6	12-15
Oxygen	34.7	49.9	0
Density at 15°C, g/cm	0.789	0.794	0.695-0.779
Boiling Temperature, °C	78.5	65	~27-225
Flash Point, °C	13	11	-43
Auto Ignition Temperature, °C	423	464	257
Flammability Limits, vol %			
Lower	3.3	6.7	1.4
Higher	19.0	36	7.6
Heating Value, Lower kJ/kg	25,360	19,930	43,960
Heating Value, Lower kJ/dm ³	21,080	15,760	32,150
Latent Heat of Vaporization, kJ/kg	921	1,177	~349
Vapor Pressure, kPa at 33°C	17.2	31.9	48-103
Stoichiometric A/F ^b	9.0	6.4	14.2-14.8
Water Solubility	Infinite	Infinite	Insoluble

^a Taken from Ref. 492.

^b Air/fuel ratio for complete combustion.

C. Historical Background

Fermentation ethanol has been blended with gasoline in many countries, primarily as an outlet for surplus farm products and to reduce oil dependence; ethanol blends are currently being used in Brazil, South Africa and Cuba. In Brazil, ethanol/gasoline blends have been used in motor vehicles since the 1920's (531). Compulsory addition of alcohol to gasoline started in the 1930's to help stabilize sugar prices. A national alcohol program was launched by the Brazilian government in 1975; its goal is to achieve a level of 20 vol % alcohol added to gasoline, corresponding to a blend containing 16.7 vol % alcohol, throughout the country.

The use of alcohol as a fuel for internal combustion engines was first considered about 80 years ago in Germany to determine whether alcohol could be used in place of gasoline for motor cars which were just being developed (478, 499). In World War I, because of serious petroleum shortages, the Germans used mixtures of alcohol, benzene and any available gasoline as motor fuels. In 1932, Cities Services Oil Company, Ltd. was the first to market an alcohol mixture, Koolmotor Blend, in Great Britain. Cleveland Petroleum Products Company followed with their "Cleveland Discol" blend in 1934.

The first real incentive to use ethanol as a motor fuel in the United States was brought about by the passage of the 1906 Industrial Denatured Alcohol Act, which exempted the tax on ethanol used for industrial purposes. The first alcohol blend marketed in the United States was sold

under the trade name of "Agrol" in Illinois, Kansas and Missouri during the period of 1935-1939 (497). Use of the blend was discontinued because its producers were unable to compete in price with the cheaper gasoline. Following test marketing in Nebraska of "Gasohol", a blend of 10 vol % ethanol in unleaded regular gasoline, commercial marketing was initiated in Illinois about year end 1977. The sale of gasohol has since spread to Nebraska, Iowa and several other states. The U.S. Energy Tax Act passed in 1978 exempted gasoline blended with at least 10% alcohol from the federal excise tax of 4 cents/gallon, thus providing 40 cents/gallon support for the contained alcohol. Alcohol in this context includes methanol and ethanol, provided they are not produced from petroleum, natural gas or coal. In December 1978 the U.S. Environmental Protection Agency removed a barrier to gasohol by allowing a waiver for blends containing 10% ethanol from prohibitions of the Clean Air Act against new fuels or additives. At this writing, gasohol is reported to be also exempt from part or all of state gasoline taxes in ten states: Arkansas, Colorado, Iowa, Kansas, Maryland, Missouri, Nebraska, North Dakota, South Dakota and Wyoming.

II. PRELIMINARY APPRAISAL OF POTENTIAL PROBLEMS OF ETHANOL USE

A. Basis of Problem Definition

A preliminary appraisal of potential problems with ethanol-containing fuels and remedies was based on a thorough literature review, discussion with other investigators and experiences and findings obtained from our previous DOE contract work on methanol.

References to most of the literature reviewed and some of the private communications are given in the bibliography. The reference serial numbers are not consecutive because those under 450 were taken from the methanol file without changing the assigned number. All new references were assigned numbers of 450 and above; private communications were assigned numbers above 800.

As in the methanol contract work, the scope of the project was intentionally limited in certain respects. Ethanol consumption was considered only in four-cycle spark ignition (SI) engines. Because gas turbines are not yet in commercial highway vehicle service, ethanol use as turbine fuel, although attractive, was not considered. The use of ethanol as diesel fuel or a diesel fuel supplement as well as its use in two-cycle engines were not considered. Also the current production cost of fermentation ethanol and its unfavorable energy balance (except when prepared from sugar cane) must be considered major problems which could hinder ethanol use. These latter problems were also considered to be outside the scope of this study.

B. Potential Problems

The potential problems considered in the preliminary appraisal are listed in Table 2. Also included are estimates of the probability of each problem occurring in the absence of corrective measures and the relative seriousness of the consequences if it did occur, all based on information available prior to experimental work. Also listed in the table are indications of whether: A. the problem was to be studied further in the project; B. further study was deemed desirable, but was either underway or likely to be undertaken in other laboratories, and beyond the scope of time and budget for this project; or C. study under this project was deemed unnecessary or inappropriate. The consequences of a problem are assigned an estimated severity rating of 1 to 3 where 1 is major, i.e., it is likely to result in vehicle inoperability, serious damage to engine or distribution equipment, serious increase in personal hazard or substantial loss of fuel availability. The lower ratings represent lesser degrees of performance loss, damage, hazard or other undesirable effects.

As in the methanol contract study, an extensive literature review was made prior to beginning experimental work. However, an in-depth written review of the available literature on each of the potential problems with ethanol fuel is beyond the scope of this project. Each problem will be discussed briefly; a list of references for each topic, derived from the computerized classification of the bibliography will be found in Appendix I, Table I-7.

This brief preliminary discussion of potential problems is based only on information available from the literature and does not include any of the findings of the present study.

Preliminary Appraisal of Potential Problems with the use of
Ethanol as a Motor Vehicle Fuel

Problems	Estimate of Risk		Study Indicated ^b
	Probability of Occurrence	Consequences ^a	
<u>Distribution and Handling</u>			
Phase Separation	Definite	1	A
Incompatibility with Gasoline	Possible	2	A
Hygroscopicity	Definite	2	A
Volume Change in Blending	Probable	3	A
Storage Stability	Possible	2	A
Susceptibility to Micro-organisms, Blends	Possible	2	A
Renaturing	Definite	2	A
<u>Compatibility with Materials</u>			
Metal Corrosion	Definite	1	A
Non-metal Compatibility	Definite	1	A
Lubricant Compatibility	Possible	2	B
Internal Engine Wear and Engine Rust	Possible	1	B
Fuel Pump Wear	Possible	2	A
Paint Daage	Probable	3	A
Dirt Loosening and Filter Plugging	Probable	3	A
Gasoline Additives	Possible	3	C
<u>Vehicle Performance</u>			
Cold Startability, Neat	Definite	1	A
Warm-Up Driveability	Definite	1	A
Warmed-Up Driveability, Neat	Definite	1	C
Vapor Lock ^c	Probable	1	A
Preignition	Possible	3	C
Octane Requirement Increase, ORI	Unlikely	3	C
Volumetric Fuel Economy	Definite	2	B
High Sensitivity ^d	Definite	3	A
Diesel - Low Cetane quality	Definite	1	B
<u>Environmental Effects</u>			
Exhaust Emissions			
Unburned Ethanol	Definite	3	B
A/F Effect on Emissions	Probable	2	B
Aldehyde	Definite	2	B
Odor	Probable	3	C
Evaporative Emission Control, Vehicular	Possible	2	B
Vapor Recovery in Distribution System	Unlikely	3	C
Environmental Effect of Spills	Definite	2	B
<u>Toxicity and Safety Precautions</u>			
Toxicity	Definite	2	C
Vapor Explosivity, Neat	Definite	2	A
Fire Problem, Neat	Possible	2	A
<u>Economic Factors</u>			
Tax Parity with Gasoline	Definite	2	C
Economics Relative to Alternative Fuels	Definite	1	C

a 1 = Major problem; 2 = moderate problem; 3 = minor problem.

b A = Study indicated, this project. B = Study elsewhere underway or desirable.

C = No further study indicated at this time.

c Including the hot operating problems such as hot stalling or difficult hot starting.

d Difference between Research and Motor Octane Numbers.

Phase Separation - Phase separation in the presence of water or at low temperatures is the most disturbing problem with alcohol blends. Water is commonly present in gasoline storage tanks and more can be absorbed from the air or enter from rain on tanks, marine or pipeline operations and from other sources. The addition of as little as 0.2% water to blends containing 10 vol % of anhydrous ethanol has been reported to cause phase separation (477). With phase separation, not only would ethanol be lost from the fuel, but operation of distribution facilities would be upset, the aqueous phase would be difficult to dispose of, corrosion of some equipment would probably be aggravated and customers' cars would be apt to stall unpredictably. In field experience, vehicles would not start or operate on a 10 vol % ethanol blend with a separated bottom phase (509, 536). It was reported that if an engine is warm, it will continue to operate on a separated blend because the alcohol concentration in the water layer is high enough to support combustion (509).

Incompatibility with Gasoline - Methanol/gasoline blends were found to be incompatible with straight gasoline because phase separation could occur under certain circumstances if the two were mixed. Similar incompatibility has not been reported in the literature but may also hold true for ethanol/gasoline blends.

Hygroscopicity - Some substances absorb moisture from moist air (10, 476). Ethanol/gasoline blends can pick up enough moisture to cause phase separation (879). The rate of water absorption of ethanol blends is markedly influenced by the alcohol content and by surface-to-volume ratio. However in commercial storage tests in the 1930's, a steady decline in critical solution temperature and therefore of water content were observed. This behavior was attributed to the removal of water by evaporation of a ternary azeotropic mixture of hydrocarbon, alcohol and water (476).

Volume Change in Blending - When two mutually soluble liquids are mixed, the final volume will not necessarily be the sum of the original volumes of the two components. Ethanol and gasoline are reported to expand slightly on blending (422, 476). If so, allowances must be made by marketers for the volume increase, and such a volume increase should be considered in calculating fuel economy of blends.

Storage Stability - Any vehicle fuel must be able to withstand long-term storage without undue deterioration either from oxidative or microbial attack. Studies indicate a tendency for alcohol/gasoline blends to form more gums during storage than the base gasolines from which they were made (186). One report stated that ethanol is of value as an inhibitor in the formation of gum in some kinds of cracked gasolines (476). The use of suitable chemical inhibitors are reported to control gum formation in alcohol blends. There are also reports of somewhat increased induction system deposits with blends made with some gasolines (499).

Susceptibility to Microorganisms - Neat ethanol, like methanol, is not attacked by microorganisms; in fact it is toxic to many microorganisms. Gasoline can be attacked by certain microorganisms in the presence of water bottoms and serious problems have sometimes been caused by dispersion of the resulting products. It seems doubtful that the blends would be susceptible to attack because the concentration of ethanol in water bottoms would probably be too high to support either gasoline- or ethanol-dependent microorganisms.

Metal Corrosion - Corrosivity of ethanol and its blends with gasoline can cause moderate to severe damage to several metals used in distribution or automotive fuel systems. Metals reported to have suffered damaging corrosion from ethanol-containing fuels under various conditions are zinc, galvanized iron, iron, brass, copper and lead (477, 489, 499, 518). Corrosion with alcohols is aggravated by the presence of water. Many fleet tests have been run with ethanol/gasoline for extended periods with no apparent corrosion problems except those caused by impurities in the ethanol (e.g., corrosive denaturants such as pyridine).

Non-Metal Compatibility - Because ethanol is a good solvent, like methanol, compatibility with non-metallic fuel system materials can be a problem. A number of synthetic and natural non-metallic materials are used in fuel systems. Polyester bonded fiberglass laminants which are used in many underground fuel storage tanks, cork, leather, Viton and polyurethane were found to be adversely affected by methanol. Many of these materials may also be damaged by ethanol-containing fuels.

Lubricant Compatibility - Crankcase emulsions have been observed with operation of bench engine tests on straight methanol with low oil sump temperatures, as in ASTM Sequence IIC tests (49°C). No information was found for neat ethanol but it is conceivable that a similar problem will occur. Lubricant compatibility with alcohol blends as engine fuel is under study at Southwest Research Institute (SWRI)^a.

Internal Engine Wear - It has been reported that very few engine wear problems result from the use of neat ethanol as a motor fuel (530, 570). With ethanol blends, a study made in the 1930's showed increased cylinder wear in a fleet of vehicles used in intermittent service (499). Others report no unusual engine wear with the use of ethanol/gasoline blends (186, 451, 525). Engine wear and lubrication with alcohol fuels is under study at Southwest Research Institute.

Fuel Pump Wear - Bosch roller-vane fuel pumps were found to lose pressure and fail from internal wear more rapidly when used with methanol than with gasoline. Fuel pump wear has not been reported with ethanol fuels but it appears that wear problems could arise with use of ethanol-containing fuels.

Paint Damage - Damage is reported when methanol- and ethanol-containing fuels are spilled on lacquer type and other finishes in refueling cars (477, 518). This was confirmed for methanol on several types of automotive paints in the previous contract work. Although paint damage is a minor problem, it would be desirable to eliminate it if possible by some fuel or other modification.

a Under a DOE interagency agreement with the U.S. Army Fuels and Lubricants Research Laboratory, operated at SWRI.

Dirt Loosening and Filter Plugging - Alcohol is a good solvent for gasoline gum and can loosen other materials deposited on fuel system surfaces (110, 476, 477). The ability of alcohols to dissolve gum and loosen dirt can lead to plugged filters and screens when alcohol blends are first used in a gasoline fuel system. This may be a short term minor problem which only occurs immediately following changeover of fuels.

Gasoline Additive - There is no reported evidence of incompatibility between ethanol and gasoline additives. However, results of the methanol contract study showed that methanol in gasoline blends interferes with the action of carburetor detergent additives. Therefore, it is possible that ethanol may similarly interfere with the action of these gasoline additives.

Cold Startability - Ethanol is a single intermediate-boiling compound, 78.5°C, while gasoline is a wide mixture of compounds with boiling points ranging from 0° to 225°C. The vapor pressure of ethanol is so low at ambient temperatures that it cannot vaporize sufficiently, even under choked conditions, to provide a flammable mixture and enable a cold engine to start below about 15°C (543). Cold starting problems with neat ethanol, as was found with neat methanol, can probably be alleviated by the addition of light hydrocarbons as starting aids. The use of ethanol/gasoline blends was found to have no adverse effects on cold starting as compared to straight gasoline above 0°C, although easier starting was found with gasoline as compared to 10 vol % ethanol blends below -23°C (474).

Warm-Up Driveability - Good car driveability includes quick starting (especially at low temperatures), stall-free engine warm-up, smooth idle, hesitation-free response of throttle opening, surge-free operation under cruise conditions and freedom from vapor lock at high temperatures. Tests using ethanol/gasoline blends were reported to degrade driveability, e.g., more severe and/or frequent stumbles, surges and stall, than gasoline alone (9, 477). Because of the oxygen content of ethanol, substitution of a blend for gasoline without adjusting the carburetor results in a leaner air/fuel mixture in the engine; leaning is known to impair driveability, with effects most noticeable during the engine warm-up period.

Warmed-Up Driveability - Driveability after warm-up appears to be no problem with ethanol blends. On vehicles with carburetion and intake system modified to give satisfactory fuel distribution during warm-up on ethanol-rich fuels, warmed-up driveability also appears to be satisfactory. The basic modifications necessary to permit starting and acceptable warm-up driveability also satisfy the warmed-up driveability requirements.

Vapor Lock - The vapor locking tendency of a fuel is related to its front-end volatility. The addition of methanol to gasoline was found to increase front-end volatility and therefore the vapor locking tendency of the gasoline. The addition of ethanol to gasoline does not appear to increase front-end volatility as drastically as the addition of methanol and therefore should have less tendency to cause vapor lock than does the use of methanol. Most studies showed that ethanol/gasoline

blends would have a higher tendency to cause vapor lock than would gasoline (186, 474, 477, 499, 559). Vapor lock problems have been reported in several customers' cars which were fueled on gasohol during the summer of 1978 (567).

(Preignition - No references on the subject of preignition with ethanol-containing fuels have been found. Because preignition does not appear to be a problem with methanol/gasoline blend, we do not expect it to be a problem with ethanol/gasoline blends.

Octane Requirement Increase - The octane requirement of an automobile usually increases several numbers as combustion chamber deposits accumulate during the first several thousand kilometers of driving. No ORI data have been found in the literature for cars run on ethanol/gasoline blends, but ORI should be no greater with blends than with gasoline. Straight ethanol burns more cleanly than gasoline and should therefore leave less deposits in the combustion chamber; this suggests that ORI is likely to be small.

Volumetric Fuel Economy - Although cars are reported to be operating on straight ethanol in Brazil, no data are available on their fuel economy. At equal efficiency, other things being equal, ethanol would give 65-66% as great fuel economy as gasoline, based on the heats of combustion. With high compression ratio engines designed for ethanol, economy is expected to be better but still less than that with gasoline.

)

Fuel economy with ethanol/gasoline blends has been measured frequently, with differing results. Blending ethanol with gasoline both reduces the fuel energy content and, if carburetion is not adjusted for the change, leans the air/fuel mixture supplied the engine. Because most late model cars already run lean, further leaning does not usually help and may even hurt thermal efficiency. Gains of 5 to 7% in fuel economy have been claimed for gasohol from some fleet tests, but in uncontrolled tests that did not assure equal driving severity and, in some cases, used different car groups for the two test fuels, thus confounding vehicle, driving pattern and fuel variables. Recent measurements on 10% alcohol blends vs. gasoline in government laboratories under controlled conditions -- same cars and same driving pattern -- have shown an average loss in fuel economy of 3% for the ethanol blends and 5% for the methanol blends, in close agreement with the decrease in fuel energy content (108, 529, 532, 536, 551, 881).

Octane Sensitivity - Although ethanol has very high Blending Research Octane Numbers (BRON's) its Blending Motor Octane Numbers (BMON's) are much lower; it therefore increases the sensitivity difference between RON and MON of gasoline blends containing it. Automobiles vary not only in their octane requirement but also in whether their requirements are more responsive to RON or MON; unfortunately recent model cars are generally more responsive to MON than RON. Therefore ethanol blends made to just pass commonly used specifications for $(RON + MON)/2$ at a level satisfactory with gasoline could, because of their high sensitivity, cause knock in cars especially responsive to MON.

Diesel-Low Cetane Quality - Compression ignition engines cannot run directly on ethanol because they require a fuel with a low autoignition temperature (high cetane number). Ethanol would have a very low cetane number as compared to diesel fuels.

Regulated Exhaust Emissions - Hydrocarbon (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) are affected by changes in the carburetor air/fuel settings of the engine. Lean operation of an engine (with more than the stoichiometric amount of air) will tend to reduce CO or hold it constant, reduce HC, and may increase or decrease NO_x , depending on the original carburetor setting. Because of the leaning effect from the use of ethanol blends, substantial decreases in CO and HC have been observed (481, 519, 532, 551, 558). In general, slight increases in NO_x are also found.

Exhaust Aldehydes and Ethanol - Increased emissions of aldehydes have been detected from cars operating on ethanol/gasoline blends (481, 532, 551). Some ethanol also appears with the unburned fuel. Aldehydes, though currently unregulated, are photochemically very reactive and could contribute significantly to smog formation.

Exhaust Odor - Odor from either ethanol fuels or ethanol/gasoline blends is not known to be a problem. Aldehydes, if present at a detectable level, would have an unpleasant odor.

Evaporative Emission Control - In recent model cars, vapors formed by the evaporation of gasoline from the fuel tank, and in some cases, from the carburetor also, are adsorbed in a canister of charcoal.

The vapors are drawn into the fuel system again and burned during vehicle operation. Increases in evaporative emissions have been reported with 10% ethanol blends relative to gasoline (481, 519); the average increase in an extensive series of tests arranged by EPA to evaluate gasohol emissions was 49% (558). Even a blend with base stock reduced in volatility gave 46% greater evaporative emissions than a gasoline of equal RVP.

The previous methanol study showed that the adsorptive capacity of charcoal for vapor from a 20% methanol/80% gasoline blend was not significantly less than for gasoline vapor. Because of its higher molecular weight, ethanol is adsorbed more strongly than methanol (113). The increase in evaporative emission with ethanol blends must therefore be caused simply by the increased quantity of low-boiling fractions in a blend being so great as to overload canisters designed for gasoline, not from failure to adsorb the alcohol. (Low-boiling fractions are increased by ethanol/hydrocarbon azeotropes.) If gasohol comes to be widely used, this problem may require the use of larger capacity charcoal canisters. Because methanol increases low-boiling fractions more than ethanol, it can be expected that methanol blends will increase evaporative emissions even more than ethanol blends.

