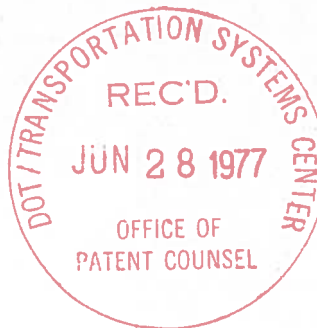


H. Farmer REFERENCE USE ONLY TSC 1411

9



REPORT NO. DOT-TSC-OST-77-31

METHANOL AS AN AUTOMOTIVE FUEL

With Special Emphasis On Methanol-Gasoline Blends

A. Landman

U.S. Department of Transportation
Transportation Systems Center
Kendall Square
Cambridge MA 02142



APRIL 1977
FINAL REPORT

DOCUMENT IS AVAILABLE TO THE U.S. PUBLIC
THROUGH THE NATIONAL TECHNICAL
INFORMATION SERVICE, SPRINGFIELD,
VIRGINIA 22161

Prepared for

U.S. DEPARTMENT OF TRANSPORTATION
OFFICE OF THE SECRETARY
Office of the Assistant Secretary for
Systems Development and Technology
Office of Systems Engineering
Washington DC 20590

141 327

NOTICE

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

NOTICE

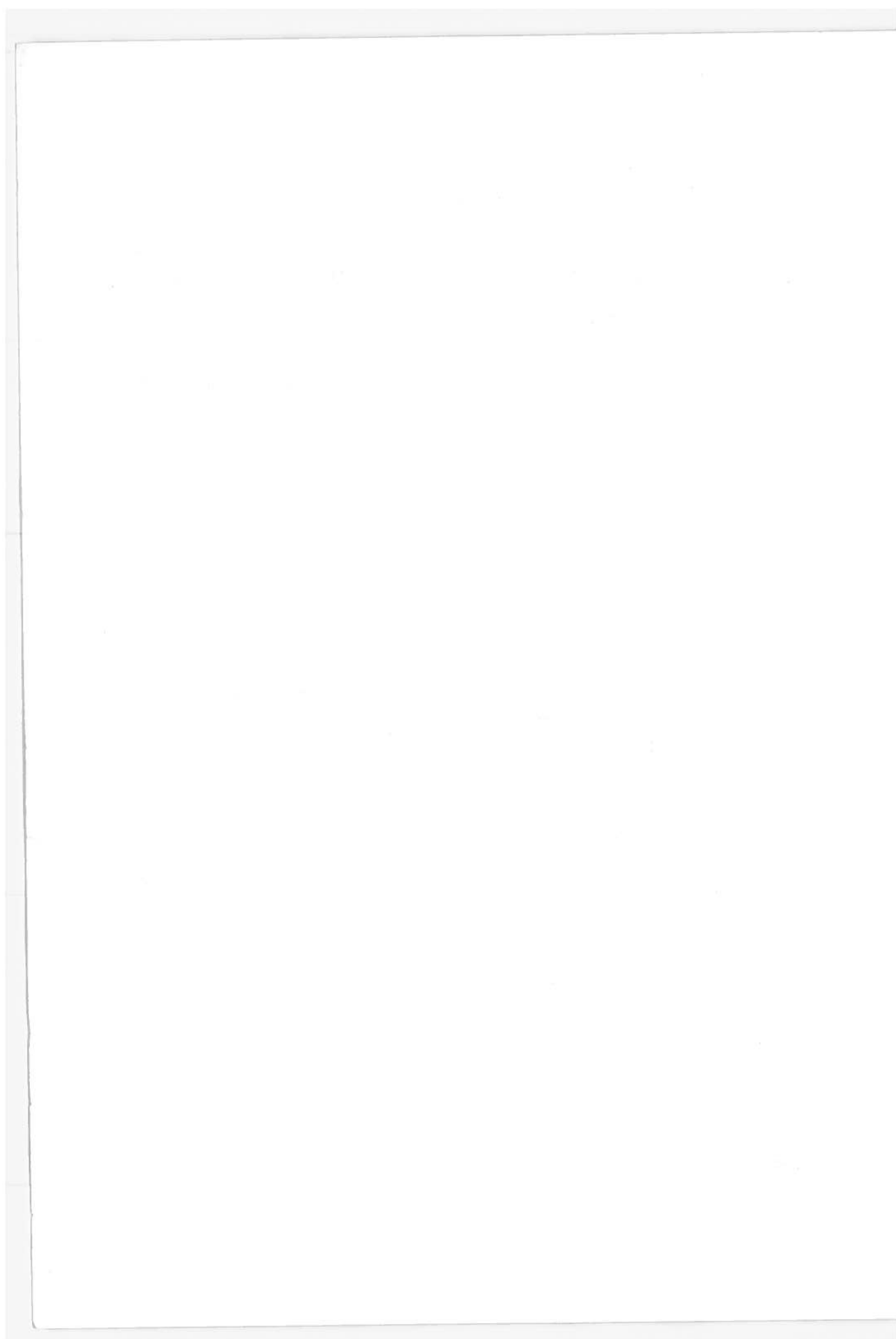
The United States Government does not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

ERRATUM

Preface, page iii, line 13 should read "Figures 5-1 through 5-8...." See attached sheet.

IN: Landman, A., Methanol as an Automotive Fuel (with Special Emphasis on Methanol-Gasoline Blends), DOT-TSC-77-31, Cambridge, MA, Final Report, April, 1977.

Attachment



TECHNICAL REPORT STANDARD TITLE PAGE

1. Report No. -TSC-OST-77-31	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle ANOL AS AN AUTOMOTIVE FUEL Special Emphasis on Methanol- line Blends		5. Report Date April 1977
		6. Performing Organization Code
7. Author(s) Landman		8. Performing Organization Report No. DOT-TSC-OST-74-38
9. Performing Organization Name and Address . Department of Transportation Transportation Systems Center Hall Square Cambridge MA 02142		10. Work Unit No. OS514/R7508
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address . Department of Transportation Office of the Secretary Office of the Assistant Secretary for Systems Development and Technology, Off. of Sys. Eng. Washington DC 20590		13. Type of Report and Period Covered Final Report June 1974-October 1974
		14. Sponsoring Agency Code
15. Supplementary Notes		
16. Abstract <p>This report reviews the available information on methanol as related to its potential use as an automotive fuel. Information is critical to assessment and future decisions are delineated and suggestions made for necessary R&D efforts. In this context, methanol is characterized and the results of various studies on methanol and methanol-gasoline blends, throughout the United States and elsewhere, are presented and compared. These studies encompass blends and their use and effects in engines and vehicles. Cost information, although limited, is given as available. The report also describes and summarizes methanol production processes; their promise and expansion possibilities in relation to potential requirements. Various raw material sources are considered in the light of future production potential needs.</p>		
17. Keywords Methanol Methanol-Gasoline Blends Alternative Fuels for Automobiles		18. Distribution Statement <p>DOCUMENT IS AVAILABLE TO THE U.S. PUBLIC THROUGH THE NATIONAL TECHNICAL INFORMATION SERVICE, SPRINGFIELD, VIRGINIA 22161</p>
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 94
22. Price		

PREFACE

This report summarizes work on methanol and methanol-gasoline blends as possible automotive vehicle fuels. The report also covers present attitudes and delineates the technical information yet to be determined necessary to fill in critical gaps and support future decision considerations.

Dr. Norman Rosenberg's critical comments have been very helpful in formulating this report. The author is also grateful to various participants in the 1974 Engineering Foundation Conference on Methanol as an Alternative Fuel, who by informal and other communications contributed significantly to this work. Special thanks are due to Dr. Thomas Reed of the Massachusetts Institute of Technology who was very generous in providing information.

Figures 6 through 13 in this Report have been reproduced with permission from SAE Paper 720692, entitled Engine Performance and Exhaust Emissions: Methanol versus Isooctane, by G.D. Ebersole and F.S. Manning. That permission is gratefully acknowledged.

METRIC CONVERSION FACTORS

Approximate Conversions from Metric Measures			
Symbol	When You Know	Multiply by	To Find
LENGTH			
mm	millimeters	0.04	inches
cm	centimeters	0.4	inches
m	meters	3.3	feet
km	kilometers	1.1	miles
		0.6	miles
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
sq in	square inches	6.5	square centimeters
sq ft	square feet	0.09	square meters
sq yd	square yards	0.8	square meters
sq mi	square miles	2.6	square kilometers
acres	acres	0.4	hectares
MASS (weight)			
oz	ounces	28	grams
lb	pounds	0.45	kilograms
	short tons (2000 lb)	0.9	tonnes
VOLUME			
tblsp	tablespoons	5	milliliters
fl oz	fluid ounces	15	milliliters
c	cups	30	milliliters
pt	pints	0.47	liters
qt	quarts	0.96	liters
gal	gallons	3.8	liters
cu ft	cubic feet	0.03	cubic meters
cu yd	cubic yards	0.76	cubic meters
TEMPERATURE (exact)			
F	Fahrenheit temperature	5/9 after subtracting 32	Celsius temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards
ha	hectares	0.4	square miles
	hectares (10,000 m ²)	2.5	acres
MASS (weight)			
g	grams	0.035	ounces
kg	kilograms	2.2	pounds
t	tonnes (1000 kg)	1.1	short tons
VOLUME			
ml	milliliters	0.03	fluid ounces
l	liters	2.1	pints
		1.06	quarts
m ³	cubic meters	0.26	gallons
		36	cubic feet
		1.3	cubic yards
TEMPERATURE (exact)			
C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature

in	inches	2.5	centimeters
ft	feet	30	centimeters
yd	yards	0.9	meters
mi	miles	1.6	kilometers
AREA			
cm ²	square centimeters	0.16	square inches
m ²	square meters	1.2	square yards



TABLE OF CONTENTS

<u>SECTION</u>	<u>Page</u>
1 INTRODUCTION.....	1-1
1.1 Findings.....	1-1
1.2 Recommendations (as of Mid-1975).....	1-3
2 DESCRIPTION AND CHARACTERISTICS.....	2-1
2.1 History and Characterization.....	2-1
2.2 Physical and Chemical Properties of Methanol and Comparison with Gasoline.....	2-3
3 USE OF METHANOL-GASOLINE BLENDS.....	3-1
Fuel Economy and Emission Effects.....	3-1
4 PROSPECTS FOR UTILIZATION OF METHANOL BLENDS.....	4-1
4.1 Prospects in Near-Term Future.....	4-1
4.2 Critical Information Gaps and Necessary Future Programs.....	4-3
5 PURE METHANOL AS AN ENGINE FUEL AND COMPARISON OF EFFECTS WITH THOSE OF GASOLINE.....	5-1
5.1 Engine/Vehicle Compatibility.....	5-1
5.2 Fuel Economy Effects and Power Output.....	5-1
5.3 Emission Effects.....	5-8
5.4 Toxicity and Safety Effects.....	5-18
5.5 Handling, Storage, and Distribution.....	5-19
5.6 Critical Information for Use of Neat (Pure) Methanol.....	5-19
APPENDIX A - METHANOL MANUFACTURE AND PRODUCTION.....	A-1
A.1 Reserves and Raw Material Sources.....	A-1
A.2 Methods of Manufacture.....	A-4
A.2.1 High-Pressure Processes.....	A-4
A.2.2 Low-Pressure Processes.....	A-5
A.2.3 Medium-Pressure Processes.....	A-6
A.2.4 Co-Product Methane-Methanol and Variations.....	A-7
A.2.5 Coal Gasification Processes.....	A-9
A.3 Production Rates, Presented and Projected....	A-9
A.4 Present-Day Uses.....	A-12

TABLE OF CONTENTS (CONT'D)

<u>SECTION</u>	<u>Page</u>
A.5 Capital and Consumer Costs.....	A-12
A.6 Impact with Other U.S. and World Energy Requirements.....	A-14
A.7 Critical Technology Gaps.....	A-14
APPENDIX B - BRIEF DESCRIPTION OF WORK BEING PERFORMED OR TO BE PERFORMED.....	B-1
APPENDIX C - GLOSSARY.....	C-1
APPENDIX D - ADDENDUM OF 1974-1975 RESULTS.....	D-1
REFERENCES.....	R-1

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
2-1	ASTM Distillation Curves for Gasoline and Alcohol...	2-4
3-1	Performance of a 1969 Toyota Corona with Methanol-Gasoline Mixtures.....	3-2
3-2	Octane Rating of Lead-Free Gasoline-Methanol Blends Obtained with ASTM Methods.....	3-4
4-1	Water Solubility and Separation with Methanol and Methyl-Blend Fuel.....	4-5
4-2	Temperature Separation of Methyl-Blends in Winter and Summer Gasoline.....	4-6
5-1	Interrelations of Power, Equivalence Ratio, and Hydrocarbon with Isooctane and Methanol at 1,000 rpm.....	5-10
5-2	Interrelationships of Power, Equivalence Ratio, and Hydrocarbon with Isooctane and Methanol at 1,800 rpm.....	5-11
5-3	Interrelations of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,000 rpm.....	5-12
5-4	Interrelations of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,800 rpm.....	5-13
5-5	Interrelations of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,000 rpm.....	5-14
5-6	Interrelations of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,800 rpm.....	5-15
5-7	Interrelations of Power, Equivalence Ratio, and Aldehydes with Isooctane and Methanol at 1,000 rpm.....	5-16
5-8	Interrelations of Power, Equivalence Ratio, and Aldehydes with Isooctane and Methanol at 1,800 rpm.....	5-17
A-1	Co-Product Plant for Methane-Methanol Production....	A-8

LIST OF TABLES

<u>TABLE</u>		<u>Page</u>
2-1	PROPERTIES OF METHANOL, ISOCTANE AND GASOLINE.....	2-5
3-1	FUEL ECONOMY AND EMISSIONS OF ENGINES USING METHANOL-GASOLINE BLENDS, COMPARED TO THE RESULTS FOR THE ENGINES USING GASOLINE.....	3-9
A-1	METHANOL SOURCES AND PRODUCTION.....	A-2
A-2	U.S. METHANOL PRODUCERS, PLANT CAPACITIES AND PROCESSES (1973).....	A-10
B-1	WORK BEING PERFORMED ON METHANOL AS AN AUTOMOTIVE FUEL 1973 - 1974.....	B-2
D-1	COMPARATIVE FUEL ECONOMY AND EMISSIONS.....	D-3

1. INTRODUCTION

1.1 FINDINGS

Methanol and other alcohols have often been proposed as fuels for internal combustion engines. Methanol has actually been used to a limited degree, especially when gasoline has been in short supply. Performance and emissions have been analyzed, but never in a systematic and co-ordinated fashion.

Methanol is qualitatively similar to isooctane as well as to other constituents of gasoline. It has a lower heating value and a higher latent heat of vaporization than gasoline so that it has a lower fuel economy (in miles per gallon) but better power performance under most conditions. Blends of 5 to 20 percent methanol with gasoline might be expected to result in intermediate behavior, but several recent studies indicate that, potentially, blends may perform better than gasoline. It is important that such initial results be verified or disproved by further investigation.

The methanol experimental data for fuel economy and emissions have been largely obtained using a CFR (Cooperative Fuels Research) one-cylinder test engine. Projections to a six cylinder engine are approximate, especially since distribution problems with methanol are more severe than with gasoline. Studies of methanol-gasoline blends have been performed using road vehicles, but experimental control was limited and there was little coordination between various efforts.

Water separation rarely presents difficulties in gasoline-powered vehicles. Methanol, because of its miscibility with water, can cause problems. In some cases, however, methanol mixed with gasoline can prove useful by combining with water to clean it up. Methyl-fuel,[®] a mixture of several alcohols of which the predominant one is methanol, may prove even more useful due to its greater solubility in gasoline, and the resultant expanded one-phase stability for the methyl fuel-gasoline-water system.

Methyl-fuel[®] also appears to be better than pure methanol for blending with gasoline. Starting and vapor lock problems are lessened and the available energy (in BTU per gallon) is greater for methyl-fuel[®] blends. Also, there is at least one process which produces methyl-fuel[®] more cheaply than methanol can be produced. The emphasis in the past has been on producing methanol as pure as possible, but some of the "impurities" that appear in methyl-fuel[®] may actually increase its value as a blending agent for gasoline.

It appears that methanol is a potential octane booster for gasoline and can replace lead or decrease the need for many of the higher-octane aromatic constituents of gasoline, some of which may be carcinogenic. Early testing suggests that engine emissions from methanol blends are generally lower in most harmful constituents (HC, CO, and NO_x)^{*} than those from gasoline, but additional tests are required to substantiate this.

Present methanol production is approximately 1% that of gasoline, and would need to be increased by a factor of ten if requirements for blends consisting of 10% methanol and 90% gasoline at today's consumption rates were to be met. Methanol manufacture in the United States could be extended somewhat by increasing the domestic production of synthesis gas, but a more significant source of raw material for the immediate future (by 1980) appears to be natural gas from the Middle East (especially Iran) that is now burnt off. One large plant recommended for Iran could provide twice the total 1973 U.S. production of methanol. Other raw material sources for methanol, especially domestic, could be tapped in the late 1970's and the 1980's. These include coal and lignite which are most plentiful and available. Methanol production could probably be increased one-hundred fold if the decision to use coal sources were to be made. Waste material and forests grown as "energy plantations" might also be contributing raw material sources for methanol in the future.

Methanol has other potential uses. These include heating, electric power generation, and use in fuel cells, and as a feedstock for chemical synthesis. There is also the intriguing but highly ^{*}Hydrocarbons, carbon monoxide and oxides of nitrogen.

speculative possibility of producing gasoline from methanol. Such gasoline might be price competitive with gasoline refined from petroleum or produced directly from coal.

Methanol-gasoline blends may be a major link in the evolution of fuel for internal combustion engines. No major change appears essential for automobile engines as they are presently constituted. Necessary, slight modifications would not require retooling and could be accomplished gradually. No significant changes in handling, transportation, and storage other than extra care in avoiding water in the fuel blends are necessary. Developments needed for gaseous fuels or refrigerated liquid fuels are unnecessary, and methanol can readily be mixed with the gasoline either at the source or at the service station.

1.2 RECOMMENDATIONS (AS OF MID-1975)

Although methanol appears as a promising candidate for improved gasoline blends, and perhaps as a gasoline substitute, there are important unresolved questions about its use in automobiles. The potential usefulness of methanol warrants further research and development to resolve these questions. In view of the immediate and critical energy problems and the long lead time to incorporate methanol into the national transportation system, such effort should be initiated soon.

The recommended research and development efforts listed below should encompass the use of various methanol fuels in conventional internal combustion engines and in new types such as the Wankel and stratified charge. The objective of such studies is to determine the operating parameters and how and to what extent they can be acceptably improved and optimized. It is important that test methods, test conditions and measurement techniques be coordinated and standardized. The recommended research and development work includes:

1. Specific aspects of engine design and operation

- Cold Start

- Vapor Lock

- Spark (Ignition) Management

Materials Compatibility
Fuel Induction
Evaporative Control
Crankcase Ventilation
Lubrication

2. Engine Performance and other characteristics

Performance

Life

Emissions

Fuel Economy

3. Driveability of methanol/gasoline fueled vehicles

4. Specific Fuel Studies

Anti Knock Qualities

Effects of Fuel Additives

Vapor Control

Optimum Blends Constituent Composition/Amounts

Water (in Fuel) Management

5. Effects of methanol/water miscibility and mechanisms to minimize negative effects

6. Impact on safety, health and environment

7. Transporting and handling systems

8. Production/availability of methanol in quantities compatible with automotive-use requirements.

If favorable results are obtained, and as larger volumes of methanol fuel become available, larger-fleet tests, representative of a wide range of climate and driving conditions, should be initiated at various locations in different parts of the United States.