Vapor Recovery in Distribution Systems - Displaced air/fuel vapor mixtures recovered from fuel transfers to or from gasoline tank trucks are usually recovered at refinery, marketing, pipeline or marine terminals. The terminal vapor recovery systems use combinations of

refrigeration, compression, absorption and adsorption techniques. In the methanol study, engineering calculations showed that methanol/gasoline blends would not overload any of the three types of vapor recovery systems tested. Because ethanol does not increase the vapor pressure of blends as much as methanol, it seems logical that ethanol/gasoline blends also would not strain the recovery capacity of such systems.

Environmental Effect of Spills - Leakage or spills of ethanol into water or land environment appear to be much less serious than similar spills of gasoline. As ethanol is completely soluble in water, rapidly dispersed and biodegradable, it should be quickly removed by natural processes. It is, however, reported to be more toxic than methanol to many forms of marine life (397).

Toxicity - Ethanol has found wide application in industry and experience shows that it is not a serious industrial poison (142, 396, 467). The Threshold Limit Value (TLV) for ethanol vapor in air has been set at 1000 ppm. Its minimum identifiable odor has been reported at 350 ppm which is well below the TLV limit. This is in contrast to methanol, where the detection limits are in the same range or higher than its TLV limits. Ethanol is oxidized rapidly in the body to carbon dioxide and water and no cumulative effects occur, also in contrast to methanol.

Vapor Explosibility - The flammability limits for ethanol (3.3 to 19.0%) are much wider than those of gasoline (1.4 to 7.6%). The saturated vapor above the liquid in a tank at 20°C contains about 6% ethanol,

which is in the explosive range, whereas that above gasoline at the same temperature is 25-50%, well above the rich explosive limit. Ethanol can present a greater hazard than gasoline if an ignition source is present.

Fire Problem, Neat - Conventional chemical foams are not suitable for fighting fires with either ethanol or methanol; a special alcohol-type foam is required. If the burning characteristics of ethanol were similar to methanol, the near invisibility of the flame would increase the fire hazard because a fire might not be detected until well advanced.

Tax Parity with Gasoline - At present, state and federal taxes on gasoline are based on fuel volume regardless of its properties. If neat ethanol or ethanol blends were taxed at the same rate, motorists using those fuels would be penalized because of the low heat of combustion and the reduced fuel economy obtained with ethanol. The federal excise tax has in fact recently been eliminated for gasohol, at least for the period from January 1, 1979 to October 1, 1984; several states have also recently introduced or increased reductions in state gasoline taxes on alcohol blends. The federal tax cancellation is not explicitly for blends of fermentation ethanol though it is effectively limited to them; it applies to blends containing at least 10% alcohol -- methanol, ethanol or presumably other alcohols -- provided that the alcohol is not derived from petroleum, natural gas or coal. Blends of methanol made from biomass would meet this requirement but they may not be used unless EPA were to permit a waiver from prohibitions of the Clean Air Act for them, as it did in December 1978 for gasohol.

Economics Relative to Alternative Fuels - Ethanol at present costs much more in bulk than gasoline for the energy contained. However, there is little doubt that as the price of gasoline increases and petroleum supplies grow short alternative fuels from shale, coal, and eventually biomass will become more competitive at some future time.

Illicit Ethanol Recovery - The production and use of ethanol is very rigidly controlled in the United States by the Bureau of Alcohol, Tobacco and Firearms. The widespread use of ethanol/gasoline blends could lead to illicit ethanol recovery or bootlegging. Ethanol can be separated from a gasoline blend with the addition of water and the separated ethanol can be further purified by charcoal treatment.

Bootlegging of ethanol from gasoline blends could be attractive for two reasons:

- (1) the recovered alcohol could be obtained at gasoline prices, and
- (2) the recovered alcohol-free gasoline which has received a gasohol subsidy can still be used as motor fuel.

III. RESULTS AND DISCUSSION

A. Problems Not Dealt With in This Study

Potential problems with ethanol were selected for investigation on the basis of a literature review, discussion with other investigators, and experience with methanol in the earlier contract study. These problems are denoted by A in the last column of Table 2. The results of investigations of these problems are reported and discussed in part B of this Section.

Problems under study elsewhere were excluded from the present work and are denoted by a B in the last column. They included: lubricant compatibility, engine wear and rust, volumetric fuel economy, diesel application, the effect of air/fuel ratio on emissions of hydrocarbons, carbon monoxide, and oxides of nitrogen, evaporative emissions, environmental effects of spills and economics relative to alternative fuels. Experimental measurement of exhaust aldehydes, originally planned, was omitted in favor of further work in other problem areas and also because aldehyde emissions from ethanol have been studied elsewhere. Certain problems were omitted because they were judged to be relatively minor or beyond the scope of this project: warmed-up driveability, preignition, octane requirement increase, exhaust odor, vapor recovery in distribution systems, toxicity, low odor level and tax parity with gasoline. All of the problems listed were treated briefly in Section II.

III.B. Problem and Solutions Studied

1. Fuel Blending, Handling and Distribution

a. Phase Studies of Several Systems

Phase studies were carried out in this contract work as in the previous methanol study in order to obtain a better understanding of phase separation from blends. Ternary phase diagrams were determined for several alcohol-gasoline-water systems which included mixtures of gasoline at three different aromatic contents, straight ethanol or denatured alcohol^(a), and water. See Appendix II.A.1. for further details.

Logarithmic relationships were used to expand the high gasoline and water concentration ends of the ternary phase diagram of these systems and this permitted a more precise definition of mutual solubility lines and tie lines. By use of this relationship for each ternary system, the mutual solubility curve and three to four tie lines, we were able to calculate the location of as many tie lines as desired. The phase relationships thus obtained were used to calculate distribution coefficients for alcohol between the aqueous and gasoline phases, respectively, as a function of water and alcohol content of the entire mixture.

(a) Completely denatured formula 19 alcohol (CDA-19) which consists of 100 gal ethanol, 4 gal methyl isobutyl ketone and 1 gal gasoline; and the Southwest Alabama Farmers' Cooperative Association (SWAFCA) special formula which consists of 89.5 gal formula 28A alcohol, 5 gal methanol, 5 gal gasoline and 0.5 gal t-butanol. (Formula 28A alcohol, in turn consists of 100 gal ethanol and 1 gal gasoline.)

The alcohol concentrations calculated for the separate phases at various overall water concentrations are shown as a function of alcohol content of the mixture in Figures II.A.1-11 to II.A.1-15. The maximum concentrations of ethanol in the aqueous phase from comparable systems were slightly lower than for methanol: 69-73 wt % for ethanol versus 79-83 wt % for methanol.

Alcohol distribution coefficients, i.e., concentration of alcohol in the aqueous phase divided by the alcohol concentration in the gasoline phase, were then calculated for the various systems and are shown as a function of alcohol content for a number of water levels (Figures II.A.1-16 to II.A.1-20). As found in the methanol work, there was no single distribution coefficient for a given system. In comparing similar ethanol and methanol systems, the distribution coefficients at the different water contents were much lower for the ethanol systems (40 to 70 versus 60 to >1000 for the methanol systems). The differences are indicative of the greater retention of ethanol in the gasoline layer. The alcohol concentrations in the aqueous phase and the distribution coefficients for the various systems in the range of 1.0 to 4.0 wt % water and 10 wt % ethanol content are listed in Table II.A.1-1. The distribution coefficients decreased (less alcohol in the water phase) with decreasing water, increasing alcohol content and increasing gasoline aromaticity. The distribution coefficients of the CDA-19 and SWAFCA alcohol formulas in gasoline and water systems were equivalent to and slightly larger than that of straight ethanol, respectively. This difference with the SWAFCA alcohol formula system was caused by the presence of methanol which is added as denaturant.

The hydrocarbon and alcohol contents of aqueous, or water-richer, phases separated from various alcohol-gasoline blends upon mixing with 1.0 wt % water are shown in Figures 1, 2 and 3 as a function of vol % alcohol in the water-free blend. The three figures are for blends with gasolines 1, 2 and 3 with 14, 26 and 38 vol % aromatics, respectively. Water contents of the aqueous phases are, of course, 100% minus the hydrocarbon and alcohol contents. Data on the compositions of separated phases used in plotting these figures were available from computer print-outs of the same tie-line data developed for use in Figures II.A.1-11, -12 and -13 and corresponding figures in the previous report on methanol fuel modification.

Figures 1 to 3 show that in general, for blends of more than about 10 vol % alcohol, the hydrocarbon content of the aqueous phase increases and the alcohol content decreases in the order: methanol; methanol plus cosolvent; ethanol. They also show that the hydrocarbon content of the aqueous phase tends to increase and the alcohol content to decrease with increasing aromatic content of the gasoline.

For a 10 vol % ethanol blend in 26% aromatic gasoline with 1.0 wt % added water, the hydrocarbon content of the aqueous phase is seen in Figure 2 to be 20 wt %, compared to 11 wt % for similar blends of methanol or methanol plus cosolvent. In a separate experiment the 10 vol % ethanol blend was equilibrated with 1.0 wt % water and the lower phase separated for analysis of the hydrocarbons by mass spectrometry. The composition showed that aromatics were concentrated in the aqueous phase, at 51% vs 26% in the original gasoline:

Paraffins, C ₆ - C ₁₀	35.2 vol %
Olefins and cycloparaffins	15.8 vol %
Benzene	3.4 vol %
Toluene	14.5 vol %
C ₈ alkyl benzenes	16.4 vol %
C ₉ alkyl benzenes	9.1 vol %
C ₁₀ alkyl benzenes	2.4 vol %
C ₁₁ alkyl benzenes	0.4 vol %
Indanes and tetralins	<u>2.8 vol %</u>
Total aromatics	51.0 vol %
	<hr/>
	100.0

FIGURE 1
**COMPOSITION OF AQUEOUS PHASE SEPARATED FROM
ALCOHOL BLENDS IN 14% AROMATIC GASOLINE
PLUS 1.0 WT% WATER**

FIGURE 2

COMPOSITION OF AQUEOUS PHASE SEPARATED FROM
ALCOHOL BLENDS IN 26% AROMATIC GASOLINE
PLUS 1.0 WT% WATER

FIGURE 3

COMPOSITION OF AQUEOUS PHASE SEPARATED FROM
ALCOHOL BLENDS IN 38% AROMATIC GASOLINE
PLUS 1.0 WT % WATER

III.B.1.b. Water Tolerance of Blends

Water tolerance measurements were made in a number of blends to examine the effects of temperature, gasoline aromatic content, and alcohol composition and concentration on water solubility. The water tolerances of an alcohol/gasoline blend is defined as the amount of water which can be absorbed by a given blend before phase separation occurs. Blends were made with gasolines of 14, 26 and 38 vol % aromatic content and with up to 15 vol % of three alcohols: (1) ethanol; (2) CDA-19 formula; and (3) SWAFCA formula. Experimental work is described in Appendix II.A.2. Data are listed in Tables II.A.2-1 to II.A.2-3; see Appendix II.A.2 for further details.

The water tolerance of ethanol/gasoline blends was found to be higher and much more responsive to alcohol concentration than that of methanol blends; only small increases in water tolerance had been found in blends with increasing methanol concentration. The water tolerances of 10 vol % blends of both ethanol and methanol in the three aromatic gasolines are shown in Figure 4. As seen in this figure, ethanol has a much higher water tolerance than methanol at equal concentration, and water tolerance with ethanol is affected relatively less by gasoline aromatic content. In contrast to methanol, ethanol blends would probably not require the use of cosolvents. A comparison of both alcohols in a 26 vol % aromatic content gasoline is given in Figure 5. This comparison shows that the water tolerance of an ethanol/gasoline blend is much more responsive to alcohol concentration than that of a methanol

blend. A blend which contained 20 vol % of an admixture of 70 wt % methanol and 30 wt % *i*-butanol as cosolvent would approximately equal the water tolerance of a 10 vol % ethanol blend. The water tolerances of blends prepared from two denatured alcohol formulas, CDA-19 and SWAFCA, were both slightly poorer than that of a blend made from straight ethanol. Water tolerances of two blends made from different ethanol/methanol combinations were drastically reduced from that of a straight ethanol blend.

FIGURE 4.
WATER TOLERANCE OF ETHANOL AND METHANOL
BLENDS VS CLOUD POINT

III.B.1.c. Cosolvent Effectiveness

Because the water tolerances of ethanol/gasoline blends are relatively high, cosolvents such as those required for good water tolerance with methanol blends are probably not needed. However, for academic purposes 1-butanol (*n*-butyl alcohol), which can be produced from grain by an alternative fermentation process (494), was tested as a cosolvent in a 1:3 ratio with ethanol. It was found to be highly effective; the water tolerance of this blend was almost double that of a blend made with straight ethanol (see Figure II.A.2-3).

III.B.1.d Volume Changes on Blending

The volume increase on blending ethanol and gasoline was determined. Expansions of about 0.23% at 10 vol % ethanol and a maximum of 0.55% at 12.5 vol % have been reported in the literature (422, 458).

The volume change of ethanol and gasoline upon mixing was measured for blends from 5 to 75 vol % ethanol. A volume increase of about 0.08 vol % at 10 vol % ethanol and a maximum increase of about 0.22 vol % at 25 vol % ethanol concentration (Figure 6) were found. Measurements were made at 20°C with a low vapor pressure gasoline^a, 50 kPa, using a set of volumetric flasks specially calibrated in our laboratory for transfer measurements.

a Gasoline number 10, listed in Table III-B, page III-4, of the report on the previous methanol study.

FIGURE 6
VOLUME INCREASE FOR
ETHANOL/GASOLINE BLENDS AT 20° C

III.B.1.e Incompatibility of Blends

Water tolerance data show that blends and gasoline should be considered potentially incompatible and should preferably not be used in the same car. An example of the incompatibility of blends is described below in more detail.

Scrutiny of Figure II.A.2-1 showed that the tolerance of a 5 vol % ethanol blend at 10° and 20°C was in every case less than half that of a 10 vol % ethanol blend with the same gasoline. This means that phase separation could take place in the tank of a car if a homogeneous 10 vol % ethanol blend nearly saturated with water is mixed with an equal or larger volume of dry straight gasoline. As with methanol, phase separation is likely to occur if the aromatic content of the straight gasoline is the same or lower than that of the gasoline in the blend.

This incompatibility was verified in the laboratory. A 10 vol % ethanol/90 vol % gasoline (38 vol % aromatic content) which contained 0.65 wt % water (versus 0.72 wt % water tolerance) was mixed with equal volumes of straight gasolines containing 14, 26 and 38 vol % aromatics at 20°C. All mixtures of blends and straight gasolines became turbid. No readily measurable lower phase was produced in any mixture; after settling, varying amounts of water droplets appeared on the bottom of the mixing vessel. More settled water was found in the mixtures with lower aromatic gasoline than with higher aromatic gasoline.

III.B.1.f. Storage Stability of Blends

The oxidation stability of a fuel is extremely important because gum formed by oxidative degradation can cause obstruction of vehicle fuel systems and air-fuel passages as well as sticking and failure of moving parts such as carburetor needle valves. An increase in the tendency for gummy deposits to occur in the induction system, which resulted from the use of ethanol/gasoline blends, has been reported in the literature (499). However, pyridine was used as a denaturant and may have aggravated the deposit formation. One reference stated that ethanol is of value as an inhibitor for gum formation in some cracked stocks (476).

A 26-week storage test was carried out as described in Appendix II.B to determine the oxidative stability of five fuels. These fuels were: Fuel SS-1, a base gasoline which was blended to have somewhat less than normal stability; Fuel SS-2, a blend of 10 vol % ethanol in Fuel SS-1; Fuel SS-3, ethanol with hydrocarbons added as cold starting aids; Fuel SS-4, an ethanol/methanol combination blend in Fuel SS-1; and Fuel SS-5, same as Fuel SS-2 with additional antioxidant. See Table III-B for properties of the fuels.

Test results showed that Fuel SS-2, 10 vol % ethanol blend, was essentially equivalent in stability to the base gasoline, Fuel SS-1. Fuel SS-5, which was similar to Fuel SS-2 except with additional DBPC^a antioxidant, formed essentially the same amount of gum as Fuel SS-2. Although the additional amount of DBPC reduced the peroxide number slightly and improved the induction period of the 10% blend after

a DBPC = 2,6-di-t-butyl-p-cresol, a highly effective gasoline antioxidant.

the 26-week storage period, the use of exceedingly large dosages of antioxidant does not appear to be necessary for good blend stability. Fuel SS-3, ethanol with starting aids, also showed good storage stability. Fuel SS-4, ethanol/methanol blend, showed slight increases in both ISD and ASTM gums which could be attributed to methanol. In the methanol study, methanol blends were more prone to gum formation than was gasoline.

In contrast to methanol, ethanol/gasoline blends appear to be equivalent in stability and will not require additional amounts of anti-oxidant to maintain storage life equivalent to that of gasoline.

III.B.1.g Susceptibility of Blends to Microbial Attack

Gasoline can be attacked by certain microorganisms found in storage tank bottom water and serious problems have sometimes been caused by the dispersion of the resulting products. No references have been found on the susceptibility of alcohol blends to microbial attack.

Microbial susceptibility tests were carried out in one-liter iron vessels fitted with screw-caps. Foul tank bottom water, 50 ml, from an unleaded gasoline storage tank was added to four fuels, 500 ml each. The fuels were:

<u>Fuel Code</u>	<u>Fuel Description</u>
MA-1	Unleaded regular gasoline No. 5
MA-2	10 vol % ethanol/90 vol % MA-1
MA-3	3.3 vol % ethanol/6.7 vol % methanol/90 vol % MA-1
MA-4	10 vol % methanol/90 vol % MA-1

The vessels were shaken weekly to simulate the agitation of tank contents caused by addition and withdrawals of fuel in normal use.

Microbial susceptibility tests showed that both ethanol and methanol act as an antiseptic to gasoline tank bottom water microorganisms. Examination of the water phase by optical microscopy showed that the straight gasoline bottom water contained live bacteria but that the waters from the three blends contained none. This was confirmed by plate culture counts which showed the gasoline bottom water to contain 1,800 counts/ml while the water from the blends were essentially void (0-2 counts/ml) of live bacteria.

These tests indicate that ethanol and methanol blends should be less susceptible to attack from microorganisms than is gasoline. The antiseptic properties of both alcohols at 40-50 vol % in the bottom water are sufficient to act as a biocide.

III.B.2.a. Dirt Loosening in Gasoline Distribution System Tanks

It was reported in the middle 1930's that when alcohol/gasoline blends are first used, the alcohol loosens rust and dirt from the walls of fuel tanks or fuel lines of an automobile (186, 477). These particles are then carried along by the fuel and plug carburetor jets and filters. Current experience with gasohol is reported to be quite similar.

The ability of two alcohol/gasoline blends and an ethanol fuel to loosen dirt, gum and rust deposits was examined in the laboratory. The four test fuels were:

<u>Fuel Code</u>	<u>Fuel Description</u>
DL-1	Unleaded base gasoline No. 4
DL-2	10 vol % ethanol/90 vol % DL-1
DL-3	3.3 vol % ethanol/6.7 vol % methanol/90 vol % DL-1
DL-4	80 vol % ethanol/5 vol % pentanes/15 vol % DL-1

The surfaces of the metal specimens were prepared to simulate deposits in a dirty gasoline tank. Iron coupons were prepared by rusting, coating with gasoline gums (obtained from aged catalytically cracked gasoline) and sand, and baking in an oven at 200°C for two hours.

Prec weighed specimens were immersed in each test fuel, in duplicate, for six days at room temperature and for four days at 48°C. After the immersion period, the specimens were gently rinsed, dried and reweighed. The results of the measurements are shown in Table 3.

All ethanol-containing fuels caused about a 9- to 12-fold increase in weight loss, i.e., "dirt loosening", compared to base gasoline alone. The three ethanol-containing fuels were essentially equivalent in their dirt loosening properties.

These results, along with those found for methanol-containing fuels, confirmed the excellent ability of the alcohols to loosen dirt and partially dissolve fuel gum deposits. To avoid any potential filter or fuel system plugging problems, a fuel distribution system which has been used in former gasoline service should be completely cleaned out before use of alcohol blends.

Table 3.

Results of Dirt Loosening Tests

<u>Fuel Code</u>	<u>Fuel Description</u>	<u>After Soak Period</u>	
		<u>Specimen^a Average Weight Loss</u> <u>mg/cm²</u>	<u>Appearances of Fuel</u>
DL-1	Unleaded base gasoline No. 4 (32% aromatic)	3.5	Amber, very light residue
DL-2	10 vol % ethanol/90 vol % gasoline No. 4	28.3	Dark orange, light residue
DL-3	3.3 vol % ethanol/6.7 vol % methanol/ 90 vol % gasoline No. 4	35.5	Dark orange, light residue
DL-4	80 vol % ethanol/5 vol % pentanes/ 15 vol % gasoline No. 4	33.5	Dark orange, light residue

a The specimens had a coated surface area of 55 cm² each.