It is also important to consider the projected cost of methanol for its automotive use in the future. This cost may vary considerably dependent on the demands that develop and the technological advances in the production of methanol.

2. DESCRIPTION AND CHARACTERISTICS

2.1 HISTORY AND CHARACTERIZATION

Methanol, CH_3OH , or methyl alcohol, is the hydroxyl derivative of methane. It can also be thought of as the reaction product to two molecules of hydrogen gas (2H_2) with one molecule of carbon monoxide (CO). It is a colorless, chemically neutral, flammable liquid at ambient temperature, and has a mild odor. It reacts with organic acids to produce an ester and water.

Methanol was originally derived as a by-product from the destructive distillation of wood (thus wood alcohol) in the manufacture of charcoal. It is now chiefly prepared synthetically from hydrocarbon raw materials such as petroleum, natural gas, or coal. The most common manufacturing process, about sixty years old, involves the catalytic hydrogenation at high pressure and temperature of a synthesis gas containing carbon monoxide. More recent processes are generally refinements of this, usually at lower pressures. A typical process used for making alcohols as well as other synthetic hydrocarbons is the Fischer-Tropsch synthesis.

Methanol is used as a solvent and as a component in the manufacture of various organic chemicals. It has also been used in racing cars and in fuel-injection piston aircraft. In Europe, during gasoline shortages in both World Wars, methanol was occasionally used for tanks, planes, and cars. One method of in-situ production in automobiles was the destructive distillation of wood chips to make alcohol vapors (including carbon monoxide and hydrogen), which were then used directly. In the Middle East, natural gas, currently flared off at the oil wells, is being studied as a source material. Plans are now under way to construct methanol plants to convert this gas to methanol at the well head to be shipped in conventional tankers.

The output of a methanol manufacturing plant can often be increased by as much as 50 percent if small amounts of other alcohols can be tolerated in the product. Such a mixture is called

methyl-fuel[®],^{1*} and contains more energy than pure methanol because of the presence of higher alcohols. Details are given in the appendix on the manufacture of methanol and methyl-fuel[®].

Methanol for commercial use is generally defined according to ASTM Standards. A typical specification, taken from the Encyclopedia of Chemical Technology,² is as follows:

ASTM: Standard D1152-58

Methyl alcohol (methanol) (99.85% grade) shall conform to the following requirements:

Specific Gravity 20/20°C	Not more than 0.7928
Color	Not more than No. 5 on the platinum-cobalt scale
Distillation Range:	
Below 64.0°C	None
Above 65.5°C	None
Nonvolatile Matter	Not more than 0.005g/100 ml
Odor	Characteristic, Nonresidual
Water	Not more than 0.15% by weight
Acidity (Free Acid as Acetic)	Not more than 0.003% by weight gram of sample
Potassium Permanganate Test	Color of added KMnO_4 must be retained at least 30 minutes at $15 \pm 0.5^\circ\text{C}$ in the dark
Acetone	Not more than 0.003% by weight.

Methanol is shipped in metal containers, drums, or tank cars which are loaded and unloaded by pump. Methanol can be shipped in the same tank cars used for petroleum products but precautions are taken in cleaning to prevent contamination. Methanol can also be transported in a pipeline.

In dry air its flammability limits are 6.7 to 36% by volume.

*References are identified in the Reference Section at the back of this report.

2.2 PHYSICAL AND CHEMICAL PROPERTIES OF METHANOL AND COMPARISON WITH GASOLINE

Methanol's properties are often compared to those of gasoline in order to assess methanol's potential as an automotive fuel. If methanol were to be used extensively as a fuel, it might be marketed as a mixture of alcohols (methyl-fuel[®])^{1,4} or possibly blended with gasoline. Pure methanol probably is the least likely possibility for wide-spread use.

Gasoline is a complex blend of hydrocarbons. For example, gasolines are composed of a range of hydrocarbons ($C_4 - C_{10}$), each of which has a different boiling point. This characteristic of gasoline results in a distillation curve which generally begins about 100°F (recovery of first distillate) and ends at about 400°F. Alcohols and other pure chemicals do not have this characteristic range of volatility. Boiling takes place at a given temperature as shown in Figure 2-1.³ Some of the more volatile constituents of gasoline begin to boil at temperatures below the boiling point of methanol.

Methanol is similar in many respects to gasoline. Its heat of combustion is lower than analogous hydrocarbons. It has a higher latent heat of vaporization and better anti-knock qualities than isooctane. Anti-knock sensitivity, defined as the difference between Research Octane Number and Motor Octane Number, is moderate.²⁰ These measures are further defined in Section 3 of this report. Methods of storage and distribution are similar to those for gasoline. Its heating value is somewhat less than half that of gasoline, and its fuel mileage per gallon is also lower, although in blends with gasoline this does not always hold, as described in Section 3. Alcohol is also miscible with water, which presents contamination and corrosion problems.

Table 2-1^{2,5,6,7} compares some of the important properties for methanol, isooctane (a representative pure hydrocarbon constituent of gasoline), and gasoline.

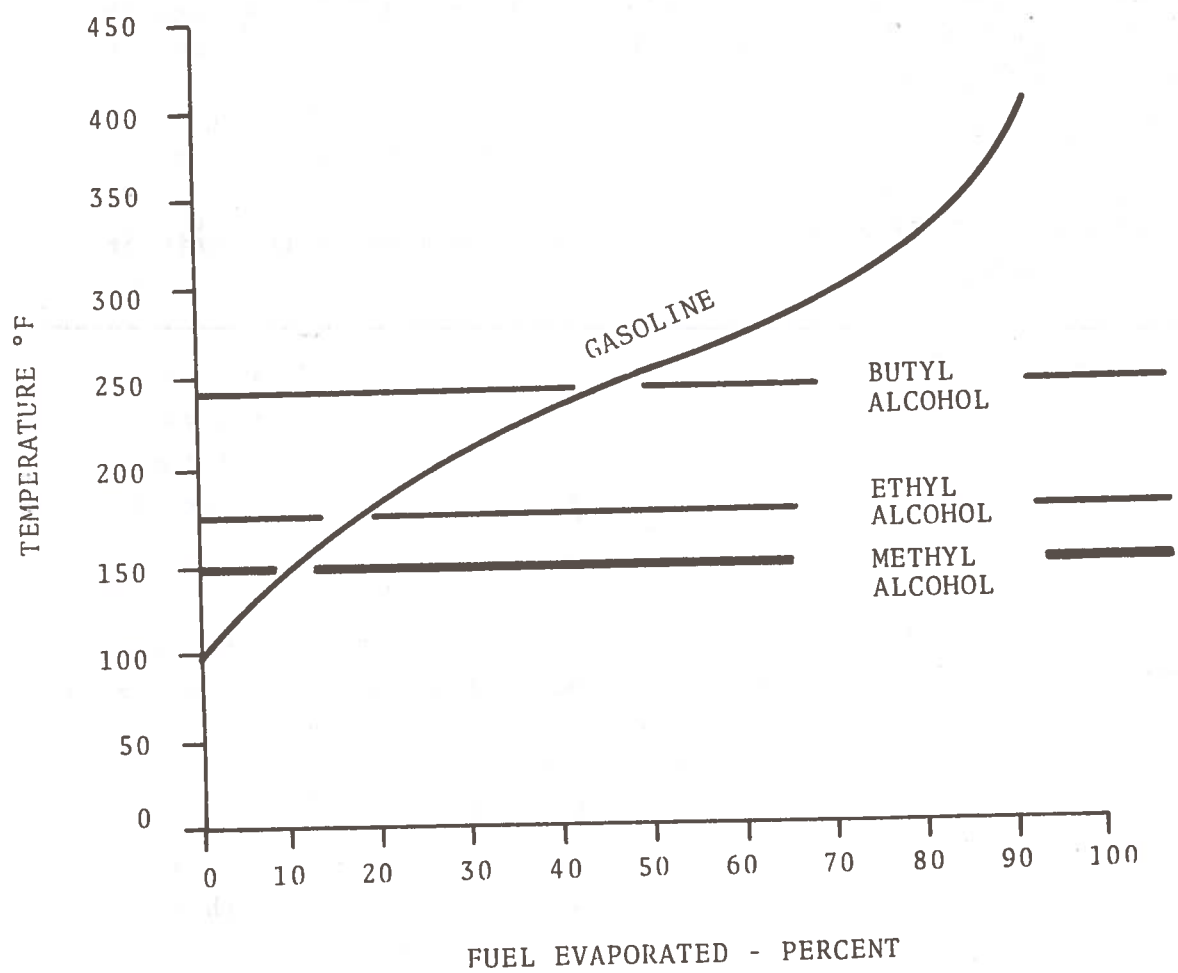
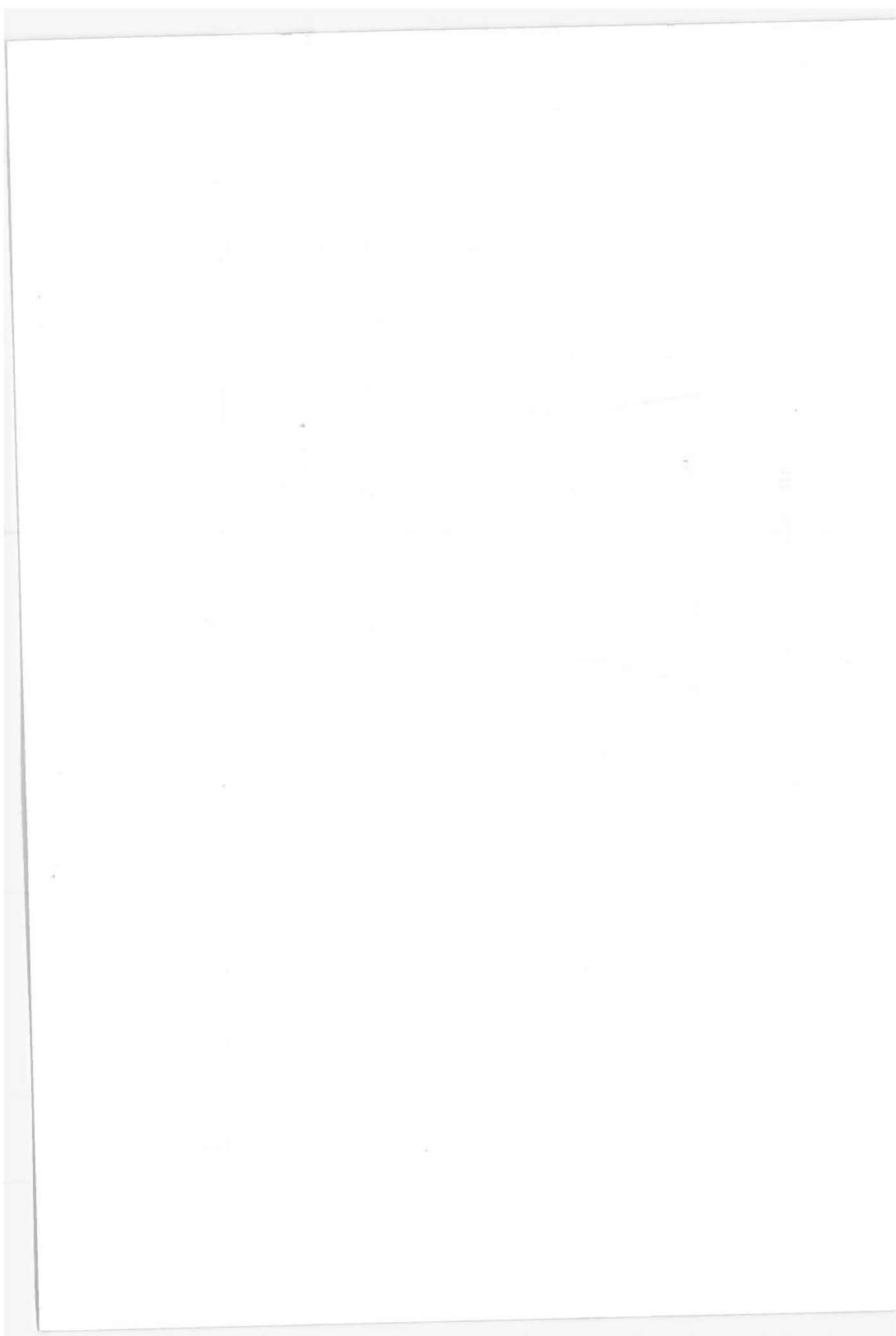


Figure 2-1. ASTM Distillation Curves for Gasoline and Alcohol ³

TABLE 2-1. PROPERTIES OF METHANOL, ISOCTANE AND GASOLINE ^{2,5,6,7}

Item Formula	Methanol CH_3OH	Isooctane C_8H_{18}	Gasoline $\text{C}_4\text{H}_{10}-\text{C}_{10}\text{H}_{22}$
Molecular weight	32.042	114.224	
Carbon to Hydrogen weight ratio	3.0	5.25	
Carbon, % by weight	37.5	84.0	
Hydrogen, % by weight	12.5	16.0	
Oxygen, % by weight	50.0	0.0	0.0
Boiling point, °F at 1 atm	148.1	210.63	100-400
Freezing point, °F at 1 atm	-144.0	-161.28	-100
Vapor pressure psi at 100°F	4.6	1.708	
Density, 60°F, lb/gal	6.637	5.795	6.2
Coefficient of expansion 1/°F at 60°F and 1 atm	0.00065	0.00065	
Surface tension, dynes/cm at 68°F and 1 atm	22.61	18.77	
Viscosity, centipoises at 68°F and 1 atm	0.596	0.503	
Specific heat of liquid, BTU/lb-F° at 77°F and 1 atm	0.6	0.5	
Heat of vaporization Btu/lb at boiling point and 1 atm	473.0	116.69	116
Heat of vaporization, Btu/lb at 77°F and 1 atm	503.3	132	
Heat of combustion, at 77°F			
Higher heating value, Btu/lb	9,776	20,556	20,260
Lower heating value, Btu/lb	8,593	19,065	
Lower heating value, Btu/gal	57,030	110,480	
Stoichiometric mixture, lb air/lb	6.463	15.13	
Research octane no.	106	100	{ Variable depending on blend
Motor octane no.	92	100	



3. USE OF METHANOL-GASOLINE BLENDS

FUEL ECONOMY AND EMISSION EFFECTS

Data currently available indicate that methanol-gasoline blends perform effectively in internal combustion engines, without requiring any modifications. Some experimental results even indicate higher fuel economy, in miles per gallon of fuel, with the blends than with gasoline alone. Pollution emissions, when using the blends, tend to be lower than with gasoline.

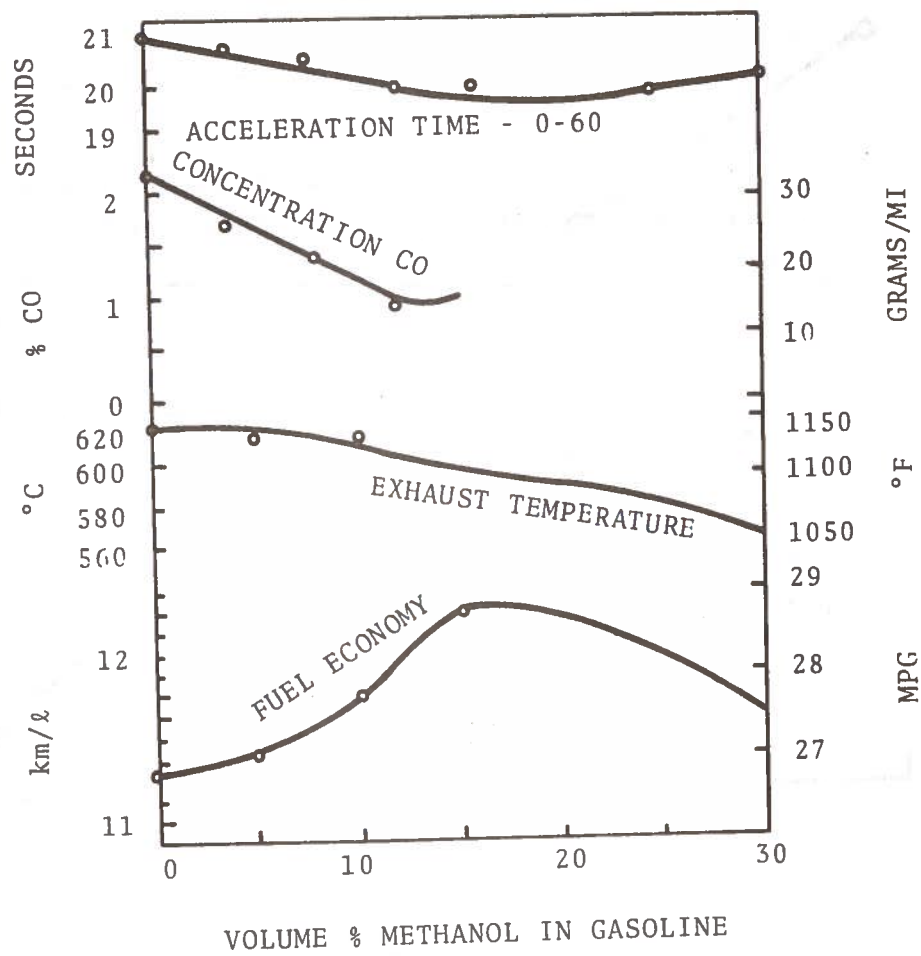
Reed and Lerner^{4,8} tested a blend of methanol/gasoline containing 5 to 30 percent methanol. A number of unmodified private cars (year models 1966 to 1972) were tested and operated over a fixed course with varying concentrations of methanol. It was found that

1. Fuel economy expressed in miles per gallon increased by 5 to 13 percent. Fuel economy in miles per BTU increased by 10 to 20 percent.
2. CO emissions decreased by 14 to 72 percent.
3. Exhaust temperatures decreased by 1 to 9 percent.
4. Acceleration (0-60 mph) increased up to about 7 percent.

The results obtained on a 1969 Toyota having a 1900 cm³ engine with an 8 to 1 compression ratio and rated at 85 BHP, are shown in Figure 3-1.

Reed and Lerner (loc. cit.) also reported the elimination of knock and dieseling in two unmodified cars when a 5 percent methanol/gasoline blend was used. Methanol has a high octane rating, about 106, which indicates good no-knock performance. An even better measure of performance when using blends containing amounts of methanol is the "blending octane value" defined by Reed and Lerner as follows:

$$BOV = \frac{O_b - O_g (1-x)}{x} ,$$



Source: Reference 4

Figure 3-1. Performance of a 1969 Toyota Corona with Methanol-Gasoline Mixtures.

in which O_b and O_g are the octane numbers of the blend and the gasoline respectively, and x is the volume fraction of methanol in the blend. A methanol volume fraction of 5% can increase the octane number of a fuel from 90 to 92, and this results in a BOV of methanol between 120 and 130.