III.B.2.b Solvent Effects of Ethanol on Automobile Paint Finishes

One of the minor problems which may be caused by the introduction of alcohols into motor fuels is damage to the vehicle paint finish from spills during refueling. The effects of nine fuel blends on four DuPont automotive paints were examined by the same methods used in the methanol study. The paints were:

- (1) acrylic lacquer ("Lucite")
- (2) polyurethane ("Imron")
- (3) acrylic enamel ("Centari")
- (4) alkyd enamel ("Dulux")

The test results and description of the test fuels are listed in Table 4.

In the test felt pads wet with the individual fuels were held against the paint surfaces for about two hours. When the pads were removed, the paint surfaces were dried and examined for signs of degradation. Polyurethane paint was not attacked by 10 vol % ethanol blends but was attacked by fuels containing higher concentration of alcohols (i.e., 20 vol % ethanol and greater). The other paints were attacked by all fuels to varying degrees.

As found in the methanol work, it is concluded that fuel spills during use of ethanol blends or ethanol containing hydrocarbon starting aids will probably cause more paint damage than is currently experienced with gasoline. It is evident that ethanol-resistant paint formulation will be preferable for cars designed to run on ethanol-containing fuels.

Table 4.

Effect of Two-Hour Wet Contact of Ethanol Fuel Blends on DuPont Automotive Paints

<u>Fuel Code</u>	<u>Fuel Blend Composition</u>	<u>"Lucite" Acrylic Lacquer 939-Y-92443</u>	<u>"Imron" Polyurethane 826-Y-2460</u>	<u>"Centari" Acrylic Enamel 934-AH181</u>	<u>"Dulux" Enamel (alkyd) 93-93774</u>
MC-1	Unleaded Base Gasoline	slightly attacked ^a	no effect	softened	slightly attacked ^a
MC-2	10 Vol % Ethanol + 90 Vol % MC-1	slightly attacked ^a	no effect	softened	no effect
MC-3	MC-2 + 0.2 wt % Water	no effect	no effect	softened	slightly attacked ^a
MC-5	3.3 vol % Ethanol + 6.7 Vol % Methanol + 90 vol % MC-1	no effect	no effect	softened	slightly attacked ^a
MC-6	80 vol % Ethanol + 5vol % Pentanes + 15 vol % MC-1	softened	wrinkled	slightly softened	slightly attacked ^a
MC-7	80 vol % 190 Proof Ethanol + 5 vol % Pentanes + 15 vol % MC-1	slightly softened	no effect	extensive damage, wrinkled	slightly attacked ^a
MC-8	20 vol % Ethanol + 80 vol % MC-1	very slightly softened	slightly wrinkled	moderate damage, wrinkled	slightly attacked ^a
MC-9	10.5 vol % CDA-19 +89.5 vol % MC-1	no effect	no effect	softened	no effect
MC-10	11.3 vol % SWAFCA Formula Alcohol + 88.7 vol % MC-1	slightly attacked ^a	no effect	softened	slightly attacked ^a

a Slight irregularity of surface evident in wetted area.

III.B.2.c Fuel Pump Wear

Because of the evidence of excessive wear of mating surfaces in Bosch roller vane fuel pumps with methanol, steel-on-steel rubbing wear tests of various ethanol-containing fuels were made with the Falex wear tester (ASTM D 2670). In this machine, two steel blocks with V-shaped grooves, which are immersed in liquid under test, are pressed against a rotating 6.1 mm diameter steel journal. Load on the blocks was reduced from the 3100-4000 Newtons force commonly used with lubricants to 220 Newtons in order to operate without seizing on the low viscosity fuels. Wear was exhibited more by scuffing of the journal and block contact surfaces than by measured closure of the blocks.

The fuels tested included unleaded base and commercial^a unleaded gasolines, formula 28-A ethanol, CDA-19 formula alcohol and SWAFCA formula alcohol. All alcohols were tested straight and in blends with base gasoline. The tests showed that ethanol, CDA-19 and SWAFCA formula alcohols, in contrast to methanol, permitted essentially no wear on the rubbing surfaces. Also 10 vol % blends of ethanol, CDA-19 and SWAFCA alcohols in both base gasoline and commercial gasoline allowed severe wear and caused seizure of the journal and block; this was also in contrast to methanol which did not affect the wear properties of gasoline. However, the addition of 1 g/l of Texaco's TFA-431, a lubricity additive for turbine fuels, to the ethanol/gasoline blends essentially eliminated the wear problem.

a Contains oleylamine, a carburetor detergent additive.

Results of these laboratory tests indicate that neat ethanol, unlike methanol, will probably not cause excessive wear of roller-vane fuel pump impellers. The addition of ethanol to gasoline, which led to failure in the laboratory test apparatus, may cause excessive wear of the pump impellers. However, this wear can be combated with the addition of a lubricity additive such as Texaco's TFA-431.

III.B.2.d. Compatibility of Ethanol Fuels With Metals

The use of neat ethanol or ethanol blends may cause problems with potential corrosion of metal fuel system materials. Corrosion of aluminum, copper, iron, lead and zinc has been reported in the literature (213, 489, 499). To measure the interaction of some common fuel system metals with ethanol-containing fuels, six metals: aluminum, brass, magnesium, steel, terne alloy and zinc were tested in seven fuels. Tests were made by immersion for six months in quiescent fuel at room temperature (23°C) and with gentle agitation of the fuel at 48°C; details are given in Appendix II.C. The fuels are described below.

MC-1	Unleaded base gasoline;
MC-2	10 vol % ethanol/90 vol % gasoline (dry);
MC-3	MC-2 + 0.2 vol % water;
MC-4	MC-2 + 1.5 vol % water (phase separation);
MC-5	3.3 vol % ethanol/6.7 vol % methanol/90 vol % gasoline;
MC-6	80 vol % ethanol/15 vol % gasoline/5 vol % pentanes;
MC-7	80 vol % 190 proof ethanol/15 vol % gasoline/5 vol % pentanes.

Results of the corrosion tests are given in Table II.C-2 in terms of both uniform, or average, corrosion rate and of visual evidence of pitting corrosion. As with the methanol fuels tested previously, there was no consistent tendency for one test condition to be more severe than the other. The averages of duplicate ratings in Table II.C-2 are

presented in Table 5, where they are compared with average ratings of related fuels tested in the methanol study. The corrosivity effects are summarized below for each metal.

Aluminum was not corroded appreciably by any of the ethanol-containing fuels; the only serious corrosion observed was with a methanol/gasoline blend with a separated aqueous phase at 48°C. Brass was not corroded significantly by any of the fuels, with or without added water, at either test condition. Steel showed severe pitting corrosion in both gasoline and an ethanol blend with a separate aqueous phase present, but was not corroded appreciably by any other fuels.

Magnesium was affected much less by a dry ethanol-rich than by a dry methanol-rich fuel, showing severe pitting in six months at both test conditions with the former vs destructive corrosion within one day with the latter. However, the presence of water did not suppress corrosion of magnesium by ethanol as it did corrosion by methanol. Ethanol blends caused more severe pitting corrosion than methanol blends, with or without phase separation, at both test conditions. Severe pitting corrosion occurred with the enriched ethanol fuel, wet or dry, and with the ethanol blend either dry or with a separated aqueous phase. Severe general corrosion also occurred in one test with dry gasoline at 23°C and severe pitting with wet gasoline at 48°C.

Terne alloy was seriously corroded by a dry methanol-rich fuel at both conditions, but not by a similar ethanol fuel; neither fuel was corrosive when it contained about 5% water. With the blends, serious pitting corrosion occurred only with a phase-separated ethanol blend.

Zinc gave anomalous and inconclusive results in the present tests. Severe pitting corrosion was observed on one coupon with each ethanol-containing fuel except the dry blends of ethanol and ethanol/methanol mixture. However, it occurred only at a milled edge of a coupon, never on one of the large sawn faces^a; a single severe pit occurred also at an edge of a coupon immersed in dry gasoline. The edge pitting with zinc is believed to have resulted from some extraneous factor rather than inherent corrosive effects of the fuels tested. This belief is based on the erratic occurrence of the pitting, its appearance only on an edge, its occurrence with dry gasoline (which is not corrosive to zinc carburetor bodies in service), and its appearance in this series of tests but not in those of the methanol study. Although zinc coupons for both studies were cut from the same zinc ingot, severe pitting in the methanol study occurred only in fuels with a separate aqueous phase, and in areas of the coupon exposed to that phase. A possible though unproved explanation for the edge pitting is that a contaminant or defect in one part of the zinc ingot that was included in several adjacent coupons for the present study made those coupons highly susceptible to local, possibly galvanic, corrosion. The fact that the edge pitting in all five specimens was centered in an area about 18-25 mm from one end of a long side is in keeping with this explanation.

a Coupons were sawed with an abrasive blade from a milled rectangular ingot of zinc.

Table 5.

Corrosivity of Ethanol and Methanol Fuels to Six Metals
(Figures are Averages from Duplicate Tests.)

Fuel	Water With Fuel, wt %	Aluminum				Brass				Magnesium			
		Average Rate		Visual		Average Rate		Visual		Average Rate		Visual	
		mm/yr X 1000		Evaluation		mm/yr X 1000		Evaluation		mm/yr X 1000		Evaluation	
		23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C
Gasoline, dry ^a	-----	0.8	0.0	2	0	0.4	0.3	0.5	0	1.9	0.5	4	1
Gasoline, dry ^b	-----	0.0	0.0	0	0	0.3	0.3	0	0	0.8	1.4	0	0.5
Gasoline + water ^b	1.3	0.9	3.4	0	1	0.1	0.5	0	0.5	3.4	210.	1	4
Alcohol Blends, dry													
10% Ethanol	-----	1.2	0.4	2	0.5	0.5	0.5	0.5	0	0.6	1.5	1	5
3.3% EtOH, 6.7% MeOH	-----	0.5	1.9	0.5	1.5	0.3	0.3	0	0	6.6	3	5	5
18% MeOH + Cosolvent ^c	-----	0.9	0.0	0	0	0.3	0.4	0	0.5	0.5	5.3	0.5	1.5
Alcohol Blends, moist													
10% Ethanol	0.2	0.5	0.0	1	0	0.4	0.3	0.5	0	0.8	0.9	1	1.5
18% MeOH + Cosolvent ^c	0.25	0.9	0.0	0	0	0.4	0.8	0	0	1.4	3.9	0.5	0.5
Alcohol Blends + Aqueous Phase													
10% Ethanol	1.5	0.5	1.1	1	1	0.4	0.4	0.5	0	9.7	51.2	3.5	4
18% MeOH + Cosolvent ^c	1.34	3.3	20.4	0.5	3	0.4	1.0	0	0.5	0.9	13.2	0	2
Enriched Alcohol, dry													
80% EtOH, 20% Hydrocarbon	-----	0.5	0.6	1.5	1	0.3	0.3	0	0	2.9	5	4	4
93% MeOH, 7% Hydrocarbon	-----	0.8	1.8	0	0.5	0.5	0.3	0	1	170,000	>450,000	6	6
Enriched Alcohol, wet													
80% EtOH ^d , 20% Hydrocarbon	6.2	0.4	0.0	0.5	0	0.1	0.3	0	0	5.8	6.5	4	4
93% MeOH, 7% Hydrocarbon	4.8	0.5	2.4	0	0.5	0.4	0.3	0	0	24.0	6.4	1	1

a Data from this study.

b Data from methanol study.

c MeOH + cosolvent mixture = 75 wt % methanol, 5 wt % ethanol, 7.5 wt % *n*-propanol, 12.5 wt % *i*-butyl alcohol.

d 190 proof alcohol, giving calculated 6.2 wt % water in blend.

e Rating code: 0 = No visible corrosion; 1 = No pitting, uniform corrosion; 2 = Slight pitting; 3 = Moderate pitting; 4 = Severe pitting; 5 = Severe general corrosion; 6 = Destructive corrosion, <24 hours.

Table 5. (Cont.)

Corrosivity of Ethanol and Methanol Fuels to Six Metals
(Figures are Averages from Duplicate Tests.)

Fuel	Water With Fuel, wt %	Steel				Terne Alloy				Zinc			
		Average Rate		Visual		Average Rate		Visual		Average Rate		Visual	
		mm/yr X 1000		Evaluation		mm/yr X 1000		Evaluation		mm/yr X 1000		Evaluation	
		23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C
Gasoline, dry ^a	-----	0.3	0.0	0	0	0.3	0.6	0	1	0.5	0.5	3 ^g	1
Gasoline, dry ^b	-----	0.3	0.4	0	0	0.3	2.2	0	0.5	0.4	0.8	0	0
Gasoline + water ^b	1.3	1.0	13.2	0	3.5	0.8	2.3	0	1	3.2	30.2	1.5	4
Alcohol Blends, dry													
10% Ethanol	-----	0.1	0.0	0	0	1.0	0.6	0.5	1	0.5	0.6	1	1.5
3.3% EtOH, 6.7% MeOH	-----	0.3	0.1	0	0	0.3	0.3	0	0	0.5	0.6	1.5	1
18% MeOH + Cosolvent ^c	-----	0.0	0.0	0	0	1.3	0.6	0.5	0	0.4	0.8	1.5	0
Alcohol Blends, moist													
10% Ethanol	0.2	0.1	0.1	0	0	0.3	0.5	0	1	0.5	0.6	3 ^g	1.5
18% MeOH + Cosolvent ^c	0.25	0.0	0.0	0	0	0.0	0.3	0	0	0.4	0.4	0	0
Alcohol Blends + Aqueous Phase													
10% Ethanol	1.5	0.1	2.7	0	4	1.3	1.0	4	2.5	0.5	1.4	2.5 ^g	3
18% MeOH + Cosolvent ^c	1.34	0.0	0.8	0	1.5	0.1	0.4	0	0	0.3	2.0	0	1
Enriched Alcohol, dry													
80% EtOH, 20% Hydrocarbon	-----	0.1	0.3	0	0	0.4	0.4	1	1.5	0.5	0.6	1	3 ^g
93% MeOH, 7% Hydrocarbon	-----	0.0	0.0	0	0	470	380	5	5	5.5	5.5	f	1
Enriched Alcohol, moist													
80% EtOH ^d , 20% Hydrocarbon	6.2	0.3	0.1	0	0	0.5	0.5	1	1	0.6	0.6	2.5 ^g	1.5
93% MeOH, 7% Hydrocarbon	4.8	0.1	0.3	0	0	1.4	1.9	0.5	0.5	0.6	1.1	1.5	1.5

a Data from this study.

b Data from methanol study.

c MeOH + cosolvent mixture = 75 wt % methanol, 5 wt % ethanol, 7.5 wt % *n*-propanol, 12.5 wt % *i*-butyl alcohol.

d 190 proof alcohol, giving calculated 6.2 wt % water in blend.

e Rating code: 0 = No visible corrosion; 1 = No pitting, uniform corrosion; 2 = Slight pitting; 3 = Moderate pitting; 4 = Severe pitting; 5 = Severe general corrosion; 6 = Destructive corrosion <24 hours.

f Crevice corrosion resulting from test method.

g Average includes rating of 4 for one specimen with pitting at coupon edge only.

III.B.2.e. Compatibility of Ethanol Fuels With Non-Metals

Experience in the 1930's showed that pump hoses and fuel pump diaphragms deteriorated more rapidly with the use of gasoline-ethanol blends than with gasoline (477, 499). Clear polyamid filter housings have recently been reported to fail in service with both ethanol and methanol blends (547, 880). In this study we examined the solvent effect of seven different ethanol-containing fuels on twelve fuel system materials. The fuels were the same as those listed in the metal compatibility tests (Section III.B.2.d.) plus Fuel MC-8, 20 vol % ethanol/80 vol % MC-1. Details of test procedure and a list of materials are given in Appendix II.D. Effects of immersion on the several materials are reported in Tables II.D-2 through II.D-13.

Seven materials (e.g., Delrin Acetal, polyethylene, Nylon 6/6, leather, paper, polypropylene and Viton) were only very slightly affected by all test fuels.

At 48°C, Buna-N and Neoprene swelled and were softened in all blends about the same amount as in gasoline, but were not affected by the ethanol fuels with hydrocarbon starting aids. Cork was badly shrunken and shriveled after immersion in all ethanol-containing fuels and subsequent drying. Fiberglass reinforced polyester specimens were yellowed and substantially softened by all ethanol-containing fuels; the reduction of hardness from about 45-50 to zero was an indication that irreversible degradation of the laminate might occur. The immersion of fiberglass specimens in all blends caused loosening of fibers around the

edges. Polyurethane was softened in all ethanol-containing fuels at 48°C and swelled somewhat more than in gasoline; specimens were badly curled and coated with a white residue by the ethanol/methanol combination blend. The immersion of polyurethane in the 190° Proof ethanol fuel resulted in specimens which were crazed, split and cracked on the convex side after drying.

At ambient temperature, fiberglass specimens immersed in the ethanol-methanol combination blend were substantially softened and yellowed; but no effect was found with the ethanol-containing fuels. Polyurethane was softened in all the ethanol-containing fuels.

The same twelve materials were also immersed for 12 weeks at 48°C in two 10 vol % ethanol blends made from denatured alcohol formulas, SWAFCA and CDA-19. There were no significant differences between effects of the denatured and undenatured alcohol blends.

As in the methanol study, it is concluded that some materials used successfully with gasoline deteriorate seriously in ethanol-containing fuels and that careful selection of suitable materials would be required to provide trouble-free fuel systems.

III.B.3.a. Cold Startability

As with methanol, the vapor pressure of ethanol below 10°C is so low that the saturated vapor is not flammable; it has been reported that the air entering the carburetor must be at least 43°C for satisfactory starting on straight ethanol (478).

Bench tests for cold startability, as described in Appendix II.E, were carried out with an equilibrium air distillation apparatus (ADA) that was designed for adiabatic rather than isothermal fuel evaporation. Flammability measurements were made on the saturated vapors from neat ethanol and ethanol with added pentanes and gasoline as starting aids. Minimum flammable temperatures falling between test temperatures were interpolated by means of the explosimeter readings and curves for vapor pressure versus temperature for ethanol and hydrocarbons.

A plot of the minimum flammable temperatures versus hydrocarbon content is shown in Figure 7. Straight ethanol did not vaporize sufficiently at air-fuel inlet temperatures below 30°C to give a flammable (startable) fuel mixture. The addition of 5, 10 and 15 vol % of a 50/50 mixture of *n*-pentane/isopentane to ethanol gave flammable fuel mixtures at supplied fuel and air temperatures down to 3.5, -10 and -27.5°C, respectively. The addition of 10, 20 and 30 vol % of a 72.4 kPa Reid Vapor pressure gasoline by interpolation gave flammable fuel mixtures down to fuel-air inlet temperatures of 12.5, 3.3 and -0°C, respectively. Ethanol with 30 vol % gasoline and 5 vol % pentanes gave flammable fuel mixtures down to -19.5°C.

The test results showed that ethanol would require much more cold starting aid to give mixtures with startability equivalent to methanol. In comparison to methanol, ethanol required the addition of about twice as much pentanes to obtain equivalent cold startability (15 vol % for ethanol versus 7-8 vol % for methanol at about -27°C). Whereas 30 vol % gasoline in methanol gave cold starting down to about -30°C , the same amount of gasoline in ethanol gave cold starting only down to 0°C .

FIGURE 7
MINIMUM FLAMMABLE TEMPERATURE FOR BLENDS OF
HYDROCARBON IN ETHANOL IN
ADIABATIC DISTILLATION AT 1.0 A/F RATIO

III.B.3.b Warm-Up Driveability Testing on a Chassis Dynamometer

Three cars were tested by the CRC driveability procedure with three experimental fuels. See Appendix II.F for description of cars, fuels and test procedures. The fuels tested were a low volatility base gasoline, a 10 vol % ethanol blend and a 22.2 vol % ethanol blend. Properties of the fuels are given in Table III-D. Results of the test are summarized in Table II.F-2 and shown in Figure 8.

The driveability performance of a Buick and a Chevelle (both used in the previous methanol study) with standard carburetors on Fuel WD-1 (base gasoline) and Fuel WD-2 (10 vol % ethanol) were somewhat clouded by the relatively poor repeatability in the total weighted demerit (TWD) values. Because of the poor repeatability of the first three base fuel runs with both the Buick and Chevelle, two additional tests were made on each car. Statistical analyses of the test results are given in Table II.F-3. The average TWD's of the Buick were slightly higher (poorer driveability) with Fuel WD-2 than with Fuel WD-1. There was a 22% probability that the TWD difference might occur by chance alone. The TWD's of the Chevelle were essentially the same on both Fuels WD-1 and WD-2. Both the Buick and Chevelle showed significant increases in TWD's on Fuel WD-3 (22.2 vol % ethanol).

The Buick with a carburetor modified to give close to the same A/F equivalence ratio with Fuel WD-3 as the standard carburetor gave with gasoline, showed a decrease in TWD's on Fuel WD-3 as compared to the runs with the standard carburetor. There was only a 12% probability

that this TWD difference occurred by chance alone. With the Chevelle the slight decrease in TWD's on Fuel WD-3 with a similarly modified carburetor was not significant.

With a Pinto equipped with a 3-way catalyst exhaust converter, both ethanol blends gave significantly higher TWD's than the base fuel, WD-1. This was somewhat surprising because it was anticipated that the oxygen sensor and closed-loop air/fuel ratio control would compensate for the leaning effect of ethanol. However, this closed-loop system is inoperative when coolant temperature is less than 52°C and when the throttle plate is either closed or wide open, and is operative only at intermediate throttle position, and with a warm engine. Therefore the closed-loop system is inoperative through most of the CRC warm-up procedure. This apparently permitted leaning by the alcohol and the poor driveability results obtained in the Pinto.

The results of these limited tests show that the use of 10 vol % ethanol blends can be expected to degrade warm-up driveability of carbureted cars to extents ranging from negligible to pronounced. At 22% ethanol, warm-up driveability was degraded significantly in all three cars tested.

FIGURE 8 **WARM-UP DRIVEABILITY IN THREE CARS** **WITH GASOLINE AND ETHANOL BLENDS**

*EXHAUST O₂ SENSOR AND CARBURETOR FEED-BACK CONTROL

III.B.3.c. Vapor Lock

Bench scale simulation tests for vapor lock, similar to those used in the methanol study, were carried out under "Hill Climb" conditions. The test procedure is described in Appendix II.G. The critical vapor/liquid ratio (V/L) in this procedure is estimated to be about 36, corresponding to borderline vapor lock in an average car, with the maximum speed in climbing a long hill at 38°C limited by vapor lock to 80 kmph. The results are summarized in Table II.G-1 and plotted in Figure 9.

Figure 9 shows that the addition of ethanol to a 56 kPa base gasoline increases the critical V/L much less than addition of the same volume of butane. This is the reverse of what was found previously with methanol and butane blends. The addition of 10 vol % ethanol accompanied by the withholding of 3 vol % butane would represent equal vapor lock, with a net gain of 7.8% in fuel volume or 4.6% in energy relative to the original blend. The increase in V/L with ethanol content is similar, relative to butane, to the increase previously found with a combination of 75% methanol and 25% cosolvent alcohols. A blend of 10 vol % ethanol with this base gasoline would be expected to be marginally vapor locking (V/L = 35-36) in an average car under the hill climbing conditions at 38°C. It would be equal to a blend of 3% butane in the same base, which would have an estimated RVP of 67 kPa, in the range of much commercial Class B gasoline. (Southeastern states summer average is 66 kPa.)

Both ethanol/methanol combination blends, as expected, were found to be severely vapor locking; critical V/L's of over 50 were obtained (see Table II.G-1).

Pure ethanol, with its high latent heat of vaporization and boiling point of 78°C was not vapor locking under the "Hill Climb" conditions.

None of the ethanol fuels enriched with hydrocarbons for cold startability would be as prone to vapor lock at 38°C as many Class B. gasolines. The highest critical V/L's measured were 19 with 15 vol % pentanes and 32 with 5 vol % pentanes plus 30 vol % gasoline.

FIGURE 9.
EFFECTS OF FUEL BLEND COMPOSITIONS ON CRITICAL
V/L RATIO IN BENCH VAPOR LOCK TEST

III.B.3.d Octane Blending Effects of Alcohols

The high octane value of ethanol is a definite asset for its use in gasoline engines. However, few data are available for the blending octane value in recent model cars on the road, specifically the Blending Road Octane Number (BRdON)^a. Also, ethanol and methanol both have much higher sensitivity, or difference between Blending Research Octane Number (BRON) and Blending Motor Octane Number (BMON), than most gasoline stocks. This suggests that present relations between car satisfaction and laboratory measurements of Research Octane Number (RON) and Motor Octane Number (MON), as used in gasoline specifications, may need to be reevaluated for alcohol-gasoline blends. The literature indicates that BRON and BMON vary considerably with the octane (and perhaps other properties) of the base stock, and to some extent (BMON more than BRON) with alcohol concentration. Current interest centers on blending values at around 10 vol % concentration in unleaded regular gasoline, typically 91-93 RON and 82-84 MON.

Blending Research, Motor and Road octane data^b measured at 10 vol % alcohol concentration in unleaded regular gasoline are shown in Table 6 for ethanol, methanol and isobutanol. Road octanes were measured in duplicate in a six-car fleet of 1975-1978 model California cars. Compared to methanol, the average values obtained for ethanol were higher in BMON but were essentially the same, probably within experimental

a Blending octane numbers for an alcohol are calculated from octane numbers measured on a blend and its gasoline component with the assumption of linear blending.

b Data developed by Union apart from the DOE contract.

error, in BRdON and BRON. Isobutanol, included as a representative cosolvent for methanol, was significantly lower than either methanol or ethanol in all three blending values.

Average blending values for methanol and ethanol from Table 6 are compared in Table 7 to relatively recent data reported in the literature for blending in unleaded regular. Most notably, the BRdON's obtained by us for both alcohols are about 15 units lower than those determined elsewhere. We are not sure of the reason or reasons for the differences, but it may be that the emission controls used to meet the more severe standards for recent model California cars reduce engine response to the alcohols as antiknocks. Further data are needed to support or refute this possibility.

It is also apparent in Table 7 that there is much more variation in values reported for BMON of the alcohols than for BRON. This is likely caused by difficulty in maintaining uniform engine operating conditions for MON determinations with alcohol blends. The variability of BMON is further indicated by tests of methanol, ethanol and isopropanol in our laboratory in two closely similar unleaded regulars (0.3 different in RON and MON) nine months apart. (The later determinations for methanol and ethanol are those reported in Table 6.) The two BRON's all agreed within 1.2 numbers, but the second measurements of BMON for the three alcohols were lower than the first by 27, 17 and 8 numbers, respectively. It appears that the MON test method is not reliable for alcohol blends.

Table 6.

Blending Octane Numbers of Alcohols
in Unleaded Regular Gasoline

	<u>Run</u>	<u>Base Unleaded Regular</u>	<u>10 V % Methanol 90 V % Base</u>	<u>10 V % Ethanol^a 90 V % Base</u>	<u>10 V % Isobutanol 90 V % Base</u>
<u>Research Octane</u>	1	90.9	95.2	95.0	92.7
	2	90.8	95.1	95.0	92.8
	Avg.	90.85	95.15	95.0	92.75
<u>Motor Octane</u>	1	82.4	83.7	84.3	83.1
	2	82.5	83.9	84.5	83.1
	Avg.	82.45	83.8	84.4	83.1
<u>Road Octanes^b</u>					
'78 Pontiac Sunbird	1	90.5	92.5	92.5	91.0
(2.47 l., 4 SM) ^c	2	90.5	92.5	92.5	91.0
'78 Pinto (2.29 l., AT) ^c	1	88.0	89.5	89.5	89.0
	2	88.0	89.5	89.5	89.0
'76 Ford Torino	1	88.0	89.0	89.0	88.7
(5.75 l., AT) ^c	2	88.0	89.0	89.0	89.0
'75 Chevelle Malibu	1	85.8	86.3	86.3	86.0
(5.74 l., AT) ^c	2	86.0	86.7	86.7	86.3
'77 Chevy Nova	1	87.4	89.0	89.0	88.4
(4.1 l., AT) ^c	2	87.4	89.0	89.0	88.2
'75 Plymouth Volare	1	87.0	88.0	88.5	88.0
(5.21 l., AT) ^c	2	87.0	88.0	88.5	88.0
6-Car Average		87.80	89.08	89.17	88.55
<u>Blending Octane Numbers</u>					
Research		----	133.9	132.4	109.9
Motor		----	96.0	102.0	89.0
Road		----	100.6	101.5	95.3

a Added as 200 proof specially denatured formula 28A, containing 0.99 V % unleaded regular gasoline.

b Measured on chassis dynamometer at 21°C and 46% relative humidity by modified Uniontown method.

c Engine displacement, liters. Transmission: 4 SM = 4 speed manual, AT = automatic.

Table 7.

Blending Antiknock Value of Alcohols

Car Fleet	Base Gasoline			Blending Values at Nominal 10%						Source
	Octane			Ethanol			Methanol			
	RON	MON	RdON	BRON	BMON	BRdON	BRON	BMON	BRdON	
6 '75-78 Calif. Models	90.9	82.5	87.3	132.4	102.0	101.5	133.9	96.0	100.6	Union, this work
4 '77 Models	90.8	83.6	84.8	----	----	116.8	----	----	----	BERC (529, 881)
4 '77 Models	86.3	79.3	80.5	----	----	115.5 ^a	----	----	----	BERC (529, 881)
4 '77 Models	81.7	74.9	76.2	----	----	122.2 ^a	----	----	----	BERC (529, 881)
None	90.6	83.5	----	129.9	95.6	----	134.8	93.5	----	BERC (546)
None ^b	92.0	84.0	----	136.0	112.0	----	138.0	120.0	----	Union, Methanol Study
None ^c	92.7	83.4	----	128.2	110.5	----	136.2	113.1	----	Union, Methanol Study
None ^d	92.0	82.4	----	135.0	108.4	----	137.0	106.4	----	Union, Methanol Study
10 '67-71 Models	90.9	82.0	88.9	----	----	----	132.9	100.0	116.9	Chevron (3)
10 '67-71 Models	91.8	83.5	89.6	----	----	----	134.8	99.5	112.8	Chevron (3)
10 '67-71 Models	90.7	82.1	89.2	----	----	----	136.7	107.1	120.5	Chevron (3)
6 '75 Models	91.1	84.6	88.5	----	----	----	----	----	113.5	BERC (108, 881)
6 '75 Models	87.1	82.1	86.4	----	----	----	----	----	117.0 ^a	BERC (108, 881)
6 '75 Models	83.8	79.7	82.7	----	----	----	----	----	131.7 ^a	BERC (108, 881)
Average, '75-78 California Models				----	----	101.5	----	----	100.6	
Average, Others				132.3	105.7	116.8	135.5	104.5	115.9	

a Excluded from average; subregular base stock.

b Base gasoline aromatic content: 14 vol %.

c Base gasoline aromatic content: 26 vol %.

d Base gasoline aromatic content: 38 vol %.

III.B.4. Safety

a. Reduction of Ethanol Explosibility by Addition of Hydrocarbons

Vapor pressure and flammability limit data indicate that the saturated vapor of ethanol, like that of methanol is flammable, or explosive, at common temperatures, the indicated flammable range being 10 to 41°C for ethanol and 9 to 41°C for methanol. The explosibility of neat ethanol vapor at room temperature, 23°C, was demonstrated in the laboratory.

Explosibility tests were carried out in an open top can which was covered with plastic food wrap. Vapors from various hydrocarbon-enriched ethanol fuels were pumped through a closed loop system to the can (and back) from a fuel reservoir which was maintained at selected test temperatures. The vapors were ignited by a spark plug which was fitted into the vapor space. In the tests various amounts of both pentanes (50/50 mixture of *n*-pentane and iso-pentane) and gasoline (Reid vapor pressure of 60 kPa) were added. The vapors over ethanol containing either 5 vol % pentanes or 20 vol % gasoline were too rich to ignite at temperatures of -10°C and above. The vapors over ethanol containing either 12.5 vol % pentanes or 35 vol % gasoline were found to be too rich to burn at -20°C and above. The addition of both pentanes and gasolines to ethanol was highly effective in alleviating the explosibility of neat ethanol.

III.B.4.b. Flame Luminosity and Visibility

The use of straight methanol would present a special safety hazard because it burns with a flame that is difficult to see in daylight. However, neat ethanol would not be a problem in this respect because it burns with a highly visible, luminous flame. The presence of either pentanes or gasoline was shown to enhance flame luminosity but the addition of hydrocarbons specifically for this purpose would be unnecessary for ethanol.

III.B.5. Renaturing and Denaturing

The U.S. Bureau of Alcohol, Tobacco and Firearms (BATF) at present permits four types of ethyl alcohol to be distributed in commerce and blended with gasoline for automotive fuel at premises other than ones that are bonded and have a permit from BATF. These are Completely Denatured Alcohol, formula 18 (CDA-18); Completely Denatured Alcohol, formula 19 (CDA-19); proprietary solvents; and a "manufactured article" denatured according to a formula approved for the Southwest Alabama Farmers' Cooperative Association (SWAFCA formula). Neither CDA-18 nor the proprietary solvents are considered suitable for long-term use in automotive fuel because of the denaturants used; the CDA-19 contains acetalcohol and "pyronate" (a product from the destructive distillation of wood), and the proprietary solvents all contain wood alcohol, a partially purified distillate from the destructive distillation of wood. CDA-19 and the SWAFCA formulas are considered more suitable. CDA-19 contains 4.0 gal methyl isobutyl ketone (MIBK) and 1.0 gal kerosene or gasoline per 100 gal ethanol; the MIBK is of some concern to fuel chemists because of its solvency, but CDA-19 has been used in much commercial gasohol. The SWAFCA formula contains 5 gal methanol, 5 gal gasoline, dye and 0.5 gal t-butyl alcohol or MIBK per 89.5 gal of specially denatured alcohol formula 28-A (SDA-28-A); the SDA-28-A in turn contains 1 gal gasoline (as defined by BATF) per 100 gal ethanol.

Three specially Denatured Alcohol formulas, SDA-1, SDA-3-A and SDA-28-A are authorized for use as automotive fuel. However, the

specially denatured alcohols may be received and blended only at bonded facilities that are subject to rigorous inventory control and BATF supervision. Of these three, SDA-28-A is preferred, since it is denatured only with gasoline. SDA-1 and SDA-3-A are denatured with 5 gal of wood alcohol or 5 gal of methyl alcohol, respectively, per 100 gal of ethanol.

Experimental work was carried out on recovering, or renaturing, of ethanol from blends made with the three denatured alcohols of most interest, CDA-19-A, SWAFCA formula^a, and SDA-28-A.^b The objective of this work was to determine whether potable ethanol could be recovered without distillation by simple extractive methods using readily available materials from blends made up from denatured alcohol formulas which have BATF approval for use in motor fuels.

Tests were carried out by extracting 200 ml of various 10 vol % ethanol/gasoline blends with 50 ml of water and washing the resulting 65-68 ml of alcohol/water extract with 30 ml of hydrocarbon solvents to remove traces of dissolved gasoline components. Both *n*-pentane and a pressure appliance fuel (PAF) were used to wash the alcohol extract. PAF, a gasoline stove and lantern fuel, is composed of hydrocarbon distillates which boil in the gasoline range and contains only about 5% aromatics. The ethanol/water extracts washed with PAF had a mild hydrocarbon odor and were therefore also air blown to reduce the odor; in contrast, the low boiling *n*-pentane washed extracts exhibited very little or no hydrocarbon odor and were not air blown.

a With the *t*-butyl alcohol rather than the MIBK option.

b A permit to operate an experimental distilled spirits plant was obtained from BATF in order to conduct this work.

Taste tests (without swallowing) were made on each of the extracts after diluting to give an ethanol concentration of approximately 15 vol %. The results showed that ethanol recovered from blends made from all three denatured alcohol formulas (especially the blends made with formula 28-A) might be deemed sufficiently palatable to drink by a determined consumer even though they contain small amounts of noxious compounds. In general, the extracts from both the CDA-19 and SWAFCA formulas were more unpleasant tasting than the formula 28-A extract but the taste of the recovered alcohols was not highly objectionable. The alcohol recovered from a blend made with the SWAFCA formula would of course be toxic because of its methanol content.

The above experiments showed that renaturing of ethanol from blends which contain approved denaturants can be accomplished by simple extractive methods and might be a problem. Therefore, experimental compounds were tested as denaturants that might serve as a greater deterrent to bootlegging. The objective was to find an additive which would give the recovered alcohol extract a highly objectionable taste. Six compounds were tested: dimethylformamide (DMF), isopropyl alcohol, *n*-butyl alcohol, iso-amyl alcohol, *t*-butyl mercaptan and an odorant (Sindar deodorant oil GD-64262). Except for the latter two compounds, all were tested at a concentration of 5 vol % in the alcohol. All compounds gave the extracted alcohols a more objectionable taste than either the SWAFCA or CDA-19 formula alcohols. However, the DMF was found to be the most effective denaturant tested; it imparted a highly objectionable and

bitter taste to the extracted alcohol. Further research is needed in this area but it appears that the use of substances such as DMF or other appropriate compounds, possibly in combination with another approved denaturant (i.e., methanol, t-butyl alcohol, etc.) may be highly effective for preventing recovery of attractive alcohol from motor fuel blends.

IV. CONCLUSIONS

A number of problems that are known or suspected to accompany the widespread use of ethanol as fuels for automobiles have been identified and studied to characterize them more fully. In general, fewer problems were found with ethanol than with methanol; the existing problems were similar but less severe than those with methanol. Only one modification of neat ethanol, the conversion to gasoline-range hydrocarbons by the Mobil process, appears to solve essentially all problems excepting that of cost.

Because of the limited availability and high cost of ethanol, along with the existence of Federal and state subsidies for blends containing 10 vol % of alcohol, the primary use of ethanol in the U.S. will probably be in blends to supplement gasoline rather than as a substitute for gasoline. The most serious problem with blends is that of phase separation on exposure to water. However, the water tolerance of ethanol blends is much higher than that of methanol. A cosolvent was found to greatly increase water tolerance of an ethanol blend, though ethanol blends do not appear to need added cosolvents. Phase separation would still be a serious problem if blends were distributed in the present gasoline distribution system. The addition of ethanol to gasoline increases the vapor locking tendency but to a much lesser extent than addition of methanol. With methanol blends in gasoline, vapor lock could be corrected by withholding butane but the amount withheld is so great as to result in a net reduction in fuel supply rather than an

increase. In contrast, withholding smaller amounts of butane from ethanol blends can correct the vapor lock problem and result in a net increase in fuel supply.

It appears that wear in roller-vane fuel injection pumps could be a problem with ethanol blends, but it appears to be one that can be alleviated by the use of additives.

As found with methanol, there are also problems with ethanol that are not responsive to fuel modifications other than conversion of the ethanol to gasoline. These problems are poorer warm-up driveability and deterioration of some metals and non-metals used in cars and in fuel distribution systems. These problems and a few others of lesser importance appear to be best treated by appropriate modifications of vehicles and fuel distribution equipment. Warm-up driveability in different carbureted cars was affected much differently by a 10 vol % ethanol blend, effects in three cars ranging from negligible to marked degradation. At 22 vol % ethanol, driveability was degraded much more, to about the same extent as with methanol when blended at an equivalent concentration (16 vol %) in terms of blend oxygen content and leaning effect. A carbureted car equipped with exhaust oxygen sensor and closed loop air/fuel control showed poor warm-up driveability with both ethanol blends because the control system on that car does not function during the warm-up period. Interchanging gasoline and ethanol/ gasoline blends in most present cars appears to be undesirable because of adverse effects on evaporative emissions and the increased likelihood of phase separation.

The widespread use of ethanol/gasoline blends might lead to problems with illicit ethanol recovery or renaturing by simple extractive methods. This problem can probably be solved with the use of new denaturants, such as dimethylformamide, which give the recovered alcohol objectionable taste.

Although ethanol/methanol combination blends were studied only in selected tests, the problems encountered with its use as fuel would generally be intermediate to those of ethanol and methanol blends. The water tolerance of mixed blends was appreciably lower than would be expected than for linear proportionality to the alcohol composition.

The leading problem with the use of neat ethanol in present cars is lack of driveability because the air/fuel ratio requirement and vaporization of the fuel are so different from gasoline that car engines will not run. Assuming suitable engine modifications were made for driveability, startability at low temperatures would continue to be a serious problem. This can be handled by the addition of substantial amounts of gasoline or light hydrocarbons, the amount depending on the temperatures expected. Ethanol, however, requires about twice as much starting aid as methanol to achieve equivalent cold starting properties. Like methanol, straight ethanol is very resistant to vapor lock and the amount of additive needed for cold startability in any climate appears to be tolerable for vapor lock in the same climate.

Addition of hydrocarbons for cold startability helps with some other problems with the use of straight ethanol as fuels. The use of

gasoline can serve as additional denaturant and would also reduce the hazards from explosibility of ethanol vapor in the presence of ignition sources other than static electricity.

Corrosion of metals and degradation of non-metal materials with the ethanol fuel were much the same as those found with blends. Problems can best be avoided by replacing ethanol-susceptible materials with more durable ones. Reduced vehicle range resulting from the low heat of combustion of ethanol could be corrected by the use of larger tanks in new cars.