Reed and Lerner attribute the improvements in anti-knock and fuel economy to dissociation of methanol during the compression stroke in the engine, which cools the charge and quenches premature combustion. It would be valuable if this supposition could be verified by direct observation of the CO and H_2 that are produced. CO and H_2 formed on dissociation might also be expected to increase the flame velocity, giving more complete and efficient combustion than with gasoline alone. (Combustion tests by Pefley and others⁹ using CO and H_2 in mixtures did not show better combustion efficiencies, so that the mechanism for methanol combustion in the automotive engine is still unclarified.)

The Reed and Lerner work also demonstrated an effective leaning of the air-fuel mixture with methanol blends, brought about by use of the same air flow rates as for gasoline. Additional performance improvement using higher compression ratios and even leaner operation may be possible.

Blends have also been studied by Breisacher and Nichols¹⁰ on a CFR engine, using ASTM Reference Fuels. These test fuels were rated by both the research and motor method,²⁰ and the results are shown in Figure 3-2. (No increase in fuel sensitivity was observed with increasing percentages of methanol additive, possibly because the lead-free gasoline contains a substantial amount of aromatics which has a fairly high sensitivity compared to paraffinic gasolines.)

A number of field tests were conducted by Breisacher and Nichols on a variety of foreign and domestic cars. The car model years ranged from 1964 and 1971. In field tests fuel tanks were filled with lead-free or low-lead gasoline. Normal operation in road tests produced engine knock, but when the methanol was added no further knocking was audible on any of the cars. The amount of

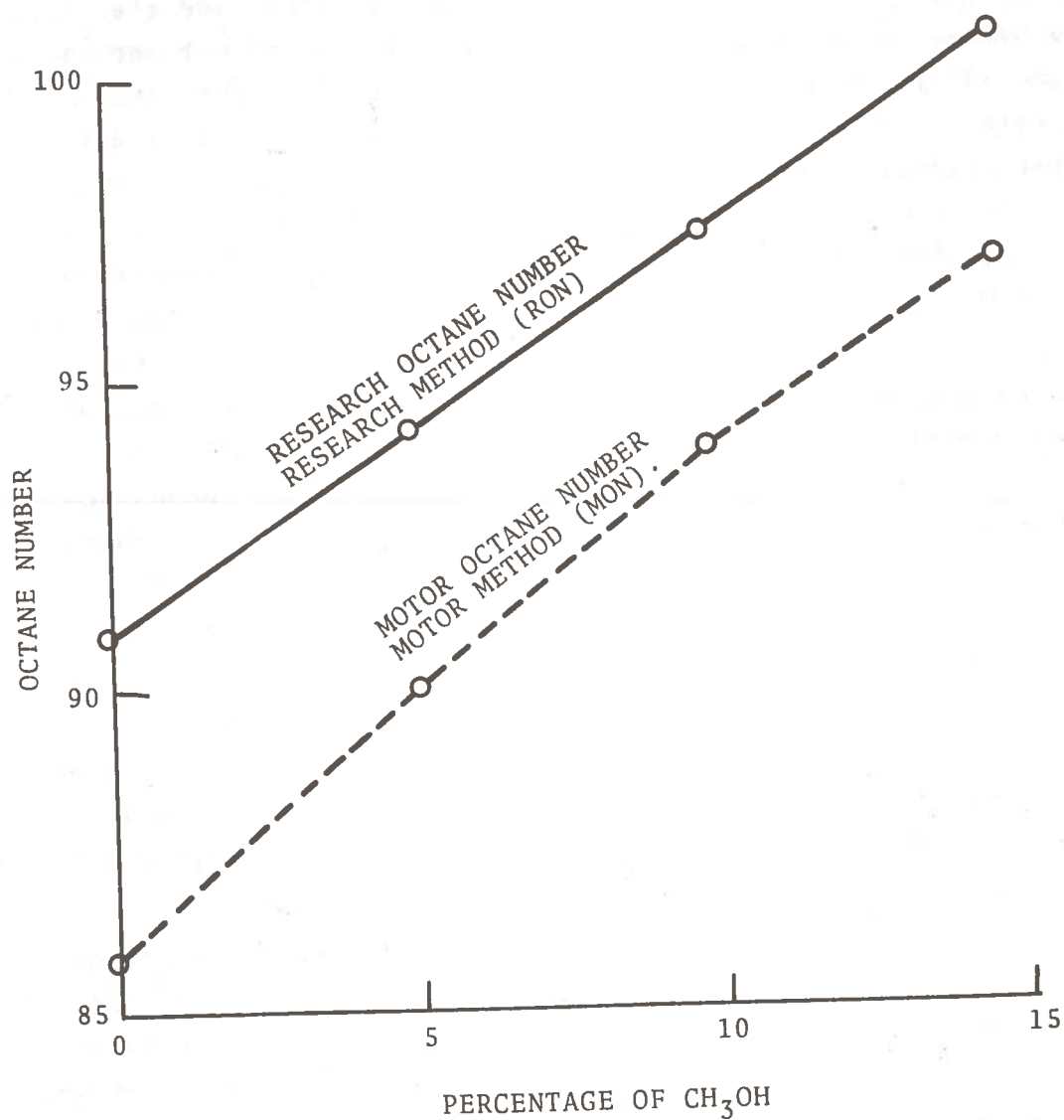


Figure 3-2. Octane Rating of Lead-Free Gasoline-Methanol Blends Obtained with ASTM Methods¹⁰

methanol required to eliminate the knocking, according to Breisacher and Nichols, ranged from 5 to 10% by volume, depending on the engine configuration and base gasoline used. Also, from a private communication received from Nichols, fuel economy seemed to be slightly better with the methanol blends.

Recent work performed at the University of Missouri, Rolla, on a CFR engine confirms the octane boosting value of methanol in a systematic quantitative fashion.¹¹ Their results show slightly better operation using methanol than the results of Reed and Lerner⁸ and about the same as those of Breisacher and Nichols.¹⁰ The apparatus used was a standard knock testing unit, consisting of a single cylinder, continuously variable-compression engine, with suitable loading and accessory equipment and instruments.

Tentative conclusions from the work so far are:

1. There is a substantial increase in the research octane number as the volume fractional concentration of methanol in the blend is increased from 2 to 25 percent, particularly for base fuels having a relatively low base octane number.
2. Blending octane values (BOV) as defined earlier in this section decrease as the volume fractional concentration of methanol in the blend is increased. Variation in BOV is quite large, with values lying between about 120 and 150.
3. Small amounts of methanol can be added to unleaded motor fuel for octane improvement. Only minor air-fuel adjustments for proper engine performance are required.

A study by Ford Motor Company¹² was made in 1970 on the variations in the chemical composition of the exhaust emissions from a single cylinder engine when up to 25% methanol was added to a fuel blend of toluene, isooctane, and n-heptane. Under fuel-rich conditions, and with increasing methanol concentrations, it was observed that unburned fuel, formaldehyde, and benzene emissions increased, acetylene emission remained constant, and propylene, iso-butylene, methane, ethylbenzene, and styrene emissions decreased. As oxygen was made more available (leaner mixtures),

methanol's influence on hydrocarbon emissions was reduced. The negative effect of methanol for the rich mixtures appears to be due to the formation and reaction of formaldehyde, an incomplete combustion product of methanol. A secondary reason is the increase in unburned toluene in the exhaust. Further work in the area of formaldehyde effects and toxicology is warranted. Lastly, this study did not show any definitive changes in carbon dioxide, carbon monoxide, oxygen, and nitric oxide emissions, which is in partial conflict with the results obtained by Reed and Lerner,⁴ and described earlier.

Studies by R.H. Lindquist et al¹³ at Chevron Research Company, using 10% methanol with gasoline as a blend, point out potential problems with fuel system materials compatibility in a methanol/gasoline environment in which there was a separation of a water-alcohol phase. Slight corrosion of the terneplate of the fuel tank (composed of soft steel with a tin/lead coating) was observed, and organic corrosion inhibitors did not seem to ameliorate this situation. In addition, magnesium-aluminum alloys were corroded by gasoline-methanol blends.

In fuel economy tests by Lindquist, results for a small fleet showed a 3-1/2% reduction in fuel economy (miles/gallon) in contradiction to the results of Reed and those of Nichols. Driveability was often poor, and stalls occurred on several occasions due to water separation.

Exhaust emission tests by Lindquist indicated higher unburned fuel and higher carbon monoxide content with the methanol blend than with straight gasoline, but lower quantities of nitrogen oxides and about the same amount of aldehydes. Use of air injection and catalytic reactors significantly reduced the amounts of all emission constituents except aldehydes, as compared to emissions from standard engines without reactors.

Studies by J. Appeldoorn et al¹⁴ at EXXON, on a set of 13 cars showed that problems due to vapor lock were more prevalent with methanol blend fueled cars than with those fueled with gasoline. Cars using gasoline-methanol blends would occasionally have

difficulty in being started when warm; stalling, surging and bucking were also sometimes experienced. Statistical data on selected cars showed that newer cars experienced more problems than older cars, and the situation was more pronounced with methanol blends than with gasoline alone. One solution to the vapor lock problem is to remove butane, pentane and similar constituents of the gasoline being used to blend with methanol. This, however, results in a loss of BTU and although the vapor lock problem is solved, in a reduction of energy efficiency in BTU/gallon.

Comparative tests at General Motors Corporation have been made by J. Colucci et al¹⁵ on vehicles using methanol-gasoline blends and gasoline alone. Driveability was found to be poorer for vehicles using methanol blends as compared to those using gasoline. The hydrocarbon and nitrogen oxide emissions were similar and the carbon monoxide emissions less using methanol blends in contrast to gasoline alone. Fuel economy in miles per gallon was slightly lower for the methanol blends. Using methanol, performance was about the same at wide-open-throttle, but worse at part-throttle. The motor octane number was boosted slightly and the research octane number was boosted significantly when methanol was used. The road octane number was only moderately higher (best improvement occurred when about 10% methanol was included in the blend). The leaning effect of adding methanol was useful, and could be adjusted to reduce the nitrogen oxide emissions, although not the hydrocarbon emissions. Leaner mixtures resulted in poorer fuel economy, however. Parenthetically, it was observed that vehicles using methanol-gasoline blends showed slightly better power outputs and thermal efficiencies when the fuel-air ratio was rich.

Colucci indicated the need to study the cars that are now becoming available, and felt that General Motors' position is that no retrofit changes should be made to use methanol-gasoline blends since modifications would be required on millions of vehicles and very little control would be possible. Colucci pointed out the problems associated with cold weather operation and gasoline-methanol separation caused by water. The work at General Motors is continuing, and more data will help to clarify the difference in Colucci's results and those of Reed and Breisacher and Nichols.

A large program to investigate the use of methanol-gasoline blends is being undertaken at the Bureau of Miles in Bartlesville, Okla., by R.W. Hurn *et al.*¹⁶ Different gasoline-methanol blends are being tested on a 40-car fleet. Gasoline components are being carefully selected from stocks to enable control of the gasoline constituents of the methanol blends. A primary objective is to determine how sensitive engine performance and emission characteristics are to gasoline blending stocks. Major consideration will be given to octane number and aromaticity. The program also includes some initial investigation using methanol-gasoline blends in a stratified charge engine.

Hurn's initial results from tests on four cars between 1972 and 1974 indicate fuel economy to be approximately the same for either 10% or 20% methanol-gasoline blends when measured in miles per gallon, but increasing up to about 10% when measured in miles per BTU, a measure that may be more significant. (See Table 3-1.)

Volkswagen studies¹⁷ using methanol and methanol-gasoline blends of up to 15% methanol show improved efficiencies in both miles/BTU and miles/gallon as compared to efficiencies when using gasoline alone.

As can be seen in Table 3-1, there is significant disagreement among the sources listed for both fuel economy and emissions in methanol blend tests. Unfortunately, quantitative data obtained by individual investigators cover a wide range, and can only be tabulated meaningfully in a qualitative fashion. Reed's results on CO emissions, for example, while given quantitatively, were limited to a few automobiles, and although all showed a decrease in CO emissions, there were large differences among the individual vehicles. Unfortunately, each investigator tested only a few automobiles, with the exception of Hurn and Volkswagen, whose tests are still being carried out.

TABLE 3-1. FUEL ECONOMY AND EMISSIONS OF ENGINES USING METHANOL-GASOLINE BLENDS (a), COMPARED WITH THE RESULTS FOR THE ENGINES USING GASOLINE

INVESTIGATOR	SINGLE CYLINDER CFR OR MULTI-CYLINDER TESTS	VEHICLES USED (ALSO NUMBER OF CYLINDERS, DRIVING CYCLE)	FUEL ECONOMY (c) (MILES PER GALLON)	FUEL ECONOMY (c) (MILES PER 10 ⁵ BTU)	CO EMISSIONS	HC EMISSIONS	NO _x EMISSIONS
Reed et al. ^{1,8}	Multi-cylinder road tests	4 cyl. 1969 Toyota 4 cyl. VW bus, Fixed course, but no drive cycle	~17 to 18 mpg 5 to 13% improvement	Significant improvement 12 to 20% est.	14 to 72% decrease	Not Measured	Not Measured
Breisacher and Nichols ¹⁰	Single-cylinder Dynamometer, Multi-cylinder road tests (road tests for fuel economy only)	VW, Cadillac, Vega No drive cycle	Small improvement (Very limited road tests)	Significant improvement	35% decrease	5% decrease	Little change
Ninomiya et al. ¹²	Single-cylinder CFR	-----	Not measured	Not measured	No change	No change to small increase	No change
Lindquist and Ingamells ¹³	Multi-cylinder road tests	4 cars, not identified 1972 FTP	~15 mpg 3% decrease	~13 mi/10 ⁵ BTU 2% average improvement	Not measured	Not Measured	Not measured
Colucci et al. ¹⁵	Multi-cylinder road tests	14 cars, 4, 6, and 8 cylinders, Different cycles, est. 1975 FTP	~12 mpg 4% decrease on average	Very slight or no improvement	38% average decrease	No significant change	8% average decrease
Hurn ¹⁶ (b)	Multi-cylinder road tests	4 cars - Vega, Maverick, Torino, Chevelle (1972 to 1974) FTP used	~12 mpg About the same	~10 mi/10 ⁵ BTU Small improvement	20% to 50% average decrease	10% to 20% increase	10% decrease
Volkswagen ¹⁷	Multi-cylinder, also Hinkel and stratified charge engines	4 cylinder VW, Passat, Porsche European Test (ECE)	8% improvement	Significant improvement 16% (estimated)	To 70% decrease	To 30% decrease	To 30% decrease

(a) Tests varied from about 5 percent to 20 percent methanol, with an average of about 10 percent in the blends.

(b) Updated to May 1975; cf. Appendix D.

(c) As a first approximation, relative improvement in fuel economy in miles per BTU is 5% greater than fuel economy expressed in miles per gallon for 10% (by volume) methanol in the blend. For methanol up to about 30% relative improvement in fuel economy in miles per BTU is 7% greater than fuel economy expressed in miles per gallon for 0% methanol in the blend.

Volkswagen is working on the corrosion and carburetor problems. They are also conducting fuel economy tests using a European driving cycle.¹⁷ "In all the tests carried out, fuel economy was improved with methanol addition up to 10 percent. A VW Passat running on regular gasoline with 15 percent by volume of methanol added, although designed to run normally on premium gasoline, none the less yielded 8 percent less fuel consumption in comparison with the premium gasoline fueled VW Passat, with no modification in the standard carburetor or ignition settings." Emissions including CO, HC, and NO_x from the VW Passat and also from a Porsche were reduced about 30 percent or more using a 20% methanol/gasoline blend as compared to gasoline alone, even after correcting for enrichment to the initial values (no methanol added).

Most of the tests referred to in Table 3-1 did not use any particular drive cycle. Each set was conducted in a self-consistent manner but was not necessarily consistent with the others. The EPA recently reported initial results of tests¹⁸ on methanol-gasoline blends using approximately 10% methanol. The Federal Test Procedure drive cycle was used. The EPA data indicated a decrease in fuel economy of around 7 to 8 percent in miles per gallon. The results for emissions were mixed.

Results on driveability are not tabulated, since they diverge so greatly. Effects of water separation are also ambiguous, with Reed reporting no rough driving problems due to water in the fuel, while some of the other investigators indicate major problems even when care was taken to avoid water in the fuel.

The results obtained by the various investigators varied widely, depending on the automobiles tested and the test conditions. This variation, arising largely from the lack of controlled experiments and standards, is a major problem in attempting to compare and assess results from different experimenters.

The problems discussed above make the need for future controlled testing very apparent. Qualitative results are indicated and summarized in this report, but quantitative information is urgently needed and can only be gained from controlled experiments.

4. PROSPECTS FOR UTILIZATION OF METHANOL BLENDS

4.1 PROSPECTS IN NEAR-TERM FUTURE

The use of methanol could probably be implemented rapidly once the supply of methanol is provided for blending, either at distribution centers or at gasoline-methanol service stations. A detailed discussion of methanol production and on-stream capability is presented in an appendix to this report.

Some of the possible advantages in the utilization of methanol are listed here:

a. The actual behavior of fuels in an internal combustion engine may differ significantly from predicted behavior for a variety of reasons. Fuel economy is only one factor, and is usually determined from specific fuel consumption measurements made on a dynamometer or in actual automobile mileage tests. Octane rating and antiknock performance are also significant factors. The importance of understanding fuel antiknock quality relative to fuel economy is essential for a meaningful evaluation of the potential usefulness of methanol. Knocking is a manifestation of nonuniform and incomplete combustion within the engine cylinders. The resultant pressure spikes are converted to waste heat instead of work with detrimental effects on fuel economy and, subsequently, on engine components. Fuels with high octane ratings (good anti-knock) will burn efficiently in high compression engines. High research octane numbers correspond well with good low speed road rating, and high motor octane values indicate good high speed road rating. Methanol may be exceptionally useful because of its high blending octane value referred to earlier in this report.

b. In a number of the methods employed to manufacture methanol, the output of the plant can sometimes be increased substantially if small amounts of other alcohols can be included. This is especially true of the Vulcan-Cincinnati process.¹ This mixture is called methyl-fuel,[®] and contains more energy than

pure methanol because of the presence of ethanol, propanol, and isobutanol. It can be produced in large quantities at a lower price than pure methanol and, in general, has some superior properties as a fuel.⁴

c. Methanol can be used to clean up water in gasoline storage. 10,000 gallons of gasoline will dissolve 1 gallon of water, 1,000 gallons of a mixture of 90% gasoline with 10% methanol will dissolve 1 gallon of water, and 100 gallons of a mixture of 90% gasoline and 10% methyl-fuel[®] will dissolve 1-gallon of water. Thus, what has been thought to be a disadvantage may turn out to be beneficial in some instances.

d. The future price of methanol is projected to be comparable to or lower than that projected for gasoline. Results from a Volkswagen study, noted by Reed in private communications, indicate these projections to hold world-wide.

e. Methanol spills are less dangerous than gasoline spills, since the methanol-water miscibility permits a spill to be washed away rather quickly. Blends do not possess this quality to the same degree and spills are more comparable to those of gasoline alone.

f. Ideally, a gradual shift to the use of methanol-gasoline blends could be carried out with no large problems during the transition. However, such a transition is by no means certain (see No. 6 under "negative factors" below).

Some of the negative factors which reduce the prospects for using methanol-gasoline blends in internal combustion engines are

1. The problems of water separation from methanol blends may become severe, especially during storage. Storage tanks at gasoline stations contain varying amounts of water. If methanol is introduced the methanol will combine with both water and gasoline and, at many of the storage facilities, a large second phase will separate out. This separation can lead to corrosion problems as well as vehicle driveability problems such as stalling.

2. Vapor lock is a potentially serious problem and the removal of some of the more volatile constituents of gasoline will not remedy this situation for all weather conditions and for all the automobiles in use today. Vehicle design modifications may prove necessary to avoid vapor lock difficulties.

3. Cold starts of engines remain a difficulty in some areas.

4. Inconclusive fuel economy results on methanol-gasoline blends leave uncertainty about an automobile's driving range when using a blend. It may prove, that for a given size tank, the range is less with a blend than with gasoline alone.

5. The blending process for large quantities of methanol may entail extra efforts and costs over present gasoline manufacturing and distribution processes.

6. Sufficient methanol for large numbers of automobiles, even using a 10% blend, may be difficult or impossible to produce, especially in a reasonable time. This is discussed in detail in the appendix.

4.2 CRITICAL INFORMATION GAPS AND NECESSARY FUTURE PROGRAMS

There is a definite need for systematic data on combustion, fuel economy, and emissions of methanol-gasoline fuel blends. Such data are required for the whole range of engines (4, 6, and 8 cylinder engines of different compression ratios and displacements.)

The toxicity of methanol-gasoline blends should be investigated on a long-term basis. Effects of formaldehyde, both in terms of toxicity and reactions within the engine should be studied. Possible ill effects on personnel handling methanol-gasoline blends should be determined.

Methanol-gasoline liquid fuel injection engines operating at high compression ratios should be further studied, since such systems offer promise for good fuel economy and low emissions.

The potentialities of alcohol additives, including higher molecular weight alcohols, to reduce NO_x emissions should be investigated. There is some suggestion that mixed alcohol additives

might provide flexibility in fuel production, which also warrants study. Tests should be made using alcohol compositions in use today and those in the development stage.

The potential for using methyl-fuel[®], in particular, containing several alcohols, may be greater than methanol alone. For example, Lerner⁸ et al have worked out phase diagrams that show the phase separation of methyl-fuel[®] and gasoline and of gasoline, methyl-fuel[®], and water to be far less serious than the separation when pure methanol is used with gasoline (See Figures 4-1, 4-2). However, these data are approximate, and good phase diagrams at different temperatures are needed for the methanol-gasoline-water and methyl-fuel[®]-gasoline-water systems. This need is related to the potentially major problem that with methanol blends a water phase separates out of the gasoline in the presence of methanol. This water phase can contain a large quantity of methanol. Thus, a small amount of water (0.3% by volume) can separate out from a 10% methanol-gasoline blend and grow to a 3% (by volume) phase containing roughly 30% of the methanol present. The resulting blend can then produce "ragged" engine performance and, potentially, corrosion. Gasoline and methanol are not miscible at low temperatures, and separation at low temperatures might also result in fuels which would cause engine starting problems.¹⁴ As noted by Reed, the latter problems can usually be solved by adding a highly volatile constituent such as acetone or ether to the fuel at the carburetor, either as a spray or as a fuel additive. Problems of vapor lock at high temperatures are similar to those with engines using straight gasoline, but often more severe. The extent of the problems and the optimum methods to overcome them need careful study.

Test programs that should be systematically undertaken in the immediate future to fill critical information gaps are listed below. Test methods should be coordinated for fuel preparation, test conditions, and measurement techniques and parameters.

Vehicle-related

Cold start (Evaluation of engine starting and operation in a low-temperature environment)

2. Vapor lock is a potentially serious problem and the removal of some of the more volatile constituents of gasoline will not remedy this situation for all weather conditions and for all the automobiles in use today. Vehicle design modifications may prove necessary to avoid vapor lock difficulties.

3. Cold starts of engines remain a difficulty in some areas.

4. Inconclusive fuel economy results on methanol-gasoline blends leave uncertainty about an automobile's driving range when using a blend. It may prove, that for a given size tank, the range is less with a blend than with gasoline alone.

5. The blending process for large quantities of methanol may entail extra efforts and costs over present gasoline manufacturing and distribution processes.

6. Sufficient methanol for large numbers of automobiles, even using a 10% blend, may be difficult or impossible to produce, especially in a reasonable time. This is discussed in detail in the appendix.

4.2 CRITICAL INFORMATION GAPS AND NECESSARY FUTURE PROGRAMS

There is a definite need for systematic data on combustion, fuel economy, and emissions of methanol-gasoline fuel blends. Such data are required for the whole range of engines (4, 6, and 8 cylinder engines of different compression ratios and displacements.)

The toxicity of methanol-gasoline blends should be investigated on a long-term basis. Effects of formaldehyde, both in terms of toxicity and reactions within the engine should be studied. Possible ill effects on personnel handling methanol-gasoline blends should be determined.

Methanol-gasoline liquid fuel injection engines operating at high compression ratios should be further studied, since such systems offer promise for good fuel economy and low emissions.

The potentialities of alcohol additives, including higher molecular weight alcohols, to reduce NO_x emissions should be investigated. There is some suggestion that mixed alcohol additives

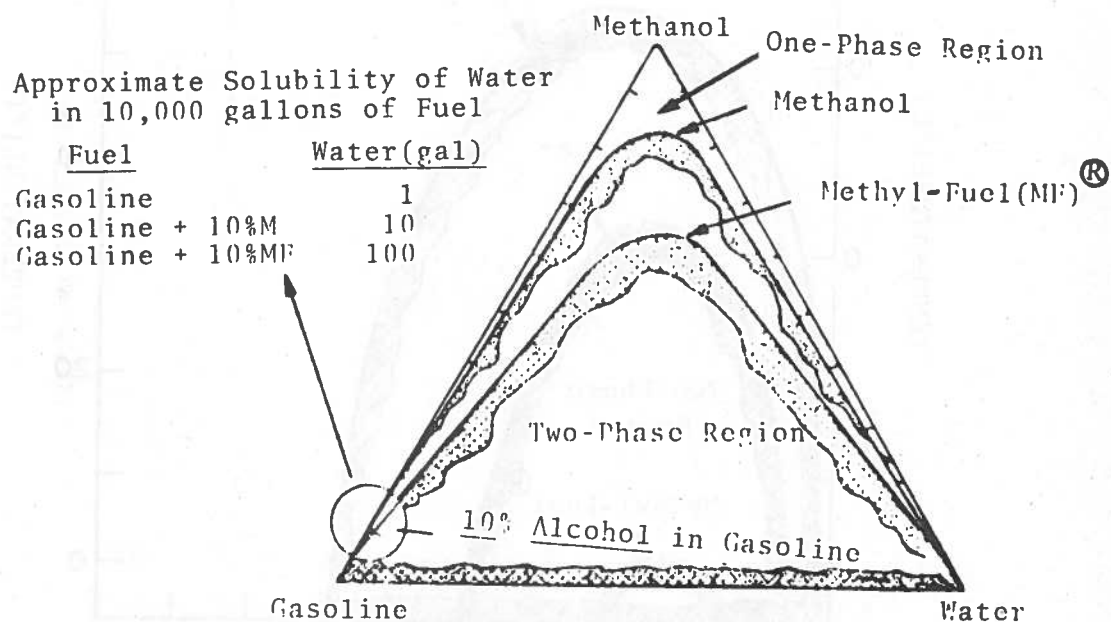
might provide flexibility in fuel production, which also warrants study. Tests should be made using alcohol compositions in use today and those in the development stage.

The potential for using methyl-fuel[®], in particular, containing several alcohols, may be greater than methanol alone. For example, Lerner⁸ et al have worked out phase diagrams that show the phase separation of methyl-fuel[®] and gasoline and of gasoline, methyl-fuel[®], and water to be far less serious than the separation when pure methanol is used with gasoline (See Figures 4-1, 4-2). However, these data are approximate, and good phase diagrams at different temperatures are needed for the methanol-gasoline-water and methyl-fuel[®]-gasoline-water systems. This need is related to the potentially major problem that with methanol blends a water phase separates out of the gasoline in the presence of methanol. This water phase can contain a large quantity of methanol. Thus, a small amount of water (0.3% by volume) can separate out from a 10% methanol-gasoline blend and grow to a 3% (by volume) phase containing roughly 30% of the methanol present. The resulting blend can then produce "ragged" engine performance and, potentially, corrosion. Gasoline and methanol are not miscible at low temperatures, and separation at low temperatures might also result in fuels which would cause engine starting problems.¹⁴ As noted by Reed, the latter problems can usually be solved by adding a highly volatile constituent such as acetone or ether to the fuel at the carburetor, either as a spray or as a fuel additive. Problems of vapor lock at high temperatures are similar to those with engines using straight gasoline, but often more severe. The extent of the problems and the optimum methods to overcome them need careful study.

Test programs that should be systematically undertaken in the immediate future to fill critical information gaps are listed below. Test methods should be coordinated for fuel preparation, test conditions, and measurement techniques and parameters.

Vehicle-related

Cold start (Evaluation of engine starting and operation in a low-temperature environment)

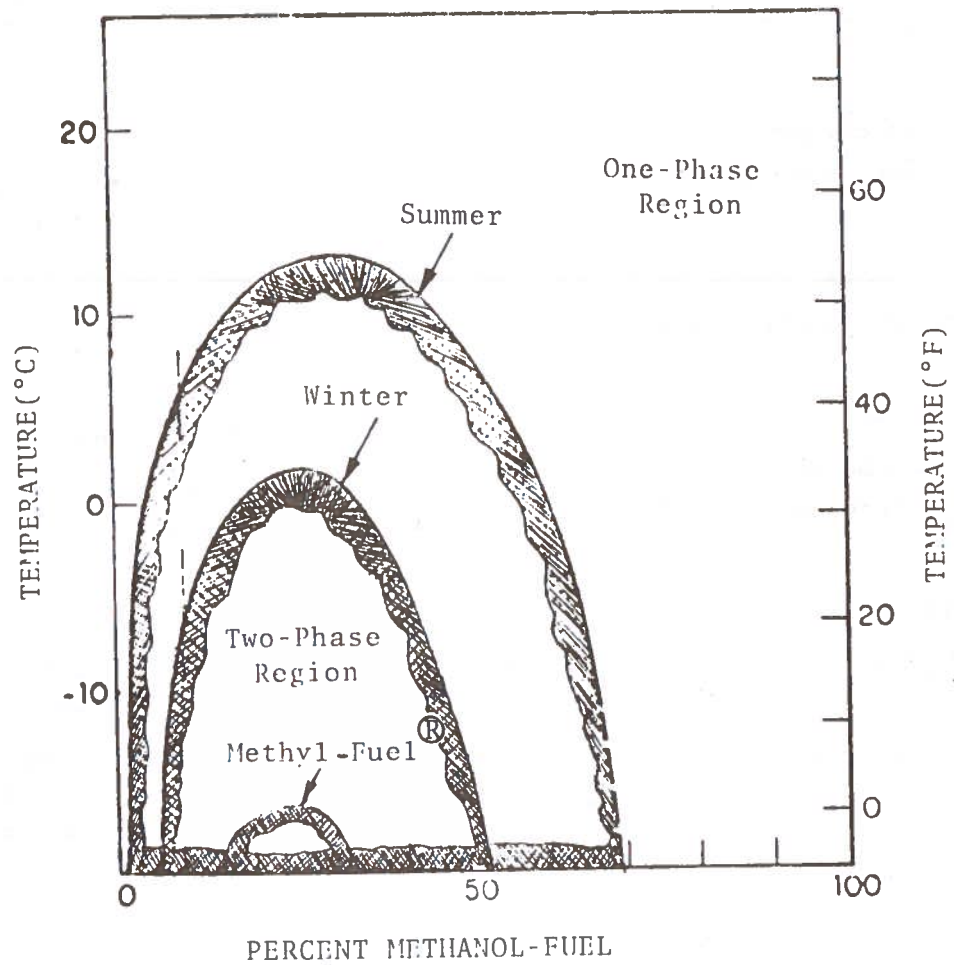


Source: Reference 8

Legend

M - Methanol
MF - Methyl-Fuel[®]

Figure 4-1. Water Solubility and Separation With Methanol and Methyl-Blend Fuel⁸



Source: Reference 8

Figure 4-2. Temperature Separation of Methyl-Blends in Winter and Summer Gasoline

Vapor lock (Study of liquid fuel flow interruption caused by fuel vaporization)

Spark management (Determination of spark position and gap for proper ignition and minimal NO_x emissions)

Materials compatibility for fuel tank and engine (Materials tests to determine fuel-related wear and corrosion mechanisms and avoidance/remedial possibilities)

Fuel induction system (Studies of methods of introducing fuel into the engine for optimum no-knock and combustion qualities)

Evaporative control system (Study of methods to maintain the engine's ratio of vapor-to-liquid fuel for good combustion and prevention of vapor lock)

Positive crankcase ventilation (Studies of effects on vapors when using methanol, and methods of removal of undesirable vapor)

Engine Life (Studies of possible harmful methanol/engine oil reactions and their effects, as well as methanol's itself, on engine life)

Emissions (Especially aldehydes) (Controlled, quantitative measurements of emissions under different experimental conditions, e.g., for different blend percentages)

Engine Operation Optimization (Quantitative, controlled measurements of performance, fuel economy and emissions, with suitably defined criteria for varying amounts of methanol and the amounts of gasoline constituents)

Driveability (Studies of stalling, surging, and bucking, including ways to prevent them)

Compatibility with existing car population (Feasibility studies of using methanol-gasoline blends in individual fleets and also in cars in general, to discover what, if any, changes must be made in engine or other vehicle design)

Water management (Study the water phase separation and its effect on engine operation, including methods to control the fuel's water content and to reduce the negative effects of water)

New engine systems (Study the use of blends in engine types other than the conventional, Otto cycle, internal combustion engine)

Fuel-related

Anti-knock (Determine octane numbers for blends containing varying amounts of methanol, and using different gasoline stocks)

Fuel additives (Determine compatibility of methanol with additives that are now used and are projected for future use in fuel)

Safety, health, and environmental effects (Study the toxic and/or other characteristics which, in handling and use of blends, introduce safety, health or environmental hazards)

Vapor control (Study the direct influence of methanol in the generation of vapors in engines, and methods for reducing undesirable effects)

Handling and transportation systems (Studies to determine problem areas, such as corrosion and solvent action of methanol)

Distribution of fuel to cylinders (Study optimum methods of fuel distribution to the engine cylinders)

Methanol composition (Quantitative studies of effects of changing methanol and methyl-fuel[®] percentages to determine optimum gasoline blends)

Volatility (Study blend volatility characteristics as a function of methanol/gasoline properties and of different gasoline stocks)

Homogeneity (Determine the importance of blend homogeneity and homogeneity lifetime of the initial blending)

Water management (Study water absorption by fuels and water separation problems in storage, handling, and distribution and the influence of temperature and climatic conditions).

5. PURE METHANOL AS AN ENGINE FUEL AND COMPARISON OF EFFECTS WITH THOSE OF GASOLINE

5.1 ENGINE/VEHICLE COMPATIBILITY

Methanol is generally compatible with present day automotive vehicles powered by spark ignition engines. Modifications to engine design for neat (pure) methanol use are discussed in this section. Methanol is suitable for use with external combustion engines such as those using the Rankine and Stirling cycles, and also with stratified charge engines and Wankel engines. It is not suitable for use with compression ignition (Diesel) engines.

Corrosion inhibitors may be necessary to prevent long-term effects on carbon steel in tankage and fuel transfer lines. Methanol is known to cause swelling of various polymers such as vinyls as well as acrylates, but is reported to be satisfactory with certain silicones, neoprene, butyl styrene butadiene, and other elastomeric compounds.

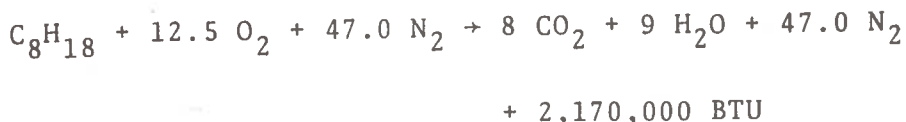
5.2 FUEL ECONOMY EFFECTS AND POWER OUTPUT

The most important factor in determining fuel economy for pure fuels such as isooctane and methanol is the heating value, given in Table 2-1. This shows methanol to have a decided disadvantage relative to isooctane. However, the effective pressure and fuel economy for methanol and methanol-gasoline blends also depend on other factors such as the latent heat of vaporization, shown in Table 2-1. The high latent heat of methanol serves as an effective internal coolant for spark ignition engines. The increased power output from methanol, relative to gasoline, can be laid to²⁰

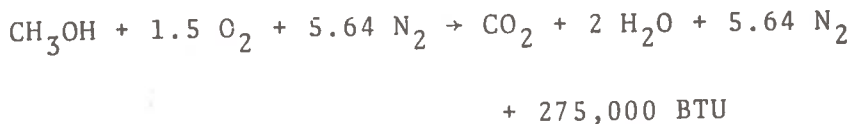
1. A higher volumetric efficiency from the cooling action;
2. Less work done on the compression stroke because vaporization holds down temperature and pressure;
3. More work done on the expansion stroke since mole product per mole mixture is higher.

An analysis of the third effect above can be made directly. If complete combustion is assumed to take place in an engine when stoichiometric fuel-air equivalence ratio mixtures* ($\phi=1.0$) have been introduced to the combustion chamber, the complete reactions (neglecting dissociation) proceed as follows:

For isooctane,



For methanol,



In the above, the assumption is made that air is 21% O_2 and 79% N_2 by volume. Two extreme conditions can now be analyzed. If the fuel enters the engine as a vapor, the ratio of moles of product to moles of reactant is determined on the "dry-basis." On the other hand, a modern engine usually does not ingest its mixture with the fuel already completely evaporated. The fuel may even be entirely unevaporated, the "wet-basis," in a direct injection engine. (Under such conditions, the moles of product depend on the number of moles of air inducted, since the fuel occupies very little of the volume.) In general, the real situation lies somewhere between the extremes.

For isooctane, the moles of products per unit mole of reactants, are:

$$\text{dry-basis} \quad -- \quad \frac{64}{60.5} = 1.058$$

$$\text{wet-basis} \quad -- \quad \frac{64}{59.5} = 1.075$$

*See Appendix C, Glossary for fuller definition of equivalence ratio.