In summary, 10 vol % ethanol blends can and are being used in current cars without modifications. Problems with filter plugging from loosened dirt and phase separation and, to a lesser extent, with cold starting, driveability, and vapor lock have been reported from field experience. Fuel modifications could help with the phase separation and vapor lock problems but long term reliable operation of most cars may require modifications of the fuel distribution system and of vehicles.

V. RECOMMENDATIONS

In order to more fully define solutions to problems from possible increased use of ethanol in gasoline and to promote the development of practical alternative automotive fuels it is recommended that further research and development be directed to the following areas.

1. A process for manufacturing ethanol and higher alcohols, in preference to methanol, by gasification of coal and catalytic conversion of the synthesis gas.

2. Sound economics for the production of fuel-grade ethanol in comparison to the economics of methanol from coal and liquid hydrocarbon fuels from oil shale and coal.

3. Vehicle evaporative control system modifications to control evaporative emissions from ethanol/gasoline blends.

4. Compatibility of blends with existing vehicle and distribution system materials, and durability of equipment under realistic conditions of use.

5. An improved denaturant package suitable for fuel use that can be approved in a completely denatured alcohol formula.

6. The water tolerance of blends at low alcohol concentrations relevant to gasohol-gasoline mixtures and potential mandating of low-level alcohol usage.

7. Fuel economy effects determined accurately and reliably under realistic conditions.

8. Properties and limits appropriate for laboratory inspection tests, and seasonally adjusted quality control specifications on blends.

9. Possible incompatibility with detergent or other gasoline additives, or any unanticipated performance problems that might be disclosed in well-monitored fleet tests.

BIBLIOGRAPHY

Abbreviations used:

API: American Petroleum Institute
BATF: Bureau of Alcohol, Tobacco and Firearms, U.S. Treasury Dept.
BERC: Bartlesville (Oklahoma) Energy Research Center
BETC: Bartlesville (Oklahoma) Energy Technology Center
CRC: Coordinating Research Council, Inc.
DOE: U.S. Department of Energy
EPA: U.S. Environmental Protection Agency
IECEC: Intersociety Energy Conversion Engineering Conference
IGT: Institute of Gas Technology
SAE: Society of Automotive Engineers
USDA: U.S. Department of Agriculture

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APPENDIX ILITERATURE, INFORMATION RETRIEVAL

Bibliographic reference material was indexed using the same computer program system used in the methanol contract study . The program can produce two types of reference listings. The first is simply a list of all bibliography reference numbers associated with given topic codes. Table I-1 is an example. The second is a listing of complete indexes for each reference called out. Table I-2 is a sample page identifying the index items.

The following three tables provide listings of the codes used, by letter or number, for the reference source (Table I-3), the author's affiliation (Table I-4, 2 pages), and the topics indexed (Table I-5, 3 pages).

A listing of all references with complete index, in alphabetic order of the first author's name, is given in Table I-6 (3 pages). The bibliographic reference numbers associated with each topic code are listed in Table I-7 (3 pages).

ETHANOL STUDY REFERENCES

3/20/79

TOTAL REFS = 138

PAGE 2

TOPIC	REFERENCES CITED
35 8	0
35 9	0
36 0	152 186 451 459 474 476 477 495 499 507 509 518 537 542 559 565
36 9	0
37 8	403 502
37 9	07 492 497
38 8	9 152 186 422 451 454 457 458 459 463 476 477 489 495 497 499 500 502 506 509 510 518 529 537 540 542 544 545 551 556 565
38 9	67 152 186 510 505
39 8	67 510
39 9	075
40 8	0
40 9	0
41 8	115 457 475 492 496 497 553
41 9	9 110 422 451 454 458 459 476 477 481 491 492 499 506 515 518 519 524 532 536 537 540 544 548 551 552 554 557
42 8	0
42 9	0
43 8	451
43 9	152 186 451 457 459 470 476 477 478 499 525 530 540 542
44 8	0
44 9	0

Topic Codes
(See Table I-5)

Reference Numbers

Table I-1.
Examples of Reference Listings by Bibliography Numbers Only

ETHANOL STUDY REFERENCES

3/20/79

TOTAL REFS = 138

PAGE 1

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SCHE	Z	75	455	41	..6..	..8..	9.....												
SCHE	Z	75	456	41	..8..	..8..	9.....												
SCHE	T	77	457	41	..8..	..8.98	9.....	..8..		..8..	8.9..								..8..
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CHRI	N	36	476	99	..1..		9.....	..X89.	8..	8.8..	9.9..								
EGLC	N	36	477	78	..8..	..8..	..X..9.	..X.9.	86..	8.8..	9.9..	9..XX			...X.	...9.			
HUKL	L	78	517	61	..8..		9.....		8.....					..998.	9.....				
STAM	L	78	529	61			9.....			..8..									
COX	X	78	546	61	..8..		9.....			..8..									
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					12345	67890	12345	67890	12345	67890	12345	67890	12345	67890	12345	67890	12345	67890	12345

Example of Reference Listing with Complete Indices

Method Listed
 Author
 Journal (Source)
 (See Table I-3)
 Year
 Reference Number
 Affiliation
 (See Table I-4)
 Topic Codes (See Table I-5)
 278 & 279
 259
 208
 (First two digits at top and bottom of column)

Table I-2.

Table I-3

Reference Source Codes

A	Am. Chem. Soc. pub (other than G, H, I or N)	N	Ind. Eng. Chem.
B	Am. Pet. Inst.	O	Inst. of Petroleum (London)
C	Am. Soc. Mech. Eng. pub	P	IECEC
D	Aut. Eng. or SAE Journal	Q	Patent
E	Auto. News	R	Private Comm.
F	Books	S	SAE Papers, or Special Publications (SP)
G	Chem. Abst.	T	Special Confs.
H	Chem. Eng, C.E. News C.E. Progress	U	Science
I	ChemTech		
J	Inst. of Fuel Journal	W	Union Oil
K	Energy Sources	X	U.S. Govt.
L	DOE Contractors' Conf.	Y	Wards Engine Update
M	Hydrocarbon Proc., or Pet. Refiner	Z	Other

Auto Engine
Manufacturers

00 Unlisted
01 Chrysler
02 Ford (& IIEC)
03 GM
04 Volvo
05 VW
06 Cummins
07 Carter Corp

Oil Companies

10 Unlisted
11 Amoco
12 British Petr.
13 Chevron
14 Continental
15 Exxon
16 Gulf
17 Mobil
18 Phillips
19 Shell
20 Skelly
21 Sun
22 Texaco
23 Union
24 Arco
25 Ashland
26 Marathon
27 Aral

Academic

30 Unlisted
31 UC, Berkeley
32 UC, Livermore
33 Purdue U.
34 Columbia U.
35 UC, Other
36 Iowa State U.
37 MIT
38 Miami, U
39 Michigan, U
40 Missouri, U
41 Nebraska U
42 Santa Clara U
43 Stanford
44 Texas A & M
45 Tulsa U
46 Penn State
47 Minnesota
48 Yale U

Institutes
Assns, Publishers

50 Unlisted
51 API
52 Battelle
53 Eng. Found.
54 Inst. Gas Tech.
55 Math Sci NW
56 Publ Staff, or
book author
57 SWRI
58 SRI
59 ASTM

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<u>Government</u>	<u>Chemical & Engineering Companies</u>	<u>Foreign (Not Otherwise Noted)</u>
60 Unlisted	70 Unlisted	90 Unlisted
61 Bartlesville ERC	71 Comm. Solv.	91 England
62 Bu. Mines	72 DuPont	92 France
63 Illinois	73 Kay Friess	93 Germany
64 DOE, ERCA (not 61)	74 Lurgi	94 Sweden
65 Texas	75 Rockwell	95 Other W. Eur.
66 Bu. Stds.	76 UOP	96 E. Europe
67 USDA	77 Bonner and Moore	97 Brazil
68 Iowa	78 Ethyl	98 Canada
69 Nebraska	79 Kellogg	99 Unknown or none of above
	80 Mid-West Solvents	
	81 Mitre Corp.	
	82 Chem. Const.	
	83 Oxirane	
	84 Gen. Elect.	
	85 Lubrizol	
	86 Engelhard Ind.	

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BOIS	G	40	214	92							9											
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36 8	152 186 458 459 474 476 477 495 499 507 509 518 537 542 559 565 567
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62 9	186 396 467 492 542
63 8	120 396
63 9	396 478 492 542 570
64 8	474 477 494 878
64 9	10 474 477 494
65 8	0
65 9	0
66 8	0
66 9	0
67 8	0
67 9	0
68 8	0
68 9	10
69 8	0
69 9	0
70 8	0
70 9	275 460 467 477 499 526 527 528 539 568 876 878
71 8	0
71 9	0
72 8	366
72 9	393
73 8	393
73 9	0
74 8	0
74 9	474
75 8	0
75 9	0
76 8	0
76 9	0
77 8	0
77 9	0
78 8	478 496
78 9	471 540
79 8	372
79 9	0
80 8	0
80 9	0
81 8	0
81 9	396 460 539 576
82 8	372 422 454 457 458 485 487 518 524 532 533 549 560 561 562 563 564 565
82 9	275 450 460 469 483 484 497 524 526 527 528 539 568
93 8	461 526 527 528 538 539 545 569
83 9	0

Table I-7 (Page 3)
Topic Index Listing

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APPENDIX IIDETAILED DESCRIPTION OF TESTS AND COMPLETE
DATA FOR SEVEN MAJOR TEST AREASA. Water Problems with Blends1. Phase Studies of Several Systems

Ternary phase diagrams were plotted for blends with three gasolines, three alcohol mixtures and water at 20°C. For the purpose of obtaining direct comparisons of ethanol solubility data with those previously obtained for methanol, it was desired to use the same three gasolines of varying aromatic contents that were used in the methanol study. Slight aging of these gasolines had apparently produced oxygenated compounds which caused some anomolous haze when the gasolines contacted water. This problem was solved, however, by treating the gasolines with activated charcoal. The three gasolines, Nos. 1, 2 and 3, had aromatic contents of 14, 26 and 38 vol %, respectively. The properties of the gasolines are given in Table III-A. The alcohols were straight ethanol and two denatured alcohol formulas: CDA-19 (100 gal ethanol, 4 gal methylisobutyl ketone, MIBK, and 1 gal gasoline) and SWAFCA (89.5 gal formula 28-A alcohol,^a 5 gal methanol, 5 gal gasoline and 0.5 gal t-butanol). The mutual solubility boundaries were determined by titrations in a Celstir flask with temperature controlled water circulated through

a Formula 28-A alcohol consists of 100 gal ethanol and 1 gal gasoline.

the jacket. Various mixtures of gasoline and alcohol or alcohol and water were titrated to turbidity with alternate additions of alcohol and the third component. Three or four tie lines were determined for each system by preparing mixtures of known composition, equilibrating at 20°C and analyzing the separated phases for water. The phase boundary curves with a few illustrative tie lines are shown on conventional triangular diagrams in Figures II.A.1-1 to II.A.1-5. With the 26 and 38 vol % aromatic gasoline and straight ethanol the phase boundary points varied in the water-rich leg with the method of titration, i.e., whether gasoline-alcohol mixture was titrated into a water-alcohol mixture or vice-versa (Figures II.A.1-2 and II.A.1-3). This was not so for the low aromatic gasoline (Figure II.A.1-1). These differences can probably be attributed to the differences in the mutual solubilities of the different aromatic gasolines in the various solutions used for the titrations. For these, the phase boundary curves were faired between the two different titration curves. Because of the MIBK and gasoline denaturants present in the CDA-19 formula and the gasoline denaturant in the SWAFCA formula, these two alcohol formulas were not completely immiscible in solutions which contained greater than about 40 wt % water (Figure II.A.1-4 and II.A.1-5).

From the above data, phase boundary curves of gasoline versus water concentration were expressed as a logarithmic function as in the methanol study.^a Plots of the five different systems, e.g., ethanol and water with 14, 26 and 38 vol % aromatic gasolines (gasoline numbers 1, 2 and 3,

a See "Methanol Fuel Modification for Highway Vehicle Use", J. L. Keller et. al., Appendix II.A.2, July 1978 for equations to calculate phase diagram data.

respectively), and two denatured alcohol formulas -- CDA-19 and SWAFCA -- with gasoline No. 2 and water, are shown in Figures II.A.1-6 to II.A.1-10. The variations in the phase boundary titrations are shown in Figures II.A.1-7 and II.A.1-8. Fortunately these occur in the area of least importance, i.e., greater than 20 wt % water on the triangular phase diagrams. End points for these curves were positioned by analyses for water in water saturated gasoline and by measuring the approximate solubility of gasoline in water.

A mathematical equation for each individual tie line was calculated from the composition of the mixture and separated gasoline phase. This equation was used to determine the intersection of the tie line with the water-rich leg of the phase boundary curve. The water phase compositions were not used because they were subject to more error and the leverage involved can unduly affect the other more critical part of the line. Intersections of each tie line with its phase boundary curve gave the coordinates of a point on the tie line determinant. These points and the tie line determinant, a least squares straight line fit to them, are shown in Figures II.A.1-6 to II.A.1-10. The plait point, where the composition of both the lower alcohol-rich phase and the upper gasoline-rich phase are the same, was determined for each system and labelled on each figure.

As in the methanol contract work, cross plots of alcohol concentrations in each phase versus alcohol concentration in the mixture for water contents of 0.125, 0.25, 0.5, 1.0, 2.0 and 4.0 wt % are shown in Figures II.A.1-11 to II.A.1-15 for the five systems.

Plots of the distribution coefficients -- the ratio of alcohol concentrations in the two phases -- versus total alcohol content for the same systems and water content levels are shown in Figures II.A.1-16 to II.A.1-20. The alcohol concentration in the water-richer phase and the distribution coefficients for the five systems in the range of most interest are listed in Table II.A.1-1.

In these ethanol/gasoline/water systems, all mixtures containing 10 wt % alcohol were miscible (single phase mixture) at water contents up to 0.5 wt % water at 20°C. The aqueous phase alcohol concentrations for ethanol-containing mixtures vary only slightly, from about 62-72 wt %. In contrast to methanol, the distribution coefficients of these ethanol systems at a given water content were much lower and did not vary widely. The distribution coefficients all decreased (less alcohol in the water phase) with decreasing water content, increasing alcohol content and increasing gasoline aromaticity.

Table II.A.1-1

Summary of Alcohol Distribution Between Phases For
Different Alcohol/Gasoline/Water Systems at 20°C

<u>Alcohol</u>	<u>Gasoline Aromatic Content, Vol %</u>	<u>Water Wt %:^a</u>	<u>10 Wt % Alcohol</u>					
			<u>Alcohol in Water-Richer Phase, Wt %</u>			<u>Distribution Coefficient^d</u>		
			<u>1.0</u>	<u>2.0</u>	<u>4.0</u>	<u>1.0</u>	<u>2.0</u>	<u>4.0</u>
Ethanol	14		71.7	72.2	65.8	11.1	18.1	25.5
Ethanol	26		68.2	70.3	63.8	9.4	15.2	24.2
Ethanol	38		66.7	68.7	62.1	8.6	13.2	20.7
CDA-19 ^b	26		64.7	67.1	62.3	8.4	15.0	25.5
SWAFCA ^c	26		68.6	70.6	64.5	9.8	16.2	27.0

a Weight % water in total mixture.

b 100 gal Ethanol, 4 gal Methylisobutyl ketone and 1 gal gasoline.

c 89.5 gal Formula 28-A alcohol, 5 gal gasoline, 5 gal methanol and 0.5 gal *t*-butanol.

d Alcohol concentration in the water-richer phase divided by the water concentration in the gasoline-richer phase.

Figure II.A.1-1

TERNARY MUTUAL SOLUBILITY DIAGRAM
AT 20° C

**ETHANOL, GASOLINE (14% AROMATIC)
AND WATER**

Figure II.A.1-2

TERNARY MUTUAL SOLUBILITY DIAGRAM
AT 20° C

**ETHANOL, GASOLINE (26% AROMATIC)
AND WATER**

Figure II.A.1-3

TERNARY MUTUAL SOLUBILITY DIAGRAM
AT 20° C

**ETHANOL, GASOLINE (38% AROMATIC)
AND WATER**

Figure II.A.1-4

TERNARY MUTUAL SOLUBILITY DIAGRAM
AT 20° C

**CDA-19 FORMULA ALCOHOL,
GASOLINE (26% AROMATIC)
AND WATER**

Figure II.A.1-5

TERNARY MUTUAL SOLUBILITY DIAGRAM

AT 20° C

SWAFCA FORMULA ALCOHOL,
GASOLINE (26% AROMATIC)
AND WATER

Figure II.A.1-6

PHASE BOUNDARY DETERMINATIONS
ETHANOL, GASOLINE NO. 1 and WATER AT 20 C

$$F(X) = \text{LN}((100 - \text{WT}\% X) / \text{WT}\% X)$$

WT% OF WATER

PHASE BOUNDARY DETERMINATIONS
ETHANOL, GASOLINE NO. 2 and WATER AT 20 C

$$F(X) = \text{LN}((100 - \text{WT}\% X) / \text{WT}\% X)$$

Figure II.A.1-8

PHASE BOUNDARY DETERMINATIONS
ETHANOL, GASOLINE NO.3 and WATER AT 20 C

$$F(X) = \ln((100 - \text{WT}\% X) / \text{WT}\% X)$$

PHASE BOUNDARY DETERMINATIONS
CDA-19, GASOLINE NO. 2 and WATER AT 20 C

$$F(X) = \ln((100 - \text{WT}\%X) / \text{WT}\%X)$$

Figure II.A.1-10

PHASE BOUNDARY DETERMINATIONS
SWAFCA, GASOLINE NO. 2 and WATER AT 20 C

$$F(X) = \text{LN} ((100 - \text{WT}\%X) / \text{WT}\%X)$$

Figure II.A.1-11

Alcohol Concentration in Separate Phases
Vs. Concentration in Mixture at 20°C
Ethanol, Gasoline No. 1 and Water

Figure II.A.1-12

Alcohol Concentration in Separate Phases
Vs Concentration in Mixture at 20°C
Ethanol, Gasoline No. 2 and Water

Figure II.A.1-13

Alcohol Concentration in Separate Phases
Vs Concentration in Mixture at 20°C
Ethanol, Gasoline No. 3 and Water

Figure II.A.1-14

Alcohol Concentration in Separate Phases
Vs Concentration in Mixture at 20°C
CDA-19, Gasoline No. 2 and Water

Figure II.A.1-15

Alcohol Concentration in Separate Phases
Vs Concentration in Mixture at 20°C
SWAFCA, Gasoline No. 2 and Water

Figure II.A.1-16

Alcohol Distribution Coefficient at 20°C
Vs Concentration in Mixture
Ethanol, Gasoline No. 1 and Water

Figure II.A.1-17

Alcohol Distribution Coefficient at 20°C
Vs Concentration in Mixture
Ethanol, Gasoline No. 2 and Water

Figure II.A.1-18

Alcohol Distribution Coefficient at 20°C
Vs Concentration in Mixture
Ethanol, Gasoline No. 3 and Water

Figure II.A.1-19

Alcohol Distribution Coefficient at 20°C
Vs Concentration in Mixture
CDA-19, Gasoline No. 2 and Water

Figure II.A.1-20

Alcohol Distribution Coefficient at 20°C
Vs Concentration in Mixture
SWAFCA, Gasoline No. 2 and Water

II.A.2. Water Tolerance Determinations

The water tolerance of an alcohol/gasoline blend is defined as the amount of water which can be absorbed by a given blend before phase separation occurs. Phase separation is first detected as an initial appearance of turbidity or cloud point. This point is determined by cooling a blend which contains a measured amount of water and noting the temperature at which cloudiness first appears.

Measurements of water tolerance versus cloud point temperature were made on blends of 5, 10, and 15 vol % ethanol in gasolines containing 14, 26 and 38 vol % aromatics, blends of two denatured alcohol formulas, ethanol/methanol combinations and ethanol with 1-butanol (*n*-butyl alcohol). The two denatured alcohol formulas were CDA-19 and SWAFCA. Except for the ethanol/methanol combinations, all blends contained 10 vol % of ethanol exclusive of any denaturants or cosolvents.

The experimental data are given in Table II.A.2-1. Each individual point on the curve for any given blend was obtained by mixing predetermined amounts of gasoline, ethanol and an ethanol/water mixture. As shown in Table II.A.2-1, some small deviations in ethanol content were obtained from the target ethanol contents. However, the differences were usually 0.01% or less and never as high as 0.1%; all points were therefore plotted as the target values. The water tolerance of ethanol/gasoline blends versus cloud point temperature is shown in Figure II.A.2-1.