For methanol, they are:

$$\text{dry-basis} \quad -- \quad \frac{8.64}{8.14} = 1.061$$

$$\text{wet-basis} \quad -- \quad \frac{8.64}{7.14} = 1.210$$

As can be seen, the methanol figures run higher, and the wet versus dry relationship is as predicted; the wet figure is larger than the dry figure and increasingly so for methanol over isooctane. This suggests that injection holds promise for increasing methanol's output even beyond that being obtained today by fuel injection of gasoline. Two other effects for methanol, resulting in larger increases in power output and probably also fuel economy as compared with isooctane, are its higher volumetric efficiency and the decreased work necessary on the compression stroke. These result from methanol's high latent heat of vaporization, which is three and one-third times that of gasoline. The higher volumetric efficiency⁵ may be minimal, but the reduction in compression work is significant. Calculations indicate twenty percent less compression work for methanol as compared to isooctane for stoichiometric and richer conditions, when assuming a wet charge, a compression ratio of 9 to 1, and intake air at 100°F.

In comparing methanol and gasoline, fuel economy expressed in miles per BTU is approximately equal whereas fuel economy expressed in miles per gallon tends to favor gasoline by about two to one, even including the considerations above. This ratio can be reduced somewhat by increasing the compression ratio, especially in the case of lower equivalence ratios than gasoline, without misfire, and thus can more readily be considered for higher compression ratio engines. Generally, increasing compression ratios from, say 8 to 1 to 12 to 1 is accompanied by a 10 to 12% increase in power at fixed stoichiometry. This is roughly equivalent to fuel savings obtained by operating with 10 to 12% leaner mixtures at fixed engine power.

Engine modifications which must be made in order to use methanol at equivalence ratios comparable to those used for gasoline

include (1) larger carburetor jet orifices, (2) heated intake manifolds, and (3) a fuel system permitting changes in fuel constituents when operating at low temperatures. A recent study of these modifications and their effects was made at Stanford University on an American Motors Gremlin by Adelman et al.²¹ The Gremlin was converted using an exhaust-heated intake manifold, a rejetted carburetor with heat exchanger for heating the fuel-air charge, a catalytic muffler, and an exhaust-port air injector. The gasoline idle and main jet orifices were each increased by a factor averaging 2.5 to give the lowest possible emissions for methanol and still retain enough power for good driveability. Comparable levels of vaporization require an order of magnitude more heat for methanol than for 60% isooctane (gasoline). This assumes the use of comparable equivalence ratios. This requirement necessitated drastic intake manifold alterations. Low temperature (40°F) starting was assured by a dashboard controlled fuel pump which injected acetone into the fuel line at the carburetor.

The experiences of Adelman²¹ et al with their Gremlin led them to further suggestions. "The cold-start tests indicate the need for further increases in heat addition to the fuel-air mixture after starting. Additional manifold heating coupled with an air preheater, as employed on some current models, could be used to improve warmup and increase fuel vaporization. To obtain a nearly wet charge, and thus extract full power at wide-open-throttle, a vacuum-controlled bypass of the air preheater could be used.

"An alternative method is to change from carburetion to fuel injection. Advantages are increased power (wet charge), uniform distribution to every cylinder, and easier starting with a shorter warmup period. The disadvantage is, of course, the increased cost and complexity.

"Even with fuel injection, it is to be expected that problems will be encountered with starting at low temperatures. The addition of a volatile component to the fuel or prevaporization, as with electric heating before starting, could improve the cold

startup.

"While no internal changes were made to the Gremlin engine, an increased compression ratio when operating on methanol might be desirable. Such an increase would take advantage of its high octane number to improve thermal efficiencies and thus increase fuel mileage."

Work done at the Chevron Research Company complements the work at Stanford.²² Chevron feels that methanol's major problem is engine starting. "On the subject of cold starting..., we have tried adding a volatile gasoline component to the methanol. We have tried this with a fuel-injected Volvo and found that it required very large quantities of light hydrocarbons, which would not be a practical solution. Prevaporization of the fuel might sound interesting; but once again, I believe the vapor would simply condense again and the same cold starting problem would still exist. Our experience indicated that one could spray large quantities of alcohol into the engine and it still would not start if the temperatures were too low. We feel that probably the best solution for the starting problem, if fuel injection is to be employed, is to use a starting fuel system. The starting fuel could simply be gasoline which would be injected in place of the alcohol through the cold start valve. The Bosch starting system is completely independent of the main system; thus, gasoline would only be injected while the engine is being cranked over. This system would require only a small tank, perhaps just one pint, another pump, and a pressure relief valve, plus very simple wiring and plumbing changes. This would require checking the start fuel supply periodically, but this is very little more complicated than all the other items that must be checked when a car is driven into a service station for gasoline.

"I have been discussing this problem in connection with the use of fuel injection, but the same sort of a system could possibly be used with carburetion. However, it might require a sophisticated type of control to determine how much and how long the starting

fuel should be injected each time the engine is started."

An extensive fuel characterization and comparison test series with a single cylinder CFR engine at a 7.5 to 1 compression ratio was performed by Ebersole and Manning.⁶ They showed the effects of spark timing and lean operating limits. In this study, the indicated specific fuel consumption for methanol was 2.5 times that for isooctane under conditions of equal power outputs and equivalence ratios. The lean misfire limits with methanol were approximately 0.2 equivalence ratios leaner than with isooctane.

A Chevron road test of a modified 6-cylinder Dodge Dart, using methanol and pre-dissociated methanol, was performed by Fitch and Kilgroe.²³ Carburetion and manifold modifications were made, and tests results showed generally rich operation and non-uniform distribution with pre-dissociated methanol. Fuel mileage was significantly reduced. The main jet diameter was increased for operation both at lean and at rich mixtures. Unfortunately, because of major difficulties encountered during the experimental program, proper assessment of the performance with methanol cannot be made.

Fitch and Kilgroe²³ also conducted laboratory tests using a single cylinder CFR variable compression-ratio research engine. The effects of compression ratio, fuel-to-air ratio, percentage of methanol dissociation, intake manifold mixture temperature, and timing on engine performance and exhaust emissions were investigated. It was found that specific fuel consumption decreased with increased compression ratio (values up to 15 to 1 were used) and the engine could be operated at very lean mixtures ($\phi = 0.65$). Slight improvement in engine brake horsepower performance was also noted with partially dissociated methanol; more definitive results were not obtained because of problems attributed to improper setup of engine conditions such as timing, intake and temperature, and other operational uncertainties.

Kilgroe⁹ and others have also conducted tests at the University of Santa Clara, on the use of dissociated methanol in the CFR engine. Results show lower thermal efficiencies for the dissociated than for undissociated methanol. Methanol and gasoline gave

comparable results, with gasoline having slightly higher thermal efficiency at lean operation and methanol slightly higher thermal efficiency at rich operation. Engine power results were also similar for gasoline and methanol.

Continental Oil Company work shows methanol to be superior to gasoline in both lower emissions of CO, hydrocarbons, and NO_x, and in fuel economy expressed in hp-hr/BTU or in miles per BTU.³⁷

Volkswagen¹⁷ has reported results of a recent study by VW and Daimler-Benz. The effective power outputs of gasoline and of methanol used in a single cylinder VW engine as a function of air-fuel equivalence ratio were determined. The methanol engine produced approximately 12 percent more power than the gasoline engine on the average. As also noted by Ebersole and Manning,⁶ the lean misfire limit of the methanol engine is displaced a long way into the lean mixture region. Volkswagen also obtained similar positive results in terms of increased output and improved exhaust emissions on full-scale engines.

The specific fuel consumption of the methanol fueled engine¹⁷ related to fuel mass was much higher than that of the gasoline fueled engine for equivalent engine output as expected, but the fuel consumption related to consumed energy was found to be considerably lower (around 10%) than that of the gasoline fueled engine. Fuel economy, expressed in miles/BTU, would be expected to be improved correspondingly, as well.

Little is known about methanol liquid fuel injection engines operating at high compression ratios. This area warrants investigation as a possible source of improvement in lean operating engine power and efficiency, with reduced pollution levels as well.

5.3 EMISSION EFFECTS

A large number of automobiles in operation now and perhaps for the next several years are equipped with engines that require fuels with an octane rating of 97 or higher. Lead alkyl additives have been used in gasoline to achieve such high anti-knock ratings, but these will not be permitted in the future. The addition of aromatic constituents to gasoline can increase the octane rating but also create some problems.¹⁰ There is usually an increase in carbon deposits when aromatic rich blends are used and it is reported that aromatics increase the reactivity and carcinogenic character of exhaust emissions. In addition, more barrels of crude oil are required to provide the same volume of fuel rich in aromatics since the crude oil has to be highly cracked and reformed in order to obtain the requisite octane number.

Recently, studies on methanol fuel exhaust pollution levels have been made which showed the use of methanol in internal combustion engines to produce less pollution than gasoline, even when compared to leaded gasoline as presently constituted and ignoring emissions directly attributable to lead.

Adelman et al²¹ at Stanford University conducted tests of their Gremlin at EPA laboratories, and demonstrated that the car surpasses the 1975-76 Federal standards for unburned hydrocarbons, carbon monoxide, and NO_x . The low emissions were due to four factors:

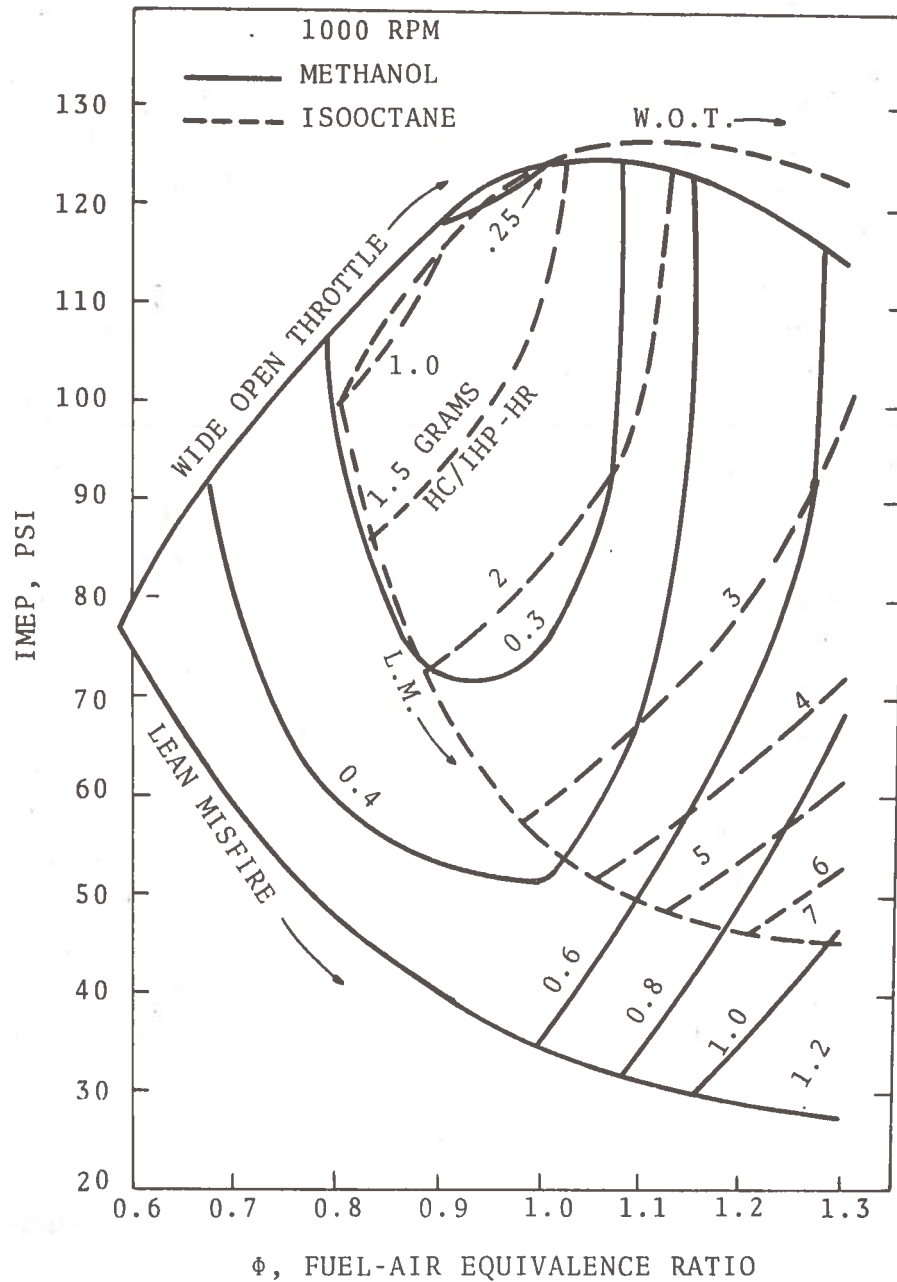
1. The apparently lower (than gasoline) lean misfire limit of methanol, which permits successful operation at $\phi = 0.75$, thus reducing HC, CO, and NO_x emissions while maintaining adequate performance.
2. The higher flame speed of methanol, which permits spark retardation resulting in lower NO_x levels.

3. The somewhat lower combustion temperatures (about 180°F at the same equivalence ratio) of methanol compared to hydrocarbon fuels, which slows the formation of NO, thus reducing NO_x. A chemical kinetic model of NO formation was developed to explain the results.
4. The use of a catalytic muffler, with air injection, to reduce HC and CO concentrations in the exhaust gas after it leaves the engine.

Fitch and Kilgroe²³ used their converted Dodge Dart with methanol to study emissions, but obtained inconclusive results, since their engine system was not optimized. They did observe high aldehyde emissions and relatively low NO_x.

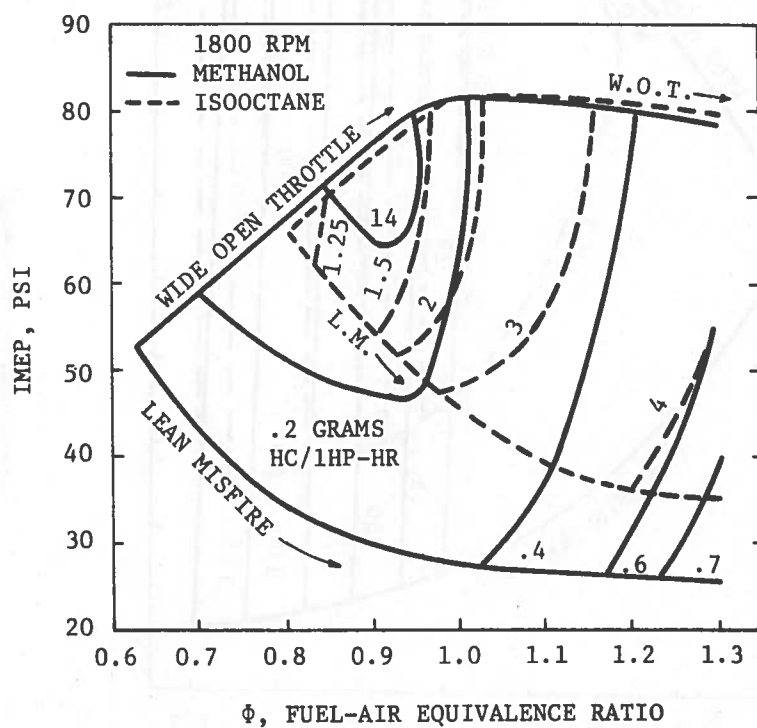
The extensive comparison test for isooctane and methanol by Ebersole and Manning⁶ with a single cylinder CFR engine at 7.5 to 1 compression ratio gives quite thorough results on emissions of hydrocarbons, carbon monoxide, nitric oxide, and aldehydes. The experiments were designed to assure good mixing and fuel vaporization. Experimental data contour maps from the work allow comparisons of power, equivalence ratio, and emissions obtained with prevaporized fuel-air mixtures. The results are summarized in chart form for data obtained at engine operating speeds of 1,000 rpm and 1,800 rpm. Figures 5-1 through 5-8 map the unburned hydrocarbons, carbon monoxide, nitric oxide, and aldehydes obtained over a range of power settings and equivalence ratios. These figures have been reprinted with the copyright permission of the Society of Automotive Engineers.

The maps take the form of parameter contours plotted on a coordinate system of indicated mean effective pressure on the y-axis and equivalence ratio on the x-axis. All possible direct comparisons between the two fuels (at the same speed) are made by superimposing the isooctane data on the methanol data. These reduced maps have three boundaries: wide open throttle, lean misfire, and $\phi = 1.3$. The area included within the three boundaries of the reduced map represents all possible combinations of indicated mean effective pressure (imep) and equivalence ratio that permit misfire-free operation at maximum-power spark timing. The large area



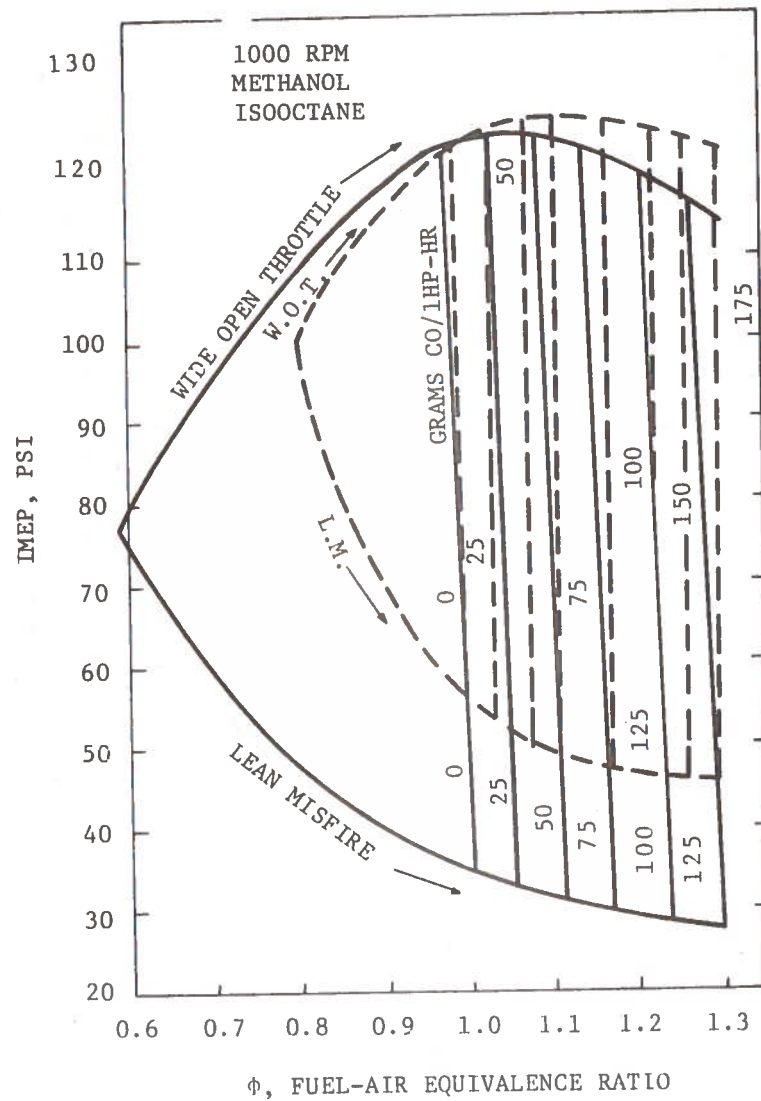
Source - Reference 6

Figure 5-1. Interrelations of Power, Equivalence Ratio, and Hydrocarbon with Isooctane and Methanol at 1,000 rpm



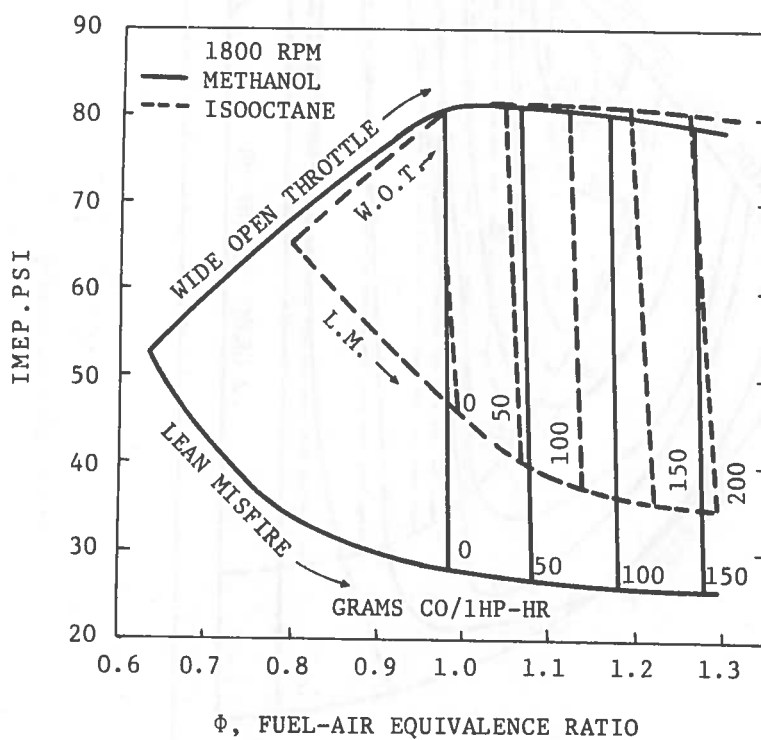
Source: Reference 6

Figure 5-2. Interrelations of Power, Equivalence Ratio, and Hydrocarbon with Isooctane and Methanol at 1,800 rpm



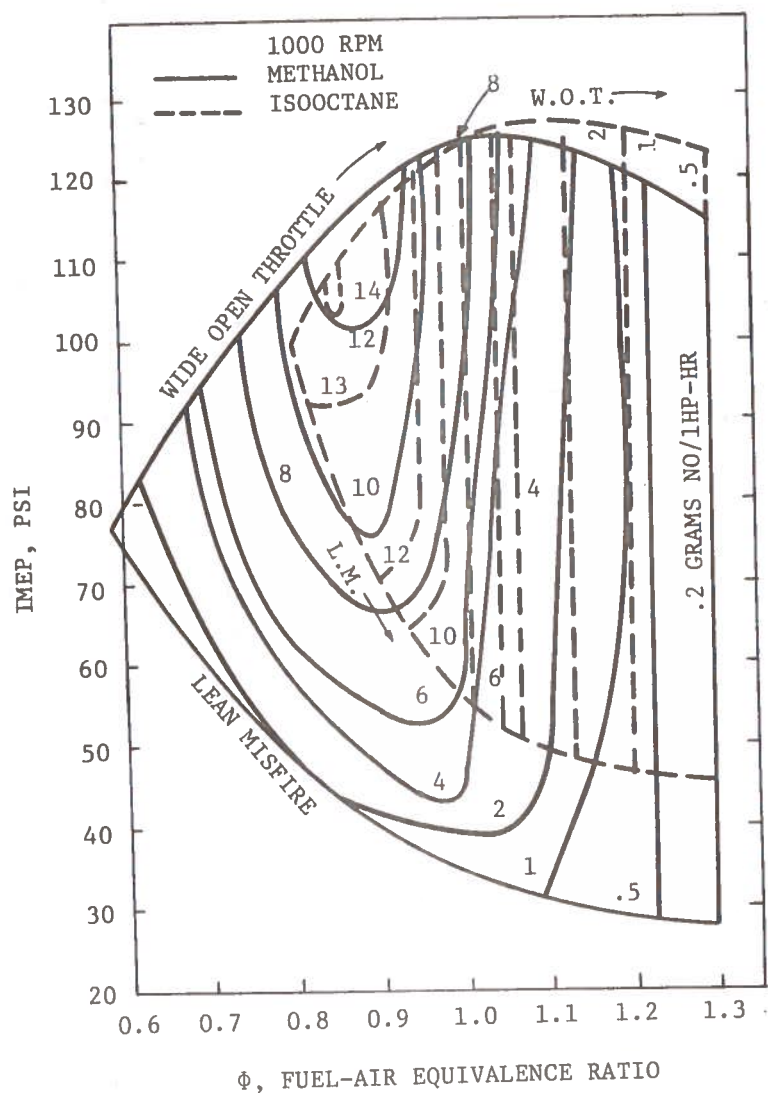
Source: Reference 6

Figure 5-3. Interrelations of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,000 rpm



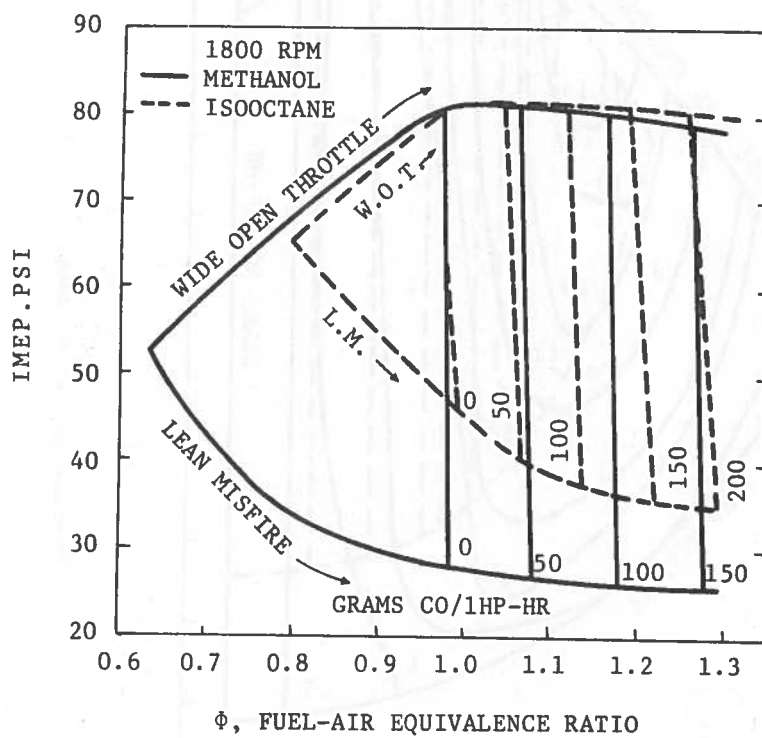
Source: Reference 6

Figure 5-4. Interrelations of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,800 rpm



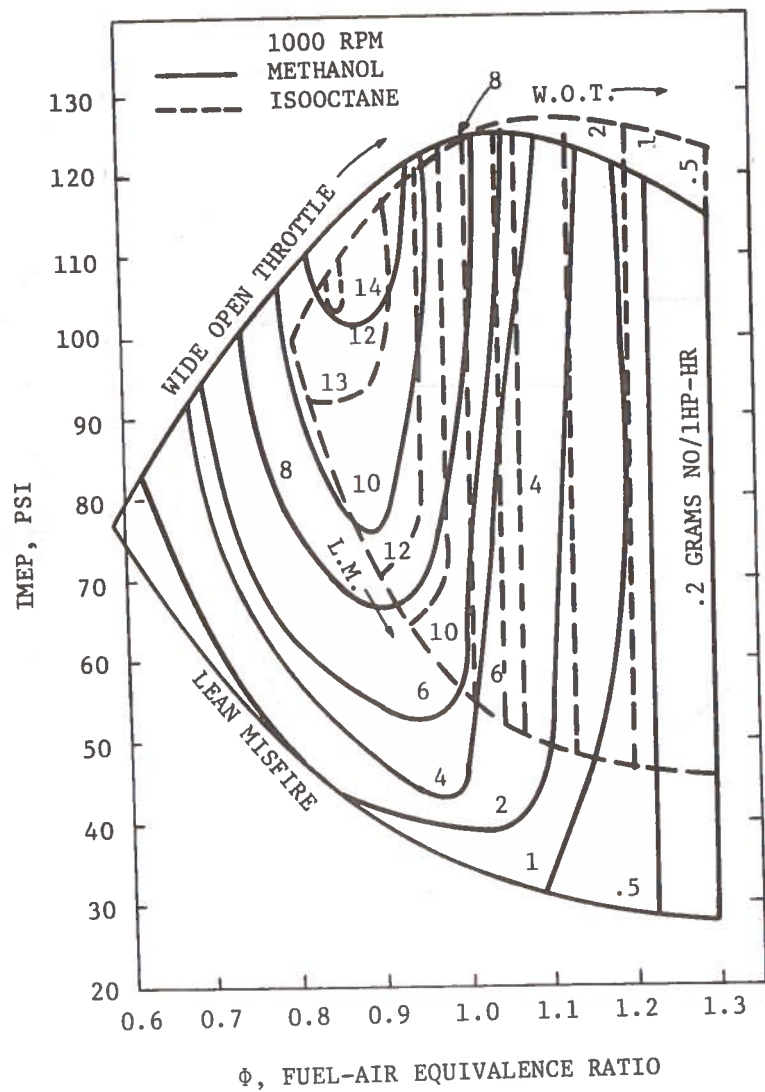
Source: Reference 6

Figure 5-5. Interrelations of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,000 rpm



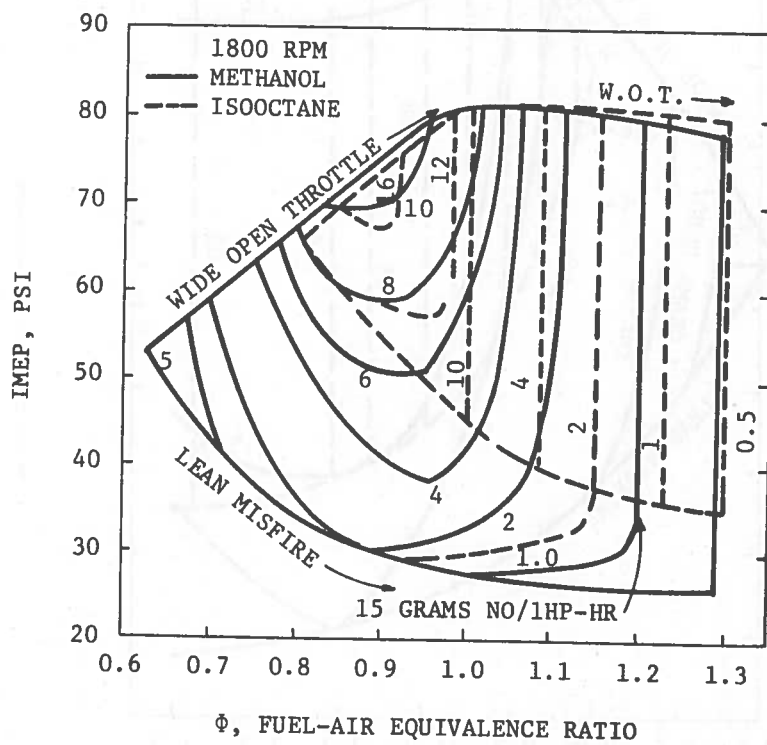
Source: Reference 6

Figure 5-4. Interrelations of Power, Equivalence Ratio, and Carbon Monoxide with Isooctane and Methanol at 1,800 rpm



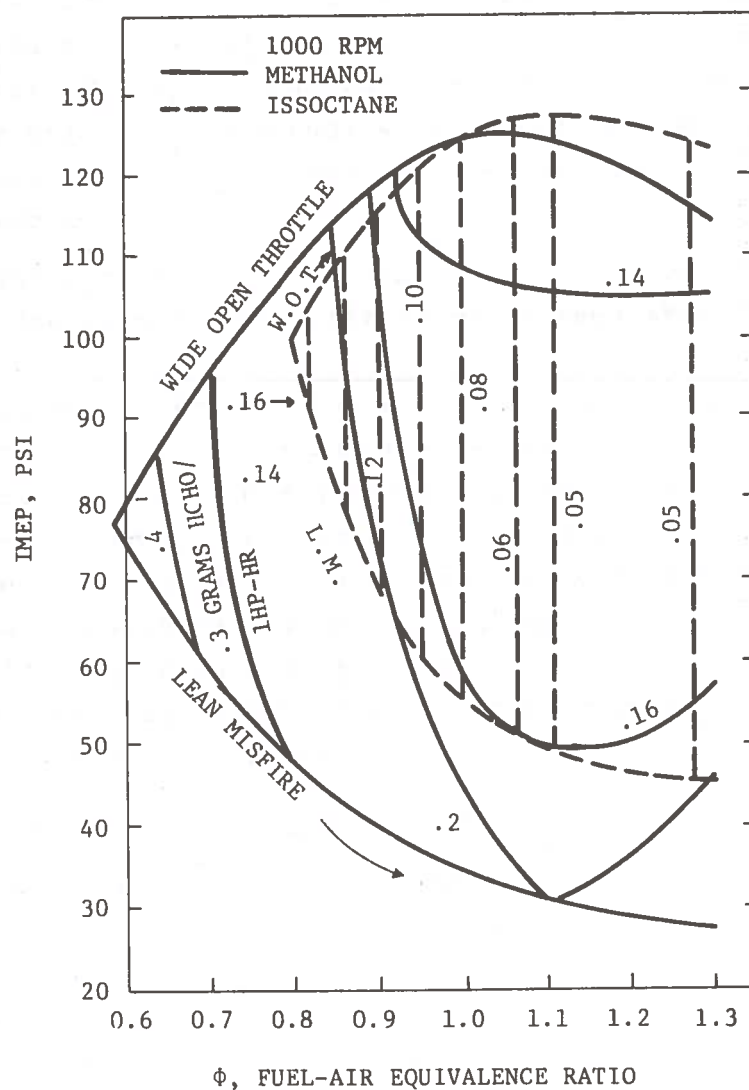
Source: Reference 6

Figure 5-5. Interrelations of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,000 rpm



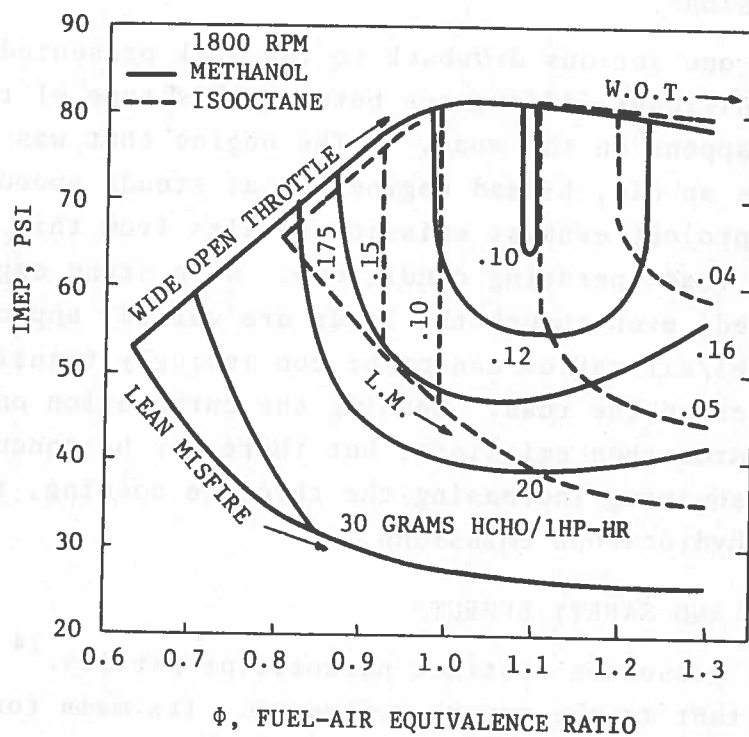
Source: Reference 6

Figure 5-6. Interrelations of Power, Equivalence Ratio, and Nitric Oxide with Isooctane and Methanol at 1,800 rpm



Source: Reference 6

Figure 5-7. Interrelations of Power, Equivalence Ratio, and Aldehydes with Isooctane and Methanol at 1,000 rpm



Source: Reference 6

Figure 5-8. Interrelations of Power, Equivalence Ratio, and Aldehydes with Isooctane and Methanol at 1,800 rpm

associated with methanol occurs because the methanol lean limits are reached at lower equivalence ratios.

The quantity of unburned fuel in the exhaust, using methanol, was 0.1 to 0.3 times that of isooctane. Negligible carbon monoxide emission levels existed with both fuels at stoichiometric and leaner mixtures. Carbon monoxide emissions with isooctane increased at a faster rate as the equivalence ratio increased. Emissions of nitric oxide with methanol were generally lower than with isooctane (one-half at midrange imep), while the inverse was true for aldehyde emissions.

There is one serious drawback to the work presented above: there are significant differences between this type of testing and what really happens on the road.²² The engine that was used, a CFR engine, is an old, L-head engine run at steady speed. It is difficult to project exhaust emission results from this setup to results under road operating conditions. On a stand engine running at steady speed, even though the loads are varied, approximate changes in fuel/air ratios cannot be convincingly translated into similar changes on the road. Leaning the carburetion on a car can reduce the hydrocarbon emissions, but there may be concurrent power loss, requiring increasing the throttle opening, thus increasing the hydrocarbon emissions.

5.4 TOXICITY AND SAFETY EFFECTS

Methanol possesses distinct narcotic properties.²⁴ It is also a slight irritant to the mucous membranes. Its main toxic effect is exerted upon the nervous system, particularly the optic nerve and possibly the retina. The permissible limits of methanol vapor for workers who are exposed on a full work-week basis over extended periods is 220 ppm. Unfortunately, the distinctive odor does not become apparent until concentrations two orders of magnitude greater are present, and thus an additional material with a distinctive odor will have to be added to methanol if it is to be used extensively. Methanol is used safely in bulk quantities at the present time, but there is a need for more information of extended lower-level exposure to methanol, a possible result of widespread

use as a motor fuel. This should include studies on the effects of formaldehyde formed when methanol is used. It should also include any effects on the skin by methanol.

Methanol is presently safely and effectively handled by observing standard precautions for handling a flammable, toxic material. Methanol fires should be easier to quench than gasoline fires because of water/methanol miscibility. The autoignition temperature of methanol (878°F) is comparable to that for gasoline. The flash point for methanol (52°F) is comparable to or lower than that of many liquid fuels, but it is much higher than that for gasoline (-40°F), which is to its advantage, since fire hazard increases as flash point decreases.