The water tolerances of the 11.3 vol % SWAFCA formula (10 vol % ethanol) in three different aromatic content gasolines are plotted in

Figure II.A.2-2 along with a plot for blends which contained 10 vol % ethanol without denaturants in the same gasolines. The experimental data on the SWAFCA blends are given in Table II.A.2-2. As shown by the plot, the SWAFCA formula reduced the water tolerance of each blend slightly as compared to blends of straight ethanol. These small reductions can probably be attributed to the presence of methanol. The water tolerance data for 10.5 vol % CDA-19 in a 26 vol % aromatic content gasoline are given in Table II.A.2-2. As with the SWAFCA formula, the water tolerance of the CDA-19 blend was reduced slightly in comparison to that of the straight ethanol blend in the same gasoline. The water tolerance was also measured of two blends which contained different ethanol/methanol combinations in a 26 vol % aromatic gasoline (see Figure II.A.2-3; data on Table II.A.2-3). The two blends were (1) 3.3 vol % ethanol/6.7 vol % methanol/90 vol % gasoline and (2) 6.7 vol % ethanol/3.3 vol % methanol/ 90 vol % gasoline. As shown in Figure II.A.2-3, the water tolerance of the two blends were drastically reduced from that of the straight 10 vol % ethanol/90 vol % gasoline blend, to values lower than would be estimated by linear interpolation between those of the ethanol and methanol blends.

Water Tolerance of Ethanol/Gasoline Blends vs Temperature

Gasoline Aromatic Content, Vol %	Ethanol Content,* Target, Vol %	Ethanol Content,* Actual, Vol %	Weight % Components			Cloud Point,**°C
			Ethanol	Gasoline	Water	
14	5.0	5.00	5.50	94.36	0.139	- 31.6
↑	↕	5.00	5.50	94.33	0.170	- 16.0
		5.00	5.50	94.29	0.216	+ 5.5
		5.0	5.49	94.25	0.263	+ 20.4
		10.0	10.93	88.79	0.282	- 33.0
		10.01	10.92	88.71	0.366	- 16.6
		9.99	10.89	88.65	0.451	- 1.8
		10.00	10.89	88.57	0.540	+ 11.6
		10.00	10.88	88.56	0.558	+ 14.8
		15.0	16.26	83.26	0.474	- 30.8
		15.00	16.24	83.13	0.627	- 13.4
↓	↕	15.01	16.22	83.03	0.748	- 1.4
		15.0	16.19	82.88	0.931	+ 14.3
14	15.0	15.01	16.19	82.88	0.931	+ 14.3
26	5.0	5.00	5.34	94.52	0.132	<- 38
↑	↕	4.98	5.32	94.54	0.147	- 35.4
		4.95	5.29	94.55	0.160	- 27.3
		4.93	5.27	94.56	0.172	- 21.0
		4.93	5.27	94.56	0.172	- 23.2
		4.95	5.28	94.50	0.222	+ 3.6
		5.00	5.34	94.42	0.247	+ 9.2
		5.0	5.33	94.40	0.265	+ 15.0
		10.0	10.61	89.06	0.327	<- 38
		10.00	10.62	89.02	0.362	- 31.4
		10.00	10.62	89.00	0.386	- 25.5
↓	↕	9.99	10.60	88.95	0.447	- 14.3
		9.99	10.59	88.92	0.494	- 6.5
		10.00	10.60	88.87	0.533	+ 0.4
		9.99	10.57	88.80	0.631	+ 14.6
		15.0	15.83	83.55	0.670	- 28.8
		14.99	15.81	83.50	0.691	- 21.4
		14.99	15.76	83.33	0.913	+ 0.8
		15.00	15.75	83.25	1.003	+ 8.3
		15.0	15.71	83.19	1.097	+ 15.8
26	15.0	14.98	15.71	83.19	1.097	+ 15.8
38	5.0	4.91	5.11	94.72	0.168	- 34.5
↑	↕	4.99	5.14	94.58	0.226	- 12.4
		5.00	5.20	94.54	0.263	+ 13.0
		5.04	5.25	94.49	0.265	+ 8.6
		5.0	5.19	94.53	0.277	+ 17.2
		10.0	10.36	89.21	0.438	- 26.6
		9.99	10.34	89.14	0.522	- 8.8
		9.99	10.32	89.06	0.619	+ 6.2
		10.0	10.33	89.00	0.674	+ 14.4
		15.0	15.47	83.86	0.677	- 34.1
		14.99	15.42	83.70	0.875	- 10.2
↓	↕	14.98	15.38	83.55	1.076	+ 6.8
		15.0	15.36	83.47	1.171	+ 14.6
38	15.0	14.99	15.36	83.47	1.171	+ 14.6

* Water-free basis

** Initial appearance of turbidity. Visible phase separation as droplets typically occurs at 0.3 - 0.6°C lower temperature.

Table II.A.2-2

Water Tolerance of Ethanol/Gasoline Blends
Containing Various Denaturants versus Temperature

Gasoline (Vol % Aromatics)	Weight Percent Components				Cloud Point, °C ^b
	Ethanol ^a	Gasoline	Denaturants	Water	
14	10.87	88.20	0.679 ^c	0.251	-35.0
14	10.86	88.10	0.678 ^c	0.361	-12.4
14	10.85	88.03	0.678 ^c	0.443	+ 0.5
14	14.84	87.91	0.677 ^c	0.579	+18.5
26	10.58	88.45	0.657 ^c	0.338	-31.5
26	10.58	88.42	0.657 ^c	0.362	-27.5
26	10.57	88.40	0.656 ^c	0.442	-12.0
26	10.56	88.33	0.656 ^c	0.521	+ 1.0
26	10.56	88.21	0.655 ^c	0.579	+13.0
26	10.55	88.16	0.655 ^c	0.630	+15.7
38	10.33	88.68	0.645 ^c	0.344	-36.6
38	10.33	88.61	0.645 ^c	0.423	-21.7
38	10.31	88.49	0.649 ^c	0.553	+ 1.0
38	10.30	88.40	0.643 ^c	0.656	+15.6
26	10.57	88.67	0.429 ^d	0.335	-37.5
26	10.56	88.62	0.429 ^d	0.389	-24.4
26	10.56	88.57	0.429 ^d	0.442	-13.4
26	10.55	88.50	0.428 ^d	0.522	- 2.0
26	10.54	88.43	0.428 ^d	0.602	+13.5
26	10.54	88.38	0.428 ^d	0.655	+19.0

a 10 vol % ethanol; water-free basis.

b Initial appearance of turbidity. Visible separation as droplets occurs at 0.3 - 0.6°C lower temperature.

c Mixture of Methanol and *t*-butyl alcohol from Southwest Alabama Farmers' Cooperative Association (SWAFCA) denatured formula.

d Methyl iso-butyl ketone (MIBK) from BATF completely denatured formula 19 (CDA-19).

Table II.A.2-3

Water Tolerance of Ethanol/Methanol/Gasoline Blends versus Temperature

Weight Percent Components			
<u>Alcohols^a</u>	<u>Gasoline^b</u>	<u>Water</u>	<u>Cloud Point, °C^c</u>
10.57 ^d	89.36	0.078	-29.2
10.56 ^d	89.32	0.118	-17.2
10.56 ^d	89.28	0.159	- 7.4
10.55 ^d	89.23	0.212	+ 6.0
10.54 ^d	89.20	0.253	+14.0
10.53 ^d	89.04	0.426	> +20.
10.61 ^e	89.23	0.159	-36.2
10.61 ^e	89.16	0.239	-14.8
10.60 ^c	89.11	0.292	- 3.0
10.59 ^e	89.04	0.373	+11.5
10.58 ^e	88.99	0.426	+20.6

a Water-free basis.

b 26 vol % aromatic content.

c Initial appearance of turbidity, Visible phase separation occurs at 0.3 - 0.6°C lower temperature.

d 3.3 vol % ethanol; 6.7 vol % methanol.

e 6.7 vol % ethanol; 3.3 vol % methanol.

Table II.A-2.4

Water Tolerance of an Ethanol/Gasoline Blend with 1-Butanol Cosolvent
versus Temperature

Weight Percent Components				Cloud Point, °C ^d
Ethanol ^a	Gasoline ^b	1-Butanol ^c	Water	
10.52	85.31	3.487	0.690	-28.4
10.50	85.19	3.482	0.822	- 9.2
10.59	85.08	3.478	0.954	+ 6.0
10.48	84.97	3.473	1.086	+22.0

a Water-free basis; 10 vol %.

b 26 vol % aromatic content.

c 1-Butanol mixed in 1:3 ratio by weight with the ethanol.

d Initial appearance of turbidity. Visible separation as droplets occurs at 0.3 - 0.6°C lower temperature.

FIGURE II.A.2-1
WATER TOLERANCE OF ETHANOL BLENDS IN VARIOUS
GASOLINES AS DETERMINED FROM CLOUD POINT
MEASUREMENTS

Figure II.A.2-2

Water Tolerance as Determined from Cloud
Point Measurements on Blends of SWAFCA Formula
Alcohol and Ethanol in Various Gasolines

FIGURE II.A.2-3
WATER TOLERANCE AS DETERMINED FROM CLOUD POINT
MEASUREMENTS ON BLENDS OF VARIOUS ALCOHOLS IN
GASOLINE NO. 2

II.A.3. Cosolvent Testing

The water tolerance of ethanol blends is much higher than that of methanol blends and probably would not require the use of cosolvents. However a test was carried out with one higher alcohol to examine the effect of a cosolvent. 1-Butanol (*n*-butyl alcohol), which can be produced from grain by an alternative fermentation process, was mixed in a 1:3 ratio by weight with ethanol. A blend of 13.2 vol % of this alcohol mixture was added to a 26 vol % aromatic gasoline. 1-Butanol was a highly effective cosolvent at this concentration. The water tolerance of this blend was almost double that of the straight ethanol as seen in the Figure II.A.2-5 plot (data on Table II.A.2-4).

II.B. Storage Stability of Blends

To judge storage stability, five fuels were stored outdoors in duplicate for 26 weeks -- October through March. The five fuels were:

<u>Fuel Code</u>	<u>Fuel Description</u>
SS-1	Base gasoline (50 vol % unleaded regular gasoline/ 50 vol % light catalytic gasoline)
SS-2	10 vol % ethanol/90 vol % SS-1
SS-3	80 vol % ethanol/5 vol % C ₅ 's/15 vol % gasoline
SS-4	3.3 vol % ethanol/6.7 vol % Methanol/90 vol % gasoline
SS-5	Same as SS-2 with additional antioxidant

The properties are given in Table III-B.

The base gasoline was blended to have somewhat poorer than normal storage stability. Fuels SS-1, SS-2, and SS-4 all contained 17 mg/l of mixed phenol-type antioxidants; Fuel SS-5 contained an additional 34 mg/l of 2,6-di-t-butyl-p-cresol (DBPC) (an effective gasoline antioxidant), for a total of 51 mg/l of antioxidant. Fuel SS-3 contained 29 mg/l of DBPC. Each fuel, in duplicate, was stored in prerusted five-gallon steel cans outdoors in the sun. This simulates severe field storage conditions. Each can was vented through a small opening that permitted air entry but excluded rain.

Stability measurements were made on all samples before and after 13- and 26-weeks storage. Fuel stability was judged by results of the following tests: Induction System Deposit (ISD)^a, ASTM existent gum, peroxide number and induction period tests. The test results are listed in Table II.B-1. Phase separation had occurred in all blends by the 13th week of storage. Results and discussion are given in Section III.B.1.f.

^a Union Oil Test Methods, published in ASTM STP No. 202 (1957).

Table II.B-1

Results^a of 26-Week Storage Stability Tests

Fuel Designation:	<u>SS-1^b</u>	<u>SS-2</u>	<u>SS-3</u>	<u>SS-4</u>	<u>SS-5</u>
DBPC ^c Antioxidant Dosage, mg/l	17.1	17.1	28.5	17.1	51.4
<u>Induction System Deposit Gums (mg/l)</u>					
Initial	7.9	9.1	17.2	7.5	7.9
26-Week	12.7	11.4	8.7	16.0	12.7
<u>ASTM Existent Gums (mg/100 ml)</u>					
Initial	<1.0	<1.0	<1.0	<1.0	<1.0
13-Week	<1.0	1.0	1.0	1.0	<1.0
26-Week	<1.0	<1.0	1.5	1.5	<1.0
<u>Peroxide Number (meq active O₂/l)</u>					
Initial	0.04	0.04	0.04	0.04	0.04
13-Week	0.07	0.08	0.06	0.11	0.07
26-Week	0.02	0.11	0.11	0.07	0.03
<u>Induction Period (minutes)</u>					
Initial	520	388	1440+	399	1038
26-Week	900	902	1440+	918	1440+

a All values are averages of two results.

b Base gasoline is a 50/50 mixture of unleaded regular gasoline and Los Angeles Refinery light fluid catalytically cracked (FCC) gasoline.

c DBPC, di-t-butyl-p-cresol.

II.C. Compatibility of Ethanol Fuels with Metals

Six different metals (i.e., aluminum, brass, magnesium, steel, terne alloy and zinc) were immersed in seven test fuels for 26 weeks to see if ethanol-containing fuels corroded the metals. See Table II.C-1 for a listing of the metals used. The fuels included:

<u>Fuel Code</u>	<u>Fuel Description</u>
MC-1	Unleaded base gasoline No. 4;
MC-2	10 vol % ethanol/90 vol % MC-1;
MC-3	MC-2 + 0.2 vol % water;
MC-4	MC-2 + 1.5 vol % water (phase separation);
MC-5	3.3 vol % ethanol/6.7 vol % methanol/90 vol % MC-1
MC-6	80 vol % ethanol/15 vol % MC-1/5 vol % pentanes;
MC-7	80 vol % 190 proof ethanol/15 vol % MC-1/5 vol % pentanes.

Because of the cost constraints of the project and the negative results obtained in the corrosion study with methanol, no corrosion inhibitors were tested. The properties of the test fuels are summarized in Table III-C.

Each metal was tested in duplicate in each fuel. One-pint jars which were compartmentalized with three pieces of glass pipe were used in the tests. Six preweighed metal specimens were placed into each jar with two specimens per compartment. Specially prepared glass rod separators were inserted to keep the specimens from touching. The samples were stored both at about 48°C in a steam-heated cabinet with mild agitation and at room temperature, 23°C, without agitation for 26 weeks. The jars were opened periodically for replenishment of air, and

the fuels were replaced at 6-week intervals. At the end of the test period the metal specimens were cleaned, reweighed and visually rated. A uniform corrosion rate for all specimens was calculated from the weight loss.

The results of the corrosion tests are summarized in Table II.C-2. Results and discussion are given in Section III.B.2.d.

Table II.C-1

Description of Metals Used in Corrosion Study

	Coupon Dimensions, <u>mm</u>	Density <u>g/cm³</u>
Aluminum - 380 Cast Alloy, SAE 308	25.4 x 51 x 3.2	2.72
Brass - Free Cutting, SAE CA-360	12.7 x 51 x 3.2	8.5
Magnesium - Die Casting Alloy	19 x 51 x 1.6	1.80
Steel - Cold Rolled Carbon Steel, AISI 1010	25.4 x 51 x 1.6	7.86
Terne - 85% Lead, 15% Tin	25.4 x 47.6 x 1.6	10.4
Zinc - Die Casting Alloy #3, SAE 903	25.4 x 51 x 3.2	7.15

Table II.C-2
Results of 26-Week Corrosivity Tests ^a

Fuel Code	Fuel Description	Aluminum				Brass				Magnesium				Steel				Terne Alloy				Zinc			
		Uniform Corrosion Rate		Visual Evaluation ^b		Uniform Corrosion Rate		Visual Evaluation ^b		Uniform Corrosion Rate		Visual Evaluation ^b		Uniform Corrosion Rate		Visual Evaluation ^b		Uniform Corrosion Rate		Visual Evaluation ^b		Uniform Corrosion Rate		Visual Evaluation ^b	
		mm/yr x 10 ³		23°C 48°C		mm/yr x 10 ³		23°C 48°C		mm/yr x 10 ³		23°C 48°C		mm/yr x 10 ³		23°C 48°C		mm/yr x 10 ³		23°C 48°C		mm/yr x 10 ³		23°C 48°C	
		23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C	23°C	48°C
MC-1	Gasoline	1.02	0.00	3	0	0.51	0.25	1	0	2.54	0.51	5	1	0.25	0.00	0	0	0.25	0.76	0	1	0.51	0.51	2	2
		0.51	0.00	1	0	0.25	0.25	0	0	1.27	0.51	3	1	0.25	0.00	0	0	0.25	0.51	0	1	0.51	0.51	4 ^c	0
MC-2	10 Vol % Ethanol/ 90 Vol % MC-1	2.03	0.51	4	1	0.51	0.51	1	1	0.76	1.52	1	5	0.25	0.00	0	0	0.51	0.76	1	1	0.51	0.76	1	2
		0.25	0.25	0	0	0.00	0.25	0	0	0.52	1.52	1	5	0.00	0.00	0	0	1.52	0.51	0	1	0.51	0.51	1	1
MC-3	MC-2 + 0.2 Wt % Water	0.51	0.00	1	0	0.25	0.25	0	0	0.76	1.02	1	2	0.25	0.00	0	0	0.25	0.51	0	1	0.51	0.51	2	1
		0.51	0.00	1	0	0.51	0.25	1	0	0.76	0.76	1	1	0.00	0.25	0	0	0.25	0.51	0	1	0.51	0.76	4 ^c	2
MC-4	MC-2 + 1.5 Wt % Water (Phase Separation)	0.00	0.00	0	0	0.51	0.25	1	0	6.35	92.46	3	4	0.00	2.54	0	4	1.02	0.51	4	1	0.51	1.02	1	3
		1.02	2.29	2	2	0.25	0.51	0	1	12.95	9.91	4	4	0.25	2.79	0	4	1.52	1.52	4	4	0.51	1.78	4 ^c	3
MC-5	3.3 Vol % Ethanol/ 6.7 Vol % Methanol/ 90 Vol % MC-1	0.75	3.81	1	3	0.25	0.25	0	0	1.78	4.06	5	5	0.25	0.00	0	0	0.25	0.25	0	0	0.51	0.51	1	1
		0.25	0.00	0	0	0.25	0.25	0	0	11.43	2.03	5	5	0.25	0.25	0	0	0.25	0.25	0	0	0.51	0.76	2	1
MC-6	80 Vol % Ethanol/ 5 Vol % C ₅ 's/ 15 Vol % MC-1	0.75	0.76	1	1	0.25	0.25	0	0	1.78	3.05	5	4	0.00	0.25	0	0	0.25	0.51	0	3	0.51	0.76	1	4 ^c
		0.25	0.51	2	1	0.25	0.25	0	0	4.06	6.86	3	4	0.25	0.25	0	0	0.51	0.25	2	0	0.51	0.51	1	2
MC-7	80 Vol % 190 Proof Ethanol/ 5 Vol % C ₅ 's/ 15 Vol % MC-1	0.00	0.00	0	0	0.25	0.25	0	0	9.14	4.06	5	3	0.25	0.00	0	0	0.51	0.51	1	1	0.51	0.51	1	1
		0.75	0.00	1	0	0.00	0.25	0	0	10.67	8.89	3	5	0.25	0.25	0	0	0.51	0.51	1	1	0.76	0.76	4 ^c	2

^a Corrosion rates in the methanol study were given in mils/year. To convert mil/yr to mm/yr x 10⁻², multiply by 25.4.

^b Coupon rating code:

0 = No visible corrosion 3 = Moderate pitting

1 = No pitting, uniform corrosion 4 = Severe pitting

2 = Slight pitting

5 = Severe general corrosion

^c Severe pitting of zinc specimens occurred only at coupon edges.

II.D. Compatibility of Ethanol Fuels with Non-Metals

The solvent effect of seven different ethanol-containing fuels on twelve fuel system materials was studied. The materials tested are listed on Table II.D-1. The fuels were the same as those used in the metal compatibility tests, Appendix II-C, plus Fuel MC-8, 20 vol % ethanol/80 vol % MC-1. The properties of the fuels are given in Appendix III-C.

The specimens were immersed in the fuels in sealed pint jars and stored at 48°C in a steam-heated cabinet on shelves that were continuously rocked. Three materials (fiberglass reinforced polyester, polyurethane, and Viton) were also stored at ambient temperature without agitation. The fuels were replenished at 6-week intervals with fresh fuel. The specimens were examined for changes in dimension, weight and hardness. The general overall condition of the specimens was also noted. Results of the observations and measurements on the individual specimens are listed in Tables II.D-2 to II.D-13. Results and discussion are given in Section III.B.2.e.