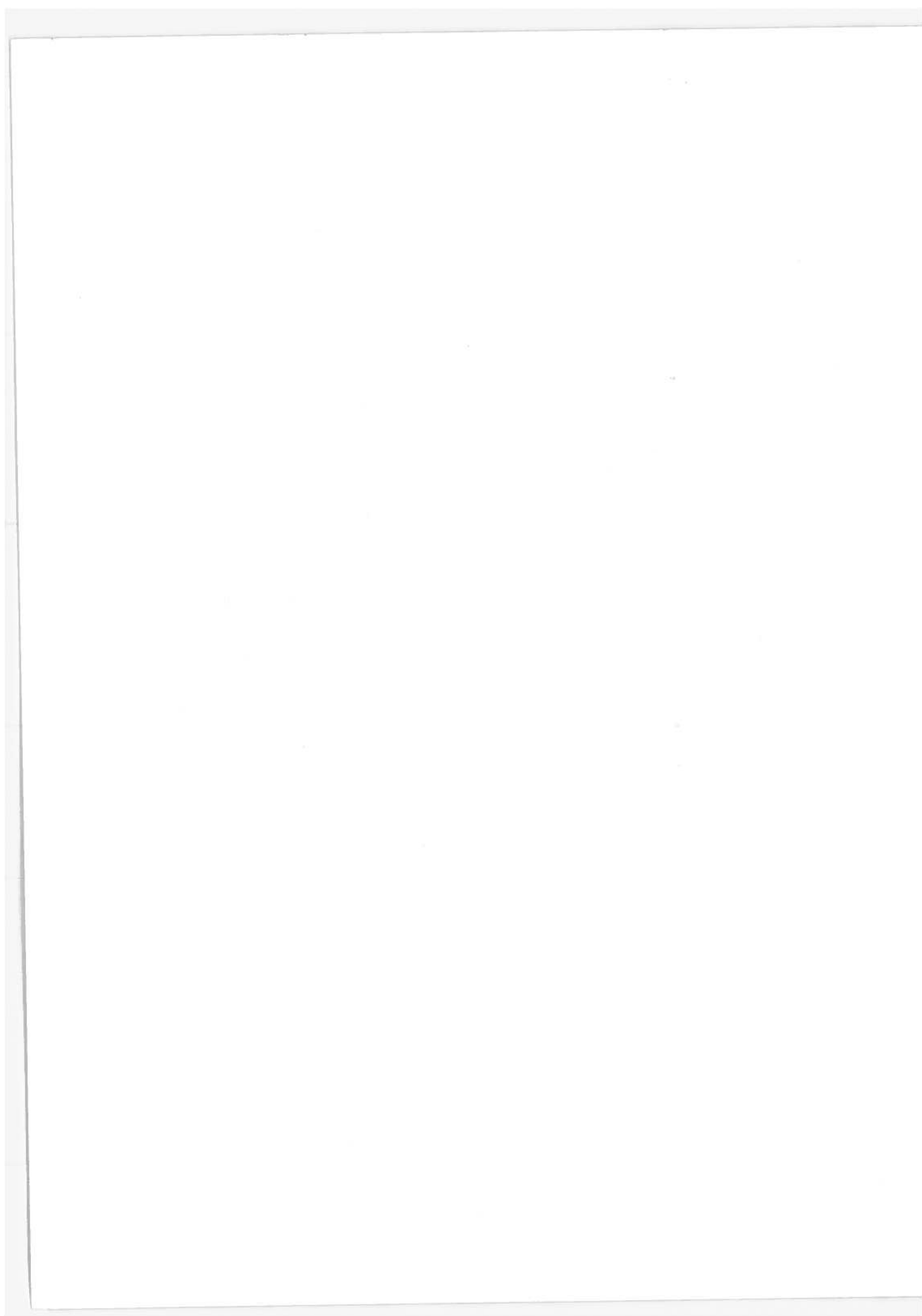
5.5 HANDLING, STORAGE, AND DISTRIBUTION

Handling, storage, and distribution differences between methanol and gasoline should be minimal. Problems related to corrosion and solvent action are not well known and need to be investigated. The miscibility of methanol and water also requires further study, particularly as it effects corrosion on metal and plastic materials after long term exposure.

5.6 CRITICAL INFORMATION FOR USE OF NEAT (PURE) METHANOL

Efficient production and distribution are prerequisites for methanol utilization on a large scale and consequently the methanol production and the distribution systems should be studied. One effort was an Exxon study²⁵ for EPA. Related studies were performed by IGT,²⁶ also for EPA. There is also a need for more systematic data on the combustion characteristics and emissions for neat methanol or methanol with fuel additives.

Some of the information gathered on methanol blends may prove useful for the use of neat methanol. However, directed pilot studies extended to small fleets will be necessary to evaluate and "prove" engine modifications. The use of neat methanol in limited fleets may even offer a partial solution to the conservation of petroleum fuels, and that aspect should be pursued in small directed research and development programs, as well as in the more extensive blend programs.



APPENDIX A

METHANOL MANUFACTURE AND PRODUCTION

A.1 RESERVES AND RAW MATERIAL SOURCES

Fossil fuels and renewable fuels are both potential sources of methanol. Fossil fuels include natural gas, petroleum, oil shale, lignite, and coal. Renewable fuels consist of municipal, agricultural, and forest refuse, as well as products of photosynthesis. The idea of recycling the products of combustion, namely CO_2 and H_2O , to obtain fuels again is also under study by the Institute of Gas Technology:²⁷ H_2O , by electrolysis, to hydrogen and oxygen, and CO_2 , by catalytic conversion, to carbon monoxide and methanol.

Practically any organic matter, including fermentable matter, can be used to produce synthesis gas (hydrogen, carbon monoxide, and often carbon dioxide) which is used for direct conversion to methanol. However, the discussion on reserves is limited to the domestic starting materials commonly used because of the current emphasis on self sufficiency. Estimates of natural gas resources total 1,412 trillion¹⁹ cu ft., which is equivalent to about 1450×10^{15} BTU. In addition, 6.8 billion barrels (27×10^{15} BTU) of natural gas liquids are believed to be recoverable. Assured crude oil reserves of approximately 36 billion barrels (210×10^{15} BTU) are known. Estimates of undiscovered resources bring the total for liquid and gas resources to 472 billion barrels (2700×10^{15} BTU). The above theoretically could lead to 40 trillion gallons of methanol.¹⁹

Coal is by far the largest and most probable single energy resource available for synthetic fuel production with an estimated total U.S. reserve of 3.2 trillion tons (80×10^{18} BTU). This represents a potential of about 500 trillion gallons of methanol (cf. Table A-1).

Other solid materials are usable besides coal. Shales in the U.S. could yield liquids that are potential fuels. One estimate is that up to 1780 billion barrels (10×10^{18} BTU) are available.²⁰

TABLE A-1 METHANOL SOURCES AND PRODUCTION

Energy/Material Resources	Process	Comment on the process	Synthesized Fuel	By-Product	Thermal Efficiency %	Comments on Pollution
<u>Coal to Methanol</u> 2 tons of coal (8Btu/lb) About 1 ton of oxygen	Use any gasifier to make synthesis gas, Lurgi and others. (Oxygen requirement varies with the process)	Coal is gasified and converted to CO + H ₂ - rich gas. The gas can be converted to methanol in presence of catalyst at about 40-50 atm and 200° to 300°C	1 ton of methanol	Small amount of higher alcohol is produced	50	Sulfur removal problems are similar to coal gasification problems.
<u>SNG to Methanol</u> 30.2 million Btu feed and fuel 75 k Whr power 7,300 SCF CO ₂ 144,016 feed water 13,200 gal cooling water	Same	Natural gas is reformed to synthesis gas. The synthesis gas is compressed to 40-50 atm and converted to methanol in presence of copper - containing catalyst at 200° - 300°	1 ton of methanol	Small amount of higher alcohol is produced	63	Minimum pollution problems.
<u>Coal or Oil Shale Derived Naphtha to Methanol</u> 1148 lb naphtha 9.7 million Btu fuel 58 k Whr power 1600 lb feed water 12,700 gal cooling water	Same	Naphtha is converted with steam to a CO and H ₂ - rich gas and then converted to methanol in presence of catalyst at 200° - 300°C	1 ton of methanol	Small amount of higher alcohol is produced	59	Sulfur removal is necessary for feedstocks containing sulfur.
<u>Coal or Oil Shale Derived Heavy Fuel Oil to Methanol</u> 2020 lb Bunker "C" (18,300 Btu/lb) 130 k Whr power 1680 lb feed water 19,800 gal cooling water	Same	Naphtha is converted with steam to a CO and H ₂ - rich gas and then converted to methanol in presence of catalyst at 200-300°C	1 ton of methanol	Small amount of higher alcohol is produced	50	Sulfur removal problems are similar to coal gasification problems.

The manufacture of methanol can be combined with waste disposal. This will extend fossil fuels, and make use of the accumulating amounts of waste material. An "oxygen refuse converter"¹⁴ that converts refuse to methanol is only one of a number of processes that have been suggested recently. The United States produces about 4×10^{11} lb. of solid refuse each year. The energy in the gas available from this refuse is 2 percent of the 7.0×10^{16} BTU consumed each year. If this gas could be entirely converted to methanol, 8 percent of the fuel for our transportation needs would be provided. Even a fraction of this amount would be significant. However, realistic projections of methanol production from waste matter in the 1980's are several orders of magnitude lower than for production from coal and two orders of magnitude lower than for production from natural gas.²⁸

Converters such as the one mentioned above can be used to convert farm waste and the waste from lumbering as well as refuse. Forests might also be grown as a raw material source for methanol. A conversion of solar energy with an efficiency close to 1 percent can be achieved by improved forest management, resulting in an energy output which could almost double our present energy supplies, provided an area of one-fourth the land area of the U.S. is used. Forests now cover more than this land area, but are not always efficiently utilized. The advantage of converting forest timber to methanol is in the conversion efficiency, and complete trees can be used, not merely those fractions that make good lumber or pulp. Steam gasification of wood char is one of the better methods to produce synthesis gas which can then be converted to methanol.

Other sources of usable gas for methanol include by-products of industrial processes. Refinery gases containing hydrogen, metallurgical process gas, and fermentation process gases are potentially available. The use of waste gases may become increasingly attractive as well, especially if the cost of available raw materials continues to increase.

Hydrogen and carbon oxides are available directly. Hydrogen can be prepared by electrolyzing water or can be obtained as a

by-product from certain electrolytic processes such as brine electrolysis. Sources for manufacture of carbon oxides include naturally occurring carbonates in the form of limestone and dolomite deposits, or even seashells and coral. The projected energy costs using these sources are excessively high at this time.

A.2 METHODS OF MANUFACTURE

As of January 1, 1971, 71% of the U.S. synthetic methanol capacity was based on high pressure processes with the remaining 29% based on low-pressure processes. Of the announced new plants and expansions, however, 96% will be based on low-pressure processes. This information and Sections 1, 2, and 3 below are mainly from the Blackford reference.²⁹

Sections A.2.4 and A.2.5 below are proposed manufacturing methods, which use a two-step sequence, namely the production of gases and then the conversion of these gases to methanol. Pilot programs for the manufacture of methanol from coal have been successful, but no significant methanol production presently uses coal as raw materials.

A.2.1 High-Pressure Processes

In high-pressure processes, pressurized synthesis gas (usually made by reforming straight natural gas and consisting of a mixture of carbon monoxide, carbon dioxide, and hydrogen) is converted into methanol according to the following:

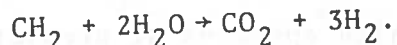
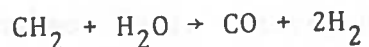


and



ΔH is the change in enthalpy.

In order for the ideal stoichiometric synthesis gas to be produced, the hydrocarbon feed to the reformer should have the empirical formula CH_2 , so that the following reactions can occur:



Most methanol manufactured in the U.S. is based on natural gas. Since natural gas contains more than the ideal amount of hydrogen, carbon dioxide is usually added to the feed to balance the excess hydrogen. In a related process, large amounts of carbon dioxide are removed from the synthesis gases used to produce ammonia. Thus, methanol plants have usually been located close to ammonia plants. Another source of carbon dioxide has been an amine scrubber which can recover CO_2 from the reformer flue (purge) gases in the methanol plant.

In a typical high-pressure process, the synthesis gas is desulfurized, cooled so that steam can be removed, compressed to a pressure of 4300 psi, mixed with recycle gas, and passed to the methanol converter via a filter which removes any oil. The conversion of synthesis gas to methanol takes place at temperatures around 300°C in the presence of a zinc-chromium oxide catalyst. The methanol-containing gases formed are cooled, condensed, and purified by distillation. The residual gases are returned to the system for reprocessing. Small amounts of dimethyl ether (light ends) and higher alcohols (high-boilers) are also formed, and can be removed by two distillation towers; the light ends may be burned in the reformer, and the high-boilers can be either recovered or burned. An overall yield of over 60% methanol of 99+% purity may be obtained by these processes using natural gas as a raw material.

A.2.2 Low-Pressure Processes

Although there are several low-pressure methanol processes in existence, the process developed by Imperial Chemical Industries Limited (ICI) of Great Britain is the one now being used in the United States. Monsanto Company brought a 100 million gallon per year plant on stream at Texas City, Texas, near the end of 1970,

based on this process, and several other companies have built plants since then.

The ICI process, which operates at pressures around 750 psi and at temperatures around 250°C, differs from high-pressure processes in several ways besides using a lower pressure. The addition of carbon dioxide to balance excess hydrogen in the feed is unnecessary in the ICI process. A highly selective copper-based catalyst is used in the converter, whose single catalyst bed makes it easier and less costly to replace the catalyst than in the high-pressure processes. The crude methanol produced by this process is much purer than the methanol produced in the high-pressure plants, allowing simpler distillation equipment to be used.

Although the cost of producing methanol in large (over 80 million gallon-per-year) high-pressure and low-pressure plants is quite similar, there is a substantial advantage in using the low-pressure process in smaller plants. Centrifugal compressors driven by steam turbines can be used in all low-pressure plants. Because of the slight cost advantages and greater simplicity of the low-pressure process, industry observers feel that it is likely that new plants will be based on low-pressure processes.

Lurgi Corporation of West Germany also has a low-pressure³⁰ methanol process, using centrifugal compressors and turbine drives, which is used in some overseas plants. This process converts carbon monoxide, carbon dioxide, and hydrogen to methanol in the presence of a copper-based catalyst, using a special patented reactor, at pressures of 600-700 psi and at temperatures of 200-300°C.

A.2.3 Medium-Pressure Processes

The medium-pressure process of Vulcan-Cincinnati, Inc., is essentially the same as a high-pressure process except that a high-activity copper-based catalyst is used, which enables use of pressures significantly lower than those used in high-pressure processes. Useable heat can be recovered at a higher temperature than is possible with the low-pressure reforming.

J.F. Pritchard & Co. of Kansas City, Missouri, Catalysts & Chemicals, Inc., of Louisville, Kentucky, ICI of Great Britain, Nihon Suiso Kogyo (NSK) of Japan, and Haldor Topsoe of Denmark have also developed medium pressure processes.

A.2.4 Co-Product Methane-Methanol and Variations³¹

There are alternative coal gasification processes to be considered in making methanol. One, a co-product process, produces both methane and methanol by using fluid bed coal gasification technology such as the Bureau of Mines Synthane Process. The other uses a higher temperature entrained gasifier to produce a synthesis gas of CO, H₂, and CO₂, without methane, which is then converted to methanol.

The Synthane Process is designed to manufacture pipeline gas and uses a fluid bed gasifier and catalytic methanator. It operates at about 1,800°F and 1,000 psi. A modification for methane and methanol production is shown in Figure A-1.

Coal feed is pretreated by steam and oxygen to prevent caking tendencies before entering the gasifier. The steam and oxygen convert the coal to a gas, which is sent to the spray tower for cleanup. In the co-product plant, a shift converter shifts the H₂ to CO ratio to 2 to 1 for methanol conversion. CO₂ is not needed in this case, since no deficiency of carbon oxides is present. Carbon dioxide (CO₂), carbonyl sulfide (COS) and hydrogen sulfide (H₂S) are scrubbed out after the shift converter. At this point in the co-product process, the gas consists of about 50% H₂, 25% CO, and 25% methane (CH₄). Fine sulfur is then removed and the gas is combined with recycle gas and sent through the converter. The product gas is sent through a condenser to obtain the methanol, and the stream is split into a portion for methane and a portion for recycle gas.

If the process is modified to produce methanol only, a synthetic fuel plant with different coal gasification process conditions would be required. An entrained-type gasifier operating at high temperature (about 2,400°F) can produce a synthesis gas with almost no CH₄, close to 60% CO, about 30% H₂, and the remainder

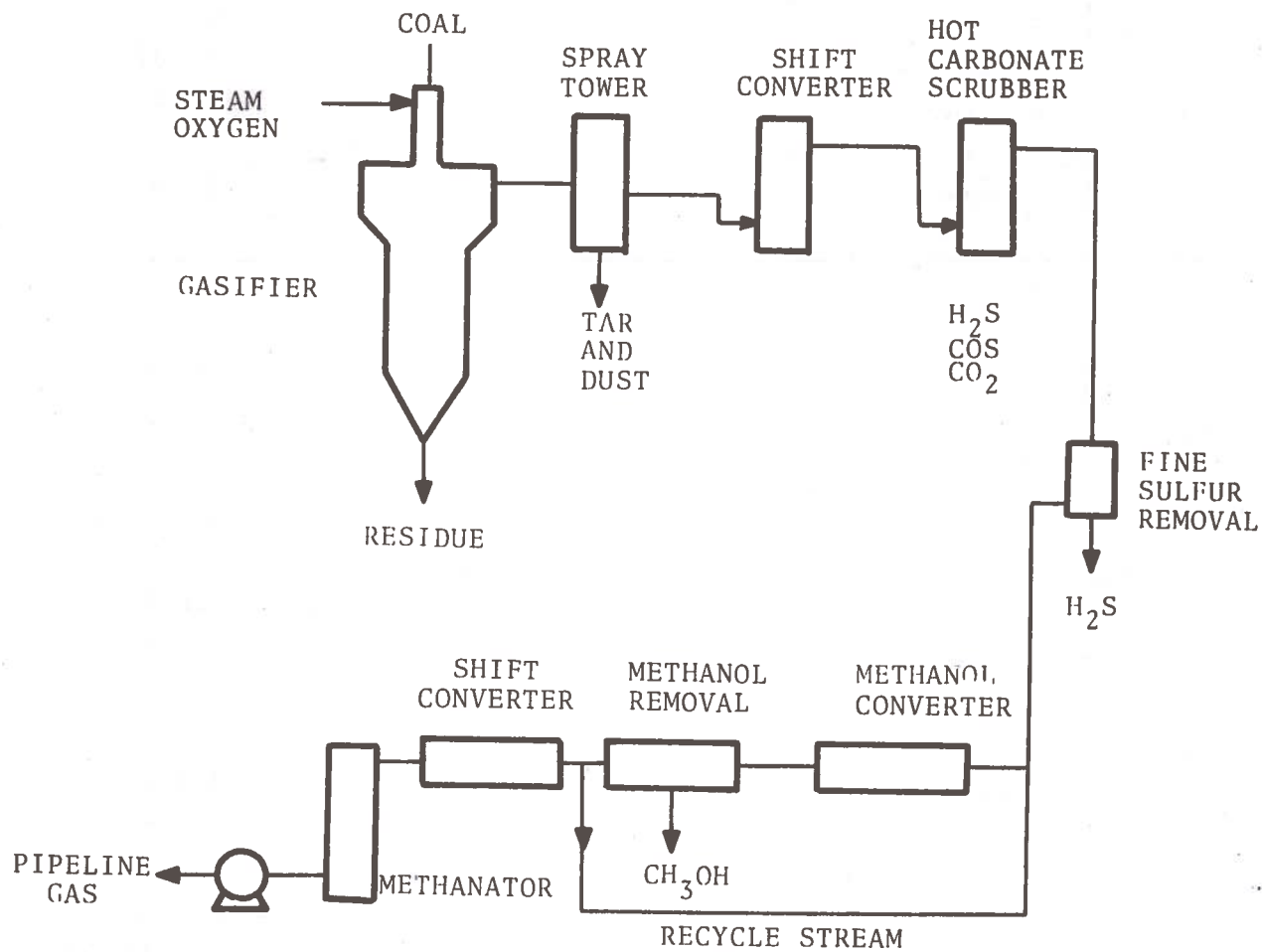


Figure A-1. Co-Product Plant for Methane-Methanol Production

mostly CO₂. The process requires cleanup of synthesis gas and a shift converter. High pressures are useful to reduce the methane even further, and some CO₂ removal may be necessary. Operation of a high-temperature entrained gasifier has been demonstrated successfully.³²

A.2.5 Coal Gasification Processes

The processes summarized below can be used to convert coal into gas, from which methanol can then be manufactured. The Bureau of Mines process described above as well as the Babcock-Wilcox entrained-type process are two of the experimental processes that show good promise. The Koppers-Totzek process is another, using an entrained-type gasifier, operating at atmospheric pressure, and using steam and oxygen. It has been used successfully commercially. Next, the Lurgi fixed bed, pressurized system is used extensively, although it cannot use caking coal. Lurgi is also working on a fixed bed process. The Winkler process, developed by Davy Powergas, Ltd., of Great Britain, is potentially useful for noncaking coals, and operates at moderate pressure.

In situ coal gasification has been suggested by Pasternak et al³³ at the Lawrence Livermore Laboratories. Steam and oxygen are prepared for injection into a carefully selected underground coal seam. Explosives are used to initiate the process, and gasification proceeds in a vertical direction. This novel approach depends heavily on the explosives technology developed at Livermore, but it is presently only in the conceptual stage. Many problems need to be solved for this process to be considered practical.

A.3 PRODUCTION RATES, PRESENT AND PROJECTED

Synthetic methanol production has increased steadily in the U.S. from about half a billion gallons per year in 1966 to about one billion gallons in 1973. One billion gallons corresponds to 60 trillion BTU. Table 4^{19,29} lists the U.S. methanol producers in 1973, the plant capacities, and the processes used. Methanol production in the United States is presently about 1% that of gasoline.

TABLE A-2. U.S. METHANOL PRODUCERS, PLANT CAPACITIES
AND PROCESSES (1973)

Company and Plant Location	Methanol Capacity (Million Gal/Year)	Process
Borden Chemical (Division of Borden Inc.) Petrochemicals Division Geismar, Louisiana Pacific Northwest location	16 (70-100)	high-pressure (scheduled for 1973 or 1974)
Celanese Corp. Celanese Chemical Co. Div. Bishop, Texas Clear Lake, Texas	 90 200	 high-pressure ICI low-pressure
E.I. DuPont de Nemours & Co., Inc. Industrial and Bio- chemicals Dept. Beaumont, Texas Huron, Texas	 200 125	 high-pressure high-pressure
Georgia-Pacific Corp. Chemical Div. Rebecca, Louisiana	 100	 ICI low-pressure
Hercules, Inc. Synthetics Dept. Plaquemine, Louisiana	 80	 high-pressure
Monsanto Co. Hydrocarbons & Polymers Div. Texas City, Texas	 100	 ICI low-pressure
Rohm & Haas Co. Deer Park, Texas	 22	 high-pressure
Tenneco, Inc. Tenneco Hydrocarbon Chemicals Div. Pasadena, Tex.	 80	 high-pressure
Union Carbide Corp. Chemicals and Plastics Div. Texas City, Tex.	 (42)	 high-pressure (shutdown in 1974)

Total

1,157 million gal/yr

SOURCE: References 19 and 20

Thus, usage of methanol blends of 5% to 10% will require an increased methanol production of an order of magnitude. This is far more feasible than attempting to use methanol alone as a fuel, since conversion to coal as a raw material will take some time to achieve, and a ten-fold increase in production would require several years. All the major producers use natural gas as feed-stock at this time, although coal gasification will probably be considered in the near future.

Significant quantities of methanol are shipped in tankers from the South, where almost all methanol capacity is located, to the northeastern United States for chemical synthesis including the production of formaldehyde. This geographical interrelationship has evolved from cost considerations.²⁹ The trend in production plants has been from smaller to larger units to improve the cost economics. Low-pressure and medium-pressure plants are being built to replace high-pressure ones, and this trend will be reinforced in the future.

The production of methanol in the Persian Gulf area for shipment to the U.S. has begun. This production is projected to be several times the present United States total production. A plant in Iran is being set up according to Reed, by Transco to produce 26,000 tons/day of methanol to be available at 12¢/gallon (26,000 tons/day corresponds to 7 million gallons/day or 2-1/2 billion gallons/year). Reed notes that a program to set up a methanol plant in the western U.S. to produce 2 billion gallons/year of methanol from lignite is in the planning stage.

Even though methanol is a bulk chemical and annual production exceeds 1 billion gallons/year at present, the availability for use as a motor fuel is limited for the immediate future. If the Iranian methanol plants are built at the scale being mentioned, an increase by an order of magnitude may be possible by 1980. Additional quantities of methanol will result from using coal as a raw material, but the time frame for completion of production plants is uncertain. Methanol from lignite could also be available in large quantities but there is no firm schedule as yet on plant construction.

A.4 PRESENT-DAY USES

The major uses for methanol² are in the synthesis of formaldehyde and other related chemicals. Other uses include solvents, antifreezes, and fuels.

A.5 CAPITAL AND CONSUMER COSTS

Several large production facilities now in operation and using the low-pressure catalyst process, have brought about a reduction in consumer prices. The costs have decreased for the following reasons:³⁴

- A. Lower production costs due to increased process material efficiency and exclusive use of turbine-driven centrifugal compressors in plants producing as little as 150 tons/day.
- B. Lower capital costs due to reductions in reforming and compressor installation costs and use of low-pressure equipment in the synthesis loop.
- C. Lower maintenance costs due to reduced compressor maintenance requirements and a simple converter design which allows rapid catalyst replacement, increasing the plant on-stream time.

Recent prices for natural gas are about 40¢/million BTU. This results in a sales value of methanol, at the plant of between 10¢/gallon and 12¢/gallon or about \$1.55/million BTU to \$1.86/million BTU.²⁰

The medium-pressure Vulcan-Cincinnati process¹ claims even lower prices for the production of Methyl-Fuel.® The estimated capital costs for a commercial size plant range from \$155 million upward depending on site conditions, auxiliary off-sites, and utilities plant requirements. The average selling price of Methyl-Fuel® in 1973 dollars, at the plant, is estimated to be \$1.02/million BTU.

The Exxon²⁵ report includes a preliminary economic analysis of methanol manufacture in a methanol/synthetic gas co-product

plant. The synthetic natural gas costs were based on a 1973 National Petroleum Council report on coal availability, which considered Lurgi gasification. The methanol cost varies according to a number of factors, including the scale of operation. Assuming a cost of \$1/million BTU for shipment, the average final consumer cost is \$2.70/million BTU.

The methanol would most likely be produced in the Western part of the United States using low-sulfur strip-mined coal. The expectation by Exxon²⁵ is that methanol could be pipelined to the mid-West and to the Gulf Coast, initially using existing oil product or crude oil pipelines. The methanol would require some purification before it could be distributed further. It is anticipated that initially methanol would be blended with gasoline. This blend would be prepared at the gasoline source and then shipped. The problem of water sensitivity and costs for overcoming it must obviously be faced at the beginning. The consumer cost should still remain under \$3/million BTU.

A detailed estimate has recently been reported³⁵ for a \$495 million, 20,000 tons-per-day coal-to methanol plant. The cost of synthesis gas, assuming coal at \$7/ton, was estimated to be 5.67¢/gallon and methanol synthesis to be 2.84¢/gallon, for a total cost of 8.51¢/gallon. If lignite at \$2/ton were used, the cost of methanol would drop to 6.4¢/gallon.

Babcock & Wilcox Company³⁶ feels that there is potential for improved efficiencies in using coal by char recycle, CO₂ recycle, and steam substitution.

The summary in the Aerospace Report¹⁹ indicates a linear decrease in projected capital costs as a function of methanol daily capacity, comparing plants producing 200 tons/day to those producing 20,000 tons/day. These cost estimates are for methanol production from natural gas.

Further economic studies are needed for producing methanol from natural gas, lignite, and coal. Future-cost assumptions for these materials will be fundamental to this study, and cost estimates will be realistic only if U.S. and international economic and political factors are carefully scrutinized.

A.6 IMPACT WITH OTHER U.S. AND WORLD ENERGY REQUIREMENTS

Methanol has potential uses in areas other than transportation fuels. These include space heat, electric power, fuel cells, and synthesis of many different materials. Wentworth⁴ of Vulcan-Cincinnati projects that large amounts of methanol will be used for utilities, and lesser amounts for sewage denitrification.

Boil-off losses, when shipping liquid natural gas, can be large. Economic studies have shown that if the shipping distance is more than about 12,000 miles, it is cheaper, on a delivered energy basis, to manufacture methanol from the gas and ship it than to ship the liquid natural gas itself.

One area that offers promise is the production of gasoline from coal-derived methanol. Methanol also might serve as the intermediary in the synthesis of many future materials since it can be synthesized from a very broad raw material base.

A.7 CRITICAL TECHNOLOGY GAPS

Coal gasification will have trace amounts of sulfur-containing-gases not present in conventional methanol synthesis gas. The effect of such gases on the methanol conversion catalyst must be determined. Work also needs to be done to find a more efficient methanol synthesis catalyst than presently is known.

Another area requiring serious study is the integration of large-scale coal processing plants employing improved gasification technology, and methanol synthesis plants.¹⁹

APPENDIX B BRIEF DESCRIPTION OF WORK BEING PERFORMED OR TO BE PERFORMED

Table B-1 summarizes some administrative aspects of various programs directed at studying methanol as an automotive fuel or fuel constituent. Some additional information follows the table as notes, keyed to the table entries by item number.

TABLE B-1. WORK BEING PERFORMED ON METHANOL AS AN AUTOMOTIVE FUEL 1973-1974

Investigator and Institution	Contract No. and Contract Title	Dollar Amount When Specified	Sponsoring Agency
1. T.B. Reed et al Mass. Inst. of Technology, Cambridge, Mass.	Study of Feasibility of Methanol Use and Production	\$100,000	Northern Pump Co., Minneapolis, Minn. J. Hawley
2. F.H. Kant, et al Exxon Research & Engineer- ing Co., Linden, N.J.	EPA Contract # 68-01-2112 Feasibility Study of Alternative Fuels for Automotive Transportation	\$149,500	EPA
3. J. B. Pangborn, et al Institute of Gas Techno- logy, Chicago, Ill.	EPA Contract # 68-01-2111 Feasibility Study of Alternative Fuels for Automotive Transpor- tation	\$135,000	EPA
4. Contractor to be determined	Impact Study of Alternative Fuels for Automotive Transpor- tation		EPA
5. R.W. Hurn et al Bureau of Mines, ERDA Bartlesville, Oklahoma	EPA-IAG-D4-0428 Experimental Study of Utilization of Methanol- Gasoline Blends in Internal Combustion Engines	\$200,000	EPA
6. R.E. Davison, D. Flamm, et al Texas A&M University Chicago Station, Texas	Internally funded studies of energy efficiency and power output of methanol blends for Ford Falcon with 6-cylinder engine		Texas A&M
7. J. Spiegel, et al Jet Propulsion Labora- tory Pasadena, Calif.	Contract on Lean Mixture Engine Testing and Evaluation	Around \$150,000, relevancy to meth- anol only in effects of using lean mixture of gasoline.	DOT-TSC
8. P. Breisacher and B.J. Nichols Aerospace Corp. El Segundo, California	Internally funded - Fuel Modifi- cation. Methanol instead of Lead as the Octane Booster in Gasoline		Aerospace

TABLE B-1. (CONTINUED)

Investigator and Institution	Contract No. and Contract Title	Dollar Amount When Specified	Sponsoring Agency
9. H.G. Adelman, R.K. Pefley, and J.D. Kilgroe U. of Santa Clara, Calif.	Internally funded - Performance and Emission Characteristics Using Blends of Methanol and Dissociated Methanol as an Auto- motive Fuel		University of Santa Clara
10. R.T. Johnson, R.K. Riley, and L.E. Stahlman University of Missouri Rolla, Missouri	DOT-OS-40104 Evaluation of Alcohol as a Vehicle Fuel Extender	\$ 56,797 3/1/74 to 6/1/75	U.S. Department of Transportation
11. J. Appeldoorn, et al Exxon Research Linden, N.J.	Internally Funded		Exxon Corp.
12. J.M. Colucci, et al Fuels and Lubricants Dept. General Motors Research Laboratories General Motors Technical Center, Warren, Mich.	Internally Funded		General Motors Corporation
13. R.H. Lindquist J.C. Ingamells, et al Chevron Research Richmond, Calif.	Internally Funded		Chevron Company
14. R.G. Jackson, et al R.M. Tillman, et al Continental Oil Co. Ponca City, Okla.	Internally Funded		Continental Oil Company
15. H. Haitland, W. Bernhardt, and W. Lee Research and Development Div. Volkswagenwerk AG Woflsburg, W. Germany	Internally Funded		Volkswagen Co.

NOTES

1. Five-point program - (1) Gasoline station including methanol blends with gasoline, set up and used to study mileage statistics and engine performance under controlled conditions, (2) Research on CFR single-cylinder engine-fuel usage, study of flame propagation speeds, other factors, (3) Alterations on full size car to study tuning problems, etc., (4) Study of phase separation, including water, both experimental and computer simulation, (5) Toxicology study, especially on skin, effects of formaldehyde, etc.
2. The main study includes background material on alternate vs. conventional fuels, domestic resource base, criteria for comparative evaluation of fuels, automotive power plants; characteristics and system economics of candidate fuels; evolutionary considerations for use of alternative fuels; fuel research data gaps; recommendations of alternative fuels and recommendations for further studies. Work on methanol is included in this study.
3. The study includes background material; a selection of potential energy sources for the future; the choice of fuels; use of synthetic fuels; cost and availability study; selection of fuels for the three periods: 1975-1985, 1985-2000, and beyond 2000; detailed cost and availability assessment, and recommendations. Work on methanol is included in this study.
4. This will be a follow-on to 2 and 3, above -- a detailed study of economic, technical, environmental, and socio-economic impact of production and use of alternative fuels, including methanol.
5. Experimental program for the engine combustion investigation of methanol-gasoline blends, coal- and shale-derived gasoline, blends of conventional petroleum-derived gasoline with shale-derived gasoline, and blends of petroleum-derived gasoline with coal-derived gasoline -- data to be obtained and analyzed -- test work on many automobiles.

6. Dynamometer studies of gasoline-methanol blends on a 6-cylinder engine, with no optimization of carburetor; computer simulation of engine output and pollution; elementary studies on phase separation of methanol, water, gasoline mixtures.
7. Lean mixture engine configurations, using gasoline for fuel were tested at discrete ratings of engine speed and torque. This will permit accurate determination of engine performance over the normal range of steady-state road loads.
8. The octane rating of methanol-gasoline blends was determined with the use of a CFR research engine and ASTM Reference Fuels. Also, road testing has been continuing on the use of blends in various automobiles-fuel economy, smooth running, etc.
9. Tests were conducted to evaluate engine performance and exhaust emissions using blends of methanol and dissociated methanol as a spark ignition engine fuel.
10. The work is to develop current information about the properties of methanol as an automotive fuel extender. The research will examine the emission characteristics of various blends of alcohol and gasoline using FTP tests and an FTP simulator. A CFR test program will be used in the development of the fuel economy and emission data to establish a basis for comparison of the fuel economy, emissions performance, and octane improving characteristics of methanol-blended fuels to gasoline. Also, an engine parameter study will be made to determine engine modifications to be made to take advantage of the presence of methanol in gasoline blends.
11. Studies of driveability, vapor lock and other problems on a fleet of 13 cars, using methanol-gasoline blends. Further work is continuing.
12. Single cylinder engine studies with pure methanol, vehicle studies with blends, and octane boosting studies with blends. Detailed testing of the leaning effect of using methanol. Measurements of emission of CO, hydrocarbons, and NO_x under

various conditions are emphasized. This work is continuing with efforts concentrated on recent and advanced cars and engines.

13. Studies of problems using methanol-gasoline blends. Emphasis on water separation, and corrosion and degradation problems. Some results have also been obtained on fuel economy. Emission measurements have been made.
14. Emission levels, performance, and fuel economy for methanol versus gasoline were measured over a range of engine operating conditions. Lean methanol operation, in particular, was emphasized.
15. Volkswagen has conducted extensive tests on use of methanol-gasoline blends in spark ignition, Wankel, and stratified charge engines. Performance, fuel economy, and emissions have been studied in detail. Further work is progressing. In addition, future prices and availability of methanol are being seriously studied.

APPENDIX C

GLOSSARY

FUEL ECONOMY IN MILES/GALLON expresses distance travelled per volume of fuel – this depends on drive cycle, which were, unfortunately, not the same for most of the results reported in this document.

FUEL ECONOMY IN MILES/BTU expresses distance travelled per unit available thermal energy input – this also depends on drive cycle.

SPECIFIC FUEL CONSUMPTION IN LB/HP-HR expresses the efficiency of converting fuel in the engine into work.

SPECIFIC ENERGY CONSUMPTION IN BTU/HP-HR expresses the efficiency of converting thermal energy into work.

VOLUMETRIC EFFICIENCY of an engine is defined as the ratio of the actual mass of air inducted by the engine on the intake stroke to the theoretical mass of air that would have been inducted by filling the piston-displacement volume with air at atmospheric temperature and pressure.

OCTANE NUMBER is a measure of the knock rating of a fuel, found by comparing the knock to that of a blend of primary reference fuels. Tests have been established which are used to measure the octane number quantitatively.

RESEARCH OCTANE NUMBER (RON) AND MOTOR OCTANE NUMBER (MON) are measured by different knock tests, with differences in engine speed, spark advance, and temperature of the intake-manifold mixture for the two methods. Research octane number measures knock resistance under less severe conditions than the motor octane number and corresponds well with low speed road rating, whereas motor octane number corresponds well with high speed road rating.

BLENDING OCTANE VALUE is defined from the expression

$$BOV = \frac{[O_b - O_g (1-x)]}{x} ,$$

in which O_b and O_g are the octane numbers of the blend and the base gasoline respectively, and x is the volume fraction of the methanol in the blend.

FUEL-AIR EQUIVALENCE RATIO, is defined