Table II.D-1

Description of Non-Metallic Specimens^a

Buna-N

Cork-gasket sheet (~1.6mm thick) from auto supply store

Delrin Acetal

High Density Polyethylene

Leather-cowhide (~3.2mm thick) from a handicraft store

Nylon 6/6

Neoprene

Paper - from a Fram gasoline filter (GC-20)

Polyester Bonded Fiberglass - specimens from Owens-Corning with
cut edges sealed with resin

Polypropylene

Polyurethane

Viton

^a Specimen size was approximately 63.5mm x 25.4mm x 3.2mm except where noted above.

Table II.D-2

Physical Changes in Buna-N After Exposure to
Various Fuels at the Reported Test Conditions^a

<u>Buna-N Specimen Numbers</u>	<u>Blend</u>	<u>Temp °C</u>	<u>Duration Weeks</u>	<u>Approximate Change, W%</u>		<u>Hardness</u>	<u>Remarks</u>
				<u>Wt</u>	<u>Length</u>		
							Original Hardness: 72 on Durometer Type A (after 3 sec.)
BN - 1 & 8	MC-1	48	25	+20	+10	48	
BN - 2 & 9	MC-2	48	25	+25	+15	45	
BN - 3 & 10	MC-3	48	25	+25	+15	46	
BN - 4 & 11	MC-5	48	25	+25	+15	43	
BN - 5 & 12	MC-6	48	25	-3	-1	72	
BN - 6 & 13	MC-7	48	25	-2	-1	67	
BN - 7 & 14	MC-8	48	25	+25	+12.5	47	

^a See the text for description of the test condition.

Table II.D-3

Physical Changes in Cork Gasket After Exposure to
Various Fuels at the Reported Test Conditions^a

Cork Gasket Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
C - 1 & 8	MC-1	48	25	+30	-1.5		Good condition after drying
C - 2 & 9	MC-2	48	25	+25	-0.5		Badly shrunken & shrivelled after drying
C - 3 & 10	MC-3	48	25	+20	+1.5		Badly shrunken & shrivelled after drying
C - 4 & 11	MC-5	48	25	-2.5 +12.5	-5) poor +3) duplicates		Badly shrunken & shrivelled after drying
C - 5 & 12	MC-6	48	25	-10	+1.5		Badly shrunken & shrivelled after drying
C - 6 & 13	MC-7	48	25	-12.5	+5		Badly shrunken & shrivelled after drying
C - 7 & 14	MC-8	48	25	+ 1.5 +45	-7.5) poor +2) duplicates		Badly shrunken & shrivelled after drying

^a See the text for description of test conditions.

Table II.D-4

Physical Changes in Delrin Acetal After Exposure to
Various Fuels at the Reported Test Conditions^a

Delrin Acetal Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
Original Hardness: 79 on Durometer Test D-2 (after 15 sec.)							
DA - 1 & 8	MC-1	48	25	+1	0.5	78	
DA - 2 & 9	MC-2	48	25	+2.5	+1	77	
DA - 3 & 10	MC-3	48	25	+2.5	+1	78	
DA - 4 & 11	MC-5	48	25	+2.5	+1	77	
DA - 5 & 12	MC-6	48	25	+2.5	+1	77	
DA - 6 & 13	MC-7	48	25	+2.5	+1	77	
DA - 7 & 14	MC-8	48	25	+3	+1.5	77	

^a See the text for description of test conditions.

Table II.D-5

Physical Changes in High Density Polyethylene After Exposure to
Various Fuels at the Reported Test Conditions^a

High Density Polyethylene Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
Original Hardness: 62 on Durometer Test D-2 (after 15 sec.)							
HDP - 1 & 8	MC-1	48	25	+7.5	+2	55	Slightly pinkish
HDP - 2 & 9	MC-2	48	25	+7.5	+2	55	Yellowed on edges
HDP - 3 & 10	MC-3	48	25	+7.5	+1.5	56	Yellowed on edges
HDP - 4 & 11	MC-5	48	25	+7.5	+1.5	53	Yellowed on edges
HDP - 5 & 12	MC-6	48	25	+2.5	+0.5	58	Traces of yellow and pink
HDP - 6 & 13	MC-7	48	25	+2.5	0	58	No color change
HDP - 7 & 14	MC-8	48	25	+7.5	+1.5	56	Traces of yellow

^a See text for description of test conditions.

Table II.D-6

Physical Changes in Leather After Exposure to
Various Fuels at the Reported Test Conditions^a

<u>Leather Specimen Numbers</u>	<u>Blend</u>	<u>Temp °C</u>	<u>Duration Weeks</u>	<u>Approximate Change, Δ%</u>		<u>Remarks</u>
				<u>Wt</u>	<u>Length</u>	
L - 1 & 8	MC-1	48	25	+5	0	
L - 2 & 9	MC-2	48	25	+10	+2	
L - 3 & 10	MC-3	48	25	+12.5	+1	
L - 4 & 11	MC-5	48	25	+12.5	+1	
L - 5 & 12	MC-6	48	25	+1	+0.5	
L - 6 & 13	MC-7	48	25	+2	+1	
L - 7 & 14	MC-8	48	25	+10	+2.5	

^a See test for description of the test conditions.

Table II.D-7

Physical Changes in Neoprene After Exposure to
Various Fuels at the Reported Test Conditions^a

Neoprene Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
Original Hardness: 72 on Durometer Type A (after 3 sec.)							
NP - 1 & 8	MC-1	48	25	+50	+15	38	
NP - 2 & 9	MC-2	48	25	+40	+15	34	
NP - 3 & 10	MC-3	48	25	+40	+15	33	
NP - 4 & 11	MC-5	48	25	+50	+15	33	
NP - 5 & 12	MC-6	48	25	-2.5	0	66	
NP - 6 & 13	MC-7	48	25	+2.5	+ 2	58	
NP - 7 & 14	MC-8	48	25	+30	+12.5	38	

^a See text for description of test conditions.

Table II.D-8

Physical Changes in Nylon 6/6 After Exposure to
Various Fuels at the Reported Test Conditions^a

Nylon 6/6							
Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
							Original Hardness: 72 on Durometer Type E-2 (after 15 sec.)
N - 1 & 8	MC-1	48	25	-0.2	-0.5	32	
N - 2 & 9	MC-2	48	25	+5	+2	72	
N - 3 & 10	MC-3	48	25	+5	+2	72	
N - 4 & 11	MC-5	48	25	+7.5	+2	70	
N - 5 & 12	MC-6	48	25	+7.5	+2	69	
N - 6 & 13	MC-7	48	25	+10	+5	69	
N - 7 & 14	MC-8	48	25	+5	+2	71	

^a See text for description of test conditions.

Table II.D-9

Physical Changes in Paper Filter After Exposure to
Various Fuels at the Reported Test Conditions^a

Paper Filter Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Remarks
				Wt	Length	
P - 1 & 8	MC-1	48	25	+2.5	0	
P - 2 & 9	MC-2	48	25	+2.5	0	
P - 3 & 10	MC-3	48	25	+2.5	0	
P - 4 & 11	MC-5	48	25	+5	+2.5	
P - 5 & 12	MC-6	48	25	-2.5	0	
P - 6 & 13	MC-7	48	25	-2.5	0	
P - 7 & 14	MC-8	48	25	+1	+0.5	

a. See text for description of test conditions.

Table II.D-10

Physical Changes in Polyester-Reinforced Fiberglass After
Exposure to Various Fuels at the Reported Test Conditions^a

Polyester Reinforced Fiberglass Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Thickness		
Original Hardness: 45-50 on Barcol Impressor Type 934-1							
GRP - 1 & 8	MC-1	48	25	0	0	43	Very slight edge delamination
GRP - 2 & 9	MC-2	48	25	+12.5	+15	0	Yellowed, fibers visible around edges
GRP - 3 & 10	MC-3	48	25	+12.5	+20	0	Yellowed, fibers very apparent around edges
GRP - 4 & 11	MC-5	48	25	+12.5	+20	0	Yellowed, fibers visible around edges, whitish at edges
GRP - 5 & 12	MC-6	48	25	+10	+15	0	Yellowed, semi-opaque
GRP - 6 & 13	MC-7	48	25	+10	+15	0	Yellowed, semi-opaque
GRP - 7 & 14	MC-8	48	25	+12.5	+20	0	Yellowed, fibers visible around edges
GRP - 15 & 22	MC-1	23	25	0	+1	49	No change
GRP - 16 & 23	MC-2	23	25	0	+1.5	48	No change
GRP - 17 & 24	MC-3	23	25	+0.5	0	45	No change
GRP - 18 & 25	MC-5	23	25	+5	+5	17	Yellowed
GRP - 19 & 26	MC-6	23	25	+0.5	+0.5	42	No change
GRP - 20 & 27	MC-7	23	25	+0.5	+0.5	44	No change
GRP - 21 & 28	MC-8	23	25	0	0	44	No change

^a See text for description of test conditions.

Table II.D-11

Physical Changes in Polypropylene After Exposure to
Various Fuels at the Reported Test Conditions^a

Polypropylene							
Specimen				Approximate Change, Δ%			
Numbers	Blend	Temp °C	Duration Weeks	Wt	Length	Hardness	Remarks
							Original Hardness: 68 on Durometer Type D-2 (after 15 sec.)
PPE - 1 & 8	MC-1	48	25	+15	+5	55	
PPE - 2 & 9	MC-2	48	25	+12.5	+5	56	
PPE - 3 & 10	MC-3	48	25	+12.5	+5	53	
PPE - 4 & 11	MC-5	48	25	+12.5	+5	53	
PPE - 5 & 12	MC-6	48	25	+ 5	+2	59	
PPE - 6 & 13	MC-7	48	25	+ 5	+2.5	60	
PPE - 7 & 14	MC-8	48	25	+12.5	+2.5	57	

^a See text for description of test conditions.

Table II.D-12

Physical Changes in Polyurethane After Exposure to
Various Fuels at the Reported Test Conditions^a

Polyurethane Specimen Numbers							
Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks	
			Wt	Length			
					Original Hardness: 44 on Durometer Type D-2 (after 15 sec.)		
UR - 1 & 8	MC-1	48	25	+20	+10	43	Darkened
UR - 2 & 9	MC-2	48	25	+40	+20	20	
UR - 3 & 10	MC-3	48	25	+40	+20	18	Curled
UR - 4 & 11	MC-5	48	25	+40	+20	10	Badly curled, white residue
UR - 5 & 12	MC-6	48	25	+30	+15	16	
UR - 6 & 13	MC-7	48	25	+30	+20	6	Crazed, split and cracked on convex side after drying
UR - 7 & 14	MC-8	48	25	+40	+20	17	
UR - 15 & 22	MC-1	23	25	+20	+10	42	Darkened
UR - 16 & 23	MC-2	23	25	+40	+15	26	
UR - 17 & 24	MC-3	23	25	+40	+15	22	
UR - 18 & 25	MC-5	23	25	+50	+20	19	
UR - 19 & 26	MC-6	23	25	+25	+10	27	
UR - 20 & 27	MC-7	23	25	+30	+15	23	
UR - 21 & 28	MC-8	23	25	+40	+15	25	

^a See text for description of test conditions.

Table II.D-13

Physical Changes in Viton After Exposure to
Various Fuels at the Reported Test Conditions^a

Viton Specimen Numbers	Blend	Temp °C	Duration Weeks	Approximate Change, Δ%		Hardness	Remarks
				Wt	Length		
Original Hardness: 73 on Durometer Type A (after 3 sec.)							
V - 1 & 8	MC-1	48	25	+5	+3	65	
V - 2 & 9	MC-2	48	25	+5	+5	60	
V - 3 & 10	MC-3	48	25	+5	+5	60	
V - 4 & 11	MC-5	48	25	+5	+5	59	
V - 5 & 12	MC-6	48	25	+2	+5	62	
V - 6 & 13	MC-7	48	25	+3	+2	62	
V - 7 & 14	MC-8	48	25	+5	+5	60	
V - 15 & 22	MC-1	23	25	+2.5	+1.5	68	
V - 16 & 23	MC-2	23	25	+5	+2.5	63	
V - 17 & 24	MC-3	23	25	+5	+3	62	
V - 18 & 25	MC-5	23	25	+5	+5	59	
V - 19 & 26	MC-6	23	25	+3	+2	63	
V - 20 & 27	MC-7	23	25	+3	+2	64	
V - 21 & 28	MC-8	23	25	+5	+3	62	

^a See text for description of test conditions.

II.E. Cold Startability of Ethanol Fuels

The cold startability tests on ethanol and ethanol with starting aids were made with the use of an equilibrium air distillation apparatus (ADA) which was used in the previous methanol study. The ADA was similar to that used for fundamental gasoline studies in the 1930's except that it was designed for isothermal fuel evaporation. The heart of the apparatus was a 5-meter coil of 12-mm diameter glass tubing surrounded by insulation and a thermally controlled and further insulated jacket. Streams of air and fuel, metered separately, were brought to test temperature in copper coils in a temperature-controlled bath and combined at the top entrance to the insulated glass coil. The temperature of the evaporatively cooled equilibrium air/fuel (A/F) mixture leaving the coil was measured in a vapor/liquid separating chamber; unevaporated fuel was measured and the fuel content of the effluent vapor was indicated by explosimeter measurements on the vapor.

In the cold startability tests, equal amounts by weight of air and fuel were used (A/F ratio = 1) to simulate the air-fuel mixture in an engine in a fully choked cold starting mode. The air and fuel rates ranged from about 8 to 11 g/min. The air-fuel mixture at a predetermined temperature was metered into the ADA until the temperature of the vapors reached equilibrium; this process usually required from one to two hours, depending on the test temperature. The run was started when the equilibrium temperature remained constant for at least five minutes.

Cold startability at the inlet temperature was inferred from explosimeter readings using a Bacharach combustible gas detector on the separated vapor.

Cold startability tests in the ADA were carried out on both straight ethanol and ethanol with hydrocarbons added as starting aids. The test data are given in Table II.E-1. Minimum flammable temperatures falling between test temperatures were interpolated by means of the explosimeter readings and curves for vapor pressure versus temperature for ethanol and hydrocarbons (Figure 2). Results and discussion are given in Section III.B.3.a.

Table II.E-1

Cold Startability Test Data on Ethanol with Added Hydrocarbons as Starting Aids

<u>Air & Fuel Inlet Temp., °C</u>	<u>Hydrocarbon Type Added, Vol %</u>	<u>Air Flow Rate, g/min.</u>	<u>Fuel Flow Rate, g/min.</u>	<u>Equilibrium Temp., °C</u>	<u>Explosimeter Reading^a</u>
+20	-----	8.94	8.89	+8.9	0.65
+24	-----	8.79	9.14	+10.0	0.77
+28	-----	8.78	9.39	+13.3	0.87
+41	-----	8.82	9.18	+18.3	>1.0
0	Gasoline, ^b 10	9.97	8.52	-7.8	0.59
0	Gasoline, 20	9.59	9.32	-7.8	0.80
0	Gasoline, 30	9.24	9.37	-7.2	~1.02
0	C ₅ 's, 5	9.06	9.38	-8.3	0.79
0	C ₅ 's, 10	9.84	9.39	-8.3	>1.0
-10	C ₅ 's, 10	10.30	9.30	-17.2	1.01
-20	C ₅ 's, 15	10.79	8.77	-22.8	>1.0
-30	C ₅ 's, 15	10.95	9.09	-32.8	0.85
-20	Gasoline, 30	10.22	9.23	-24.4	0.95
	C ₅ 's, 5				
+10	C ₅ 's, 5	8.94	9.70	+3.9	~1.0
+10	Gasoline, 10	9.56	9.59	+1.7	0.85
+10	Gasoline, 20	9.54	9.59	+0.6	1.01
+20	Gasoline, 10	9.03	9.74	+7.2	1.1

a Flammability of vapor was measured on a Bacharach combustible gas detector, Model CP220H.

Readings of 1.0 or greater indicate a combustible mixture.

b 72.4 kPa RVP gasoline.

II.F. Warm-Up Driveability Tests On a Chassis Dynamometer

Warm-up driveability tests were carried out in three cars on the chassis dynamometer with several experimental fuels. The cars selected for this work were:

	<u>Odometer Reading At Beginning of Test</u>
1975 Chevelle V-8, 5.7 l engine	55,685 km
1976 Buick Skyhawk, V-6, 3.8 l engine	58,362 km
1978 Pinto 4-cylinder, 2.3 l engine	17,428 km

The Chevelle and Buick were both used in the previous driveability testing with methanol and were equipped with standard carburetted systems. The Pinto was equipped with an exhaust oxygen sensor and carburetor feed-back control. Modified carburetors, which were adjusted for blends and were used in the methanol study, were available for both the Buick and Chevelle. These carburetors decreased the A/F ratio of the cars running on blends to the equivalence ratio of the same cars with standard carburetors running on straight gasoline.

Three test fuels were used; they were: (1) a low volatility unleaded base gasoline (59 kPa RVP), WD-1; (2) 10 vol % ethanol/90 vol % gasoline, WD-2; and (3) 22.2 vol % ethanol/77.8 vol % gasoline, WD-3 (for fuel properties, see Table III-D. The ethanol content of Fuel WD-3 gave the blend a stoichiometric A/F ratio of 13.3, approximately the same as for a blend containing 15.6 vol % methanol that was used previously in the driveability work with methanol. This fuel composition was designed for use with the modified carburetors for the Buick and Chevelle.

Tests were conducted by the CRC driveability test procedure. (See Table II.F-1.) The cars were thoroughly purged with test fuel and parked overnight at minimum temperatures from 8° to 13°C. They were then moved into the weatherized chassis dynamometer without starting the engine, and tested at 16°C air temperatures. Performance data, in the form of CRC Total Weighted Demerits (TWD)^a for the three cars and three fuels tested are listed in Table II.F-2. All fuels were tested at least in triplicate. Average results, standard deviation and the deviation from the means are listed in Table II.F-3 and are plotted in Figure 3. Results and discussion are given in Section III.B.3.b.

a TWD is the sum of the demerits incurred in cars during various driving modes in the CRC test procedure. See Table II.F-1.

Table II.F-1.

CRC Driveability Test Procedure and Data Recording Instructions1. Cold Start and Driveaway

- A. Record all necessary test information at top of data sheet. Include overnight low temperature and run temperature.
- B. Start engine per Owner's Manual procedure. Record start time.
- C. Record engine idle quality in neutral after start; with foot removed from throttle pedal (fast idle cam).
- D. If engine stalls repeat steps B and C. Record number of stalls.
- E. Allow engine to idle 15 seconds. Apply brakes (right foot), shift to normal drive range and record engine idle quality. If engine stalls, restart immediately. Record number of stalls. Idle 5 seconds in drive.

This completes the start-up portion of the procedure. Space is provided on the data sheet to record the intensity of any backfires which might occur during the start-up procedure.

- F. After 5 sec in drive, make a light throttle acceleration from 0-40 km/hr at constant throttle opening beginning at a pre-determined manifold vacuum. Cruise at 40 km/hr. At 0.32 km open throttle to the detent position and accelerate from 40 to 56 km/hr at constant throttle in high gear. Decelerate to a stop, and at 0.48 km make a WOT acceleration from 0 to 55 km/hr. Decelerate to 16 km/hr and at 0.64 km accelerate at light throttle from 16 to 40 km/hr. Manifold vacuum corresponding to the throttle position for the start of each acceleration is posted in each car.
- G. During the above maneuvers observe and record the severity of any malfunctions such as the following:
 - 1. Hesitations
 - 2. Stumbles
 - 3. Surge
 - 4. Stalls
 - 5. Backfires

Table II.F-1 (Cont.)

- H. At 0.64 km, brake moderately to a stop on the right side of the roadway. Idle for 30 seconds in drive. Record idle quality and number of stalls.
- I. Perform steps F, G, and H three times (2.4 km).
- J. After completing 30 sec idle, make a crowd acceleration (constant predetermined vacuum) from 0-72 km/hr. 0.64 km is provided for this maneuver. Decelerate from 72 to 40 km/hr, and open throttle to detent position and accelerate from 40-56 km/hr. At 3.2 km decelerate to a stop and accelerate WOT from 0 to 56 km/hr. Decelerate to 16 km/hr and accelerate 16 to 40 km/hr at light throttle. Rate and record malfunctions in these maneuvers as in step G. Idle 30 seconds in drive as in step H.
- K. Perform step J three times. Total course is 5.8 km.

CRC Driveability Demerit Rating System

<u>Malfunction</u>	<u>Demerits</u>		
Starting Time, sec	Sec. -2.0 ^a (but not less than zero)		
Stall at idle	8		
Stall when driving	32		
	<u>Trace (T)</u>	<u>Moderate (M)</u>	<u>Heavy (H)</u>
Idle Roughness	1	2	4
Surge	4	8	16
Hesitation, Stumble or Backfire	6	12	24

Total Weighted Demerits (TWD) is the sum of the demerits incurred in each of the 35 maneuvers (starting, idling and various driving modes) in the test sequence. If more than one malfunction is recorded for any particular maneuver, only the one giving the highest demerit score is counted.

a Time in seconds required to start engine minus 2.0, but record negative values as zero.

Summary of Warm-Up Driveability
Test Results

	Fuel		
	Base Gasoline, WD-1	10 Vol % Ethanol, WD-2	22.2 Vol % Ethanol, WD-3
Stoichiometric A/F Ratio	14.56	13.99	13.29
	<u>TWD^a</u>	<u>TWD^a</u>	<u>TWD^a</u>
V-6 Buick			
Run 1	61	149	599
2	257	279	468
3	173	215 ^b	260
4	90	NR ^b	NR
5	<u>143</u>	<u>NR</u>	<u>NR</u>
Average	145	214	442
Standard Deviation ^d	77	65	171
S.D. Mean	34	38	99
V-6 Buick, Mod. Carb.			
Run 1	NR	NR	257
2	NR	NR	264
3	NR	NR	<u>212</u>
Average	--	--	244
Standard Deviation ^d	--	--	28
S.D. Mean	--	--	16
V-8 Chevelle, Std. Carb.			
Run 1	63	164	304
2	264	230	286
3	222	174	403
4	172	NR	NR
5	<u>182</u>	<u>NR</u>	<u>NR</u>
Average	181	189	331
Standard Deviation ^d	75	36	63
S.D. Mean	34	21	36
V-8 Chevelle, Mod. Carb.			
Run 1	NR	NR	376
2	NR	NR	236
3	NR	NR	<u>245</u>
Average	--	--	286
Standard Deviation ^d	--	--	78
S.D. Mean	--	--	45
Pinto 4, Std. Carb. ^c			
Run 1	266	450	666
2	337	575	690
3	<u>269</u>	<u>647</u>	<u>603</u>
Average	291	557	653
Standard Deviation ^d	40	100	48
S.D. Mean	23	58	26

a Total Weighted Demerits per CRC scoring.

b NR = Not run.

c Equipped with exhaust oxygen sensor and carburetor feed-back control.

d Standard Deviation of test results.

Table II.F-3

Statistical Analyses of Driveability Test DataLegend

N = Number of test runs.

 $\overline{TWD}$ = Average Total Weighted Demerits. $S_{\overline{TWD}}$ = Standard deviation of $\overline{TWD}$. Δ = Difference between two designated values.

P = % probability.

Car	Fuel A	Fuel B	A			B			Δ				p^a	p^b
			N	$\overline{TWD}$	$S_{\overline{TWD}}$	N	$\overline{TWD}$	$S_{\overline{TWD}}$	N	$\Delta \overline{TWD}$	S_{Δ}	$\frac{\Delta}{S_{\Delta}}$	(%)	(%)
Buick	Base	10% EtOH	5	144.8	34.2	3	214.3	37.5	6	69.5	50.8	1.37	75-80	22
Buick	Base	22% EtOH	5	144.8	34.2	3	442.3	98.7	6	297.5	104.5	2.85	95-97.5	3.0
Buick	22% EtOH, Std. Carb.	22% EtOH, Mod. Carb.	3	442.3	98.7	3	244.3	16.3	4	198.0	100.0	1.98	80-90	12
Chev.	Base	10% EtOH	5	180.6	33.6	3	189.3	20.5	6	8.7	39.4	0.22	<20	83
Chev.	Base	22% EtOH	5	180.6	33.6	3	331.0	36.4	6	150.4	49.5	3.04	>97.5	2.3
Chev.	22% EtOH, Std. Carb.	22% EtOH, Mod. Carb.	3	331.0	36.4	3	285.7	45.2	4	45.3	58.0	0.78	50-60	48
Pinto	Base	10% EtOH	3	290.7	23.2	3	557.3	57.6	4	266.6	62.1	4.29	98-99	1.2
Pinto	Base	22% EtOH	3	290.7	23.2	3	653.0	25.9	4	362.3	34.8	10.4	>99.9	<0.1
Buick	10% EtOH	22% EtOH	3	214.3	37.5	3	442.3	98.7	4	228.0	105.6	2.16	90	10
Chev.	10% EtOH	22% EtOH	3	189.3	20.5	3	331.0	36.4	4	141.7	41.8	3.39	95-97.5	2.8

a Confidence that $\Delta \overline{TWD}$ is >0 based on t table for n degrees of freedom.
(Reference Croxton & Cowden, pp 651-653.)

b % Probability of this difference by chance alone.

II.G. Vapor Lock

Laboratory vapor lock tests were patterned after the "Hill Climb" procedure used previously.^a This procedure simulates the fuel flow in a car, loaded with four passengers plus luggage, that idles for several minutes at 38°C ambient temperature and then climbs a steady 6% grade with moderate acceleration. It is limited by vapor lock to 80 kmph maximum speed. Moderate acceleration in this case is defined as taking 100% more time to any speed than WOT acceleration on level road. The limiting fuel vapor/liquid (V/L) ratio was estimated to be about 36 in this procedure. The critical point in the acceleration was after 20 seconds elapsed time. Fuel temperature after 20 seconds' acceleration was therefore used to determine V/L for the test fuels under the Hill Climb conditions.

The bench-scale vapor lock test apparatus which had been used in the methanol study was reassembled for use with ethanol. The apparatus was modified slightly, mainly by replacing the peristaltic feed pump with a gear pump and a larger diameter fuel conditioning coil. These modifications improved the precision of measurements by reducing background pulsations in the fuel outlet temperature tracings. A typical temperature trace is shown on Figure II.G-1.

In the bench test, fuel from a 0°C reservoir was heated to typical fuel tank temperature and pumped by a gear pump through an insulated electrical heater (simulated fuel pump), where electrical energy was

a For a more detailed description of the vapor lock test procedure, see "Methanol Fuel Modification for Highway Vehicle Use - Final Report", J. L. Keller et al , Appendix II.H., July 1978.

added at a rate to match the net heating rate of an automobile fuel pump during hot idle. Heat capacity of the "pump" was matched to that of fuel consumed during 10 minutes idling in the same ratio as found in a typical car. A fast response shielded thermistor probe in the effluent stream was connected to a recorder and provided a continuous measurement of the temperature of the effluent fuel, liquid and vapor. After ten minutes of "idle" the fuel flow rate was increased, without changing the electrical energy input, to simulate the average consumption rate under "Hill Climb" conditions with moderate acceleration. Temperature of the effluent fuel was read after 20 seconds WOT acceleration, the critical point in the acceleration. The fuel V/L ratio corresponding to that temperature was then taken from a previously determined curve of V/L versus temperature for that fuel and interpreted as described below.

Table II.G-1 lists the fuels tested and the results. The fuels include: a base gasoline of 56 kPa RVP; blends of ethanol, ethanol-methanol mixtures and butane in the base gasoline; pure ethanol; and ethanol enriched with pentanes or pentanes plus gasoline. The properties of the vapor lock fuels are given in Tables III-E and III-F. The critical V/L ratios are plotted against the percent added component in Figure 4 for the blends of ethanol and butane in gasoline and for ethanol enriched with pentanes. (Vapor lock in an average car is estimated to occur at a V/L of 36 for the procedure being simulated.) V/L vs temperature curves for the several fuels are shown in Figures II.G-2, II.G-3 and II.G-4. Results and discussion are given in Section III.B.3.c.

Table II.G-1

Vapor Lock Test Results on Blends

<u>Fuel Designation</u>	<u>Fuel Composition</u>	<u>Temperature, °C^a</u>			<u>Equivalent V/L at Critical Condition</u>
		<u>Stabilized</u>	<u>10 Min. Idle</u>	<u>20-Second Hill Climb, Critical Condition</u>	
VL-1	Base Gasoline	54.6	73.5	64.8	23.1
VL-2	5 vol % EtOH	53.3	67.4	58.2	32.2
VL-3	10 vol % EtOH	53.3	64.6	57.2	34.2
VL-4	15 vol % EtOH	53.5	64.7	57.8	38.3
VL-5	3.3 vol % EtOH/ 6.7 vol % MeOH	51.9	60.7	54.1	63
VL-6	6.7 vol % EtOH/ 3.3 vol % MeOH	52.4	62.7	56.7	53.3
VL-7	2% Butane	53.9	73.2	63.7	32.3
VL-8	5% Butane	53.5	72.1	62.0	39.7
VL-9	EtOH	53.8	71.6	62.6	<1
VL-10	VL-9 + 5 vol % C ₅ 's	53.5	70.1	62.7	1.8
VL-11	VL-9 + 10 vol % C ₅ 's	53.3	66.8	59.0	12.2
VL-12	VL-9 + 15 vol % C ₅ 's	53.5	65.1	58	19.3
VL-13	VL-9 + 5 vol % C ₅ 's + 30 vol % Gasoline	53.4	65.2	58.4	31.7

a All temperatures are averages of at least two tests from the laboratory bench scale vapor lock test apparatus.

Figure II.G-1

Bench Scale Vapor Lock Test
Simulated Fuel Pump in Hill Climb Procedure
at 37.8°C Air Temperature

Figure II.G-2

T-V/L PLOTS OF GASOLINE AND ETHANOL BLENDS:
MEASURED OVER MERCURY

Figure II.G-3

T-V/L PLOTS OF GASOLINE AND BUTANE BLENDS:
MEASURED OVER MERCURY

**T-V/L PLOTS OF ETHANOL AND ETHANOL WITH ADDED
HYDROCARBONS: MEASURED OVER MERCURY**

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APPENDIX IIIProperties of Test Fuels

All available fuel properties are given in this Appendix for the base gasolines, alcohol/gasoline blends and ethanol fuels used in this study. The properties for a given set of fuels are grouped by the area of study. The properties of all base gasolines are given in Table III-A along with a note on the primary use of each gasoline. The three full-boiling range gasolines (Blends 1, 2 and 3 in Table III-A) are the same fuels which were blended and used in the methanol contract study; these fuels were used for phase separation studies.

Table III-A

Properties of Gasolines Used in Ethanol Study

Gasoline Blend Number:	1	2	3	4	5
Fuel Description:	Low Aromatic	Medium Aromatic	High Aromatic	Unleaded Regular Base	Unleaded Regular Base
Primary Fuel Use:	Phase Studies			Compatibility Tests	Microbial Attack Tests
Hydrocarbon Type, FIA Vol %					
Aromatics	14.0	26.3	37.6	31.5	49.7
Olefins	10.8	6.7	1.8	1.0	2.3
Saturates	75.2	57.0	60.6	67.5	48.0
Octane Number					
RON, Research Octane Number	92.0	92.3	92.6	94.2	96.3
MON, Motor Octane Number	84.2	33.8	83.4	85.6	85.4
(R+M)/2	88.1	38.1	88.0	89.9	
Density at 15°C, g/cm ³	0.7162	0.7379	0.7576	0.7433	0.7670
Reid Vapor Pressure, kPa	72.4	69.0	71.7	55.8	73.7
D-86 ASTM Distillation, °C at % Evap.					
IBP	31.1	29.4	28.3	30.0	33.3
5	40.0	40.6	40.6	47.8	46.1
10	42.7	48.3	50.0	57.8	55.6
20	60.0	62.2	66.7	77.8	74.4
30	72.8	76.7	83.3	93.3	93.3
40	85.0	88.9	97.8	103.3	106.7
50	96.1	101.7	109.4	113.3	114.4
60	105.6	113.3	120.0	123.3	122.2
70	116.1	124.4	130.0	134.4	130.6
80	133.3	141.1	142.8	148.9	141.7
90	160.6	158.3	160.6	170.0	160.0
95	177.8	175.6	177.8	190.0	196.7
EP	196.7	203.3	205.0	210.6	197.8
% Recovered	97.0	97.5	97.0	97.5	95.0
Botts	1.1	1.3	1.1	1.0	1.0

Table III-B

Properties of Fuels Used in Storage Stability Tests

Fuel Designation:	SS-1 ^a	SS-2	SS-3	SS-4	SS-5
Fuel Composition:	Base	10 vol %	80 vol %	3.3 vol %	b
	Gasoline	Ethanol	Ethanol/	Ethanol/	
		in SS-1	5 vol %	6.7 vol %	
			C ₅ 's/	Methanol	
			15 vol %	in SS-1	
			Gasoline		
			No. 4		
Density, g/cm ³ at 15°C	0.7283	0.7329	0.7790	0.7329	b
ASTM D-86 Distillation, °C at % Evaporated					
IBP	31.7	32.8	46.7	32.2	b
5	42.8	40.6	61.1	39.4	
10	48.3	45.0	72.2	42.8	
20	56.7	50.6	76.1	47.2	
30	65.0	55.0	76.7	51.1	
40	74.4	60.0	77.2	55.0	
50	85.0	63.9	77.2	65.6	
60	95.6	83.9	77.8	90.0	
70	107.8	100.6	77.8	103.3	
80	123.9	115.0	77.8	119.4	
90	148.3	143.3	77.8	142.8	
95	171.1	161.1	78.9	162.8	
EP	190.6	186.7	105.0	187.8	
% Rec.	98.0	98.0	99.0	98.0	
Botts	1.0	1.0	1.0	1.0	

a 50 Vol % unleaded regular gasoline No. 4/50 vol % Los Angeles Refinery light catalytically cracked gasoline.

b Fuel SS-5 is the same composition as Fuel SS-2 with additional antioxidant.

Table III-C

Properties of Fuels Used in Metal Corrosion,
Non-Metal Compatibility and Paint Damage Studies

Fuel Designation	MC-1	MC-2	MC-5	MC-6	MC-7	MC-8	MC-9	MC-10
Fuel Description	Gasoline No. 4	10 Vol % EtOH/ 90 Vol % MC-1	6.7 Vol % MeOH/ 3.3 Vol % EtOH/ 90 Vol % MC-1	80 Vol % EtOH/ 15 Vol % MC-1/ 5 Vol % Pentanes	80 Vol % 95% EtOH/ 15 Vol % MC-1/ 5 Vol % Pentanes	20 Vol % EtOH/ 80 Vol % MC-1	10 Vol % EtOH/ 0.4 Vol % MIBK/ ^a 89.6 Vol % MC-1	10 Vol % EtOH/ 1.3 Vol % Denaturants ^b / 88.7 Vol % MC-1
Density, g/cm ³ at 15°C	0.7433	0.7653	0.7658	0.7805	0.7986	0.7683	0.7658	0.7662
ASTM D 86 Distillation °C at % Recovered								
IBP	30	42	38	46	39	39	36	35
5	48	53	48	64	58	54	48	48
10	58	58	52	70	69	59	53	53
20	78	64	58	75	75	66	63	61
30	93	69	63	76	76	71	68	67
40	103	89	89	77	77	73	80	76
50	113	110	109	77	77	77	106	107
60	123	121	120	77	77	113	118	117
70	134	132	131	77	77	129	130	128
80	149	146	145	78	78	143	147	144
90	170	164	163	78	78	163	164	161
95	190	182	181	79	79	179	188	182
EP	211	204	202	176	132	202	197	200
% Recovered	97.5	98.0	98.0	98.0	98.0	98.0	98.0	98.0
Botts	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

a CDA-19 alcohol formula (100 gal ethanol, 4 gal methylisobutyl ketone, (MIBK), 1 gal gasoline).

b SWAFCA alcohol formula (89.5 gal formula 28-A alcohol, 5 gal gasoline, 5 gal methanol, 0.5 gal t-butanol).

Table III-D

Properties of Warm-Up Driveability Fuels

	Fuel Composition		
	Base Gasoline	10 vol % Ethanol/ 90 vol % Base	22.2 vol % Ethanol / 77.8 vol % Base
Density, g/cm ³ at 15°C	0.7666	0.7695	0.7725
RVP, kPa	57.9	59.3	57.2
FIA, vol %			
Aromatics	40.5	---	---
Saturates	54.5	---	---
Olefins	5.0	---	---
ASTM D-86 Distillation, °C at % Evap.			
IBP	33	36	36
5	52	50	50
10	61	57	58
20	81	64	67
30	96	69	71
40	109	83	79
50	118	109	88
60	127	119	99
70	139	129	123
80	152	143	138
90	172	158	153
95	187	168	168
EP	212	206	197
% Recovered	98.0	99.0	99.0
Botts	1.0	1.0	1.0

Table III-E

Properties of Vapor Lock Test Fuels

Fuel Designation:	VL-1	VL-2	VL-3	VL-4	VL-5	VL-6	VL-7	VL-8
Composition:	Base Gasoline	5% EtOH	10% EtOH	15% EtOH	6.7% EtOH/ 3.3% MeOH	3.3% EtOH/ 6.7% MeOH	2% C ₄	5% C ₄
Reid Vapor Pressure, kPa	56.0	60.6	60.2	59.5	77.9	65.5	63.4	74.2
ASTM D-86 Distillation, °C at % Evap.								
IBP	34.4	35.6	37.8	40.6	39.4	34.4	33.3	35.0
5	50.0	47.8	48.3	49.4	44.4	44.4	42.2	46.1
10	52.2	51.1	52.2	53.9	51.1	48.3	48.9	49.4
20	71.1	58.9	60.0	60.6	56.7	53.9	62.8	62.8
30	83.3	70.0	65.6	65.6	61.1	58.9	76.7	77.2
40	94.4	87.8	70.6	68.9	70.6	72.2	89.4	96.7
50	104.4	101.1	93.9	72.2	96.7	97.8	101.1	102.2
60	113.9	111.7	110.0	105.0	109.4	109.4	110.0	111.7
70	126.7	122.2	121.7	118.9	121.1	120.6	121.1	123.9
80	143.3	137.8	136.7	135.0	136.1	135.6	137.2	139.4
90	166.7	154.4	162.8	160.0	162.8	158.3	161.1	163.3
95	188.9	188.9	183.3	179.4	183.9	177.8	178.9	186.7
EP	198.9	197.8	200.0	203.3	204.4	195.0	193.3	203.9
% Recovered	98.0	98.0	98.0	98.0	98.0	98.0	98.0	97.0
Botts	0.7	1.2	1.4	1.0	1.0	1.0	1.0	1.5
V/L at (°C)								
40.6								0.8
43.3				0.7	2.5	1.0		1.6
46.1		1.1	1.4	1.1	10.5	3.0	1.3	4.4
48.9	0.6	2.7	3.3	3.0	24.3	9.9	2.6	9.7
51.7	1.1	8.5	9.9	9.1	44.7	24.6	5.6	15.7
54.4	3.1	17.8	20.1	21.0	65.4	40.1	10.3	22.2
57.2	6.9	29.5	34.1	33.8	>70.0	55.6	16.4	28.5
60.0	12.5	39.7	48.1	54.5		>70.0	22.6	34.0
62.8	18.6	51.7	65.0	>70.0			29.1	42.1
65.8	25.1	62.5	>70.0				38.2	49.2
68.4	33.2	>70.0					48.8	56.4
71.2	42.2						55.7	63.2
73.9	50.8						64.3	>70.0
76.7	58.8						>70.0	
79.5	68.6							

Properties of Vapor Lock Test Fuels

Fuel Designation:	<u>VL-9</u>	<u>VL-10</u>	<u>VL-11</u>	<u>VL-12</u>	<u>VL-13</u>
Composition:	EtOH	5% C ₅ 's	10% C ₅ 's	15% C ₅ 's	5% C ₅ 's + 30% Gasoline
Reid Vapor Pressure, kPa	12.6	31.0	48.2	57.8	62
ASTM D-86 Distillation					
°C at % Evap.					
IBP	78.0	46.1	31.1	31.1	35.6
5	78.0	70.6	47.2	47.2	50.6
10	78.0	76.1	55.6	55.6	60.0
20	78.0	76.7	75.6	77.2	71.1
30	78.0	76.7	77.2	77.2	75.0
40	78.0	77.2	77.2	77.2	76.1
50	78.0	77.2	77.2	77.2	76.7
60	78.0	77.2	77.2	77.2	77.2
70	78.0	77.2	77.2	77.2	77.8
80	78.0	77.2	77.2	77.2	78.3
90	78.0	77.2	77.2	77.2	79.4
95	78.0	77.2	77.2	77.2	162.8
EP	78.3	78.9	78.3	78.3	178.3
% Recovered	99.0	99.0	99.0	99.0	98.6
Botts	0.0	0.0	0.0	0.0	1.0
V/L at (°C)					
40.6					
43.3					
46.1				1.1	1.6
48.9			0.7	2.0	4.5
51.7			1.2	4.4	10.6
54.4			2.7	9.3	17.2
57.2			8.1	16.8	26.5
60.0			15.2	26.7	37.4
62.8		1.6	22.5	40.9	49.9
65.8		4.9	33.1	61.3	67.0
68.4		12.6	54.2	>70.0	>70.0
71.2	0	26.9	>70.0		
73.9	1.1	54.8			
76.7	5.1	>70.0			
79.5	>70.0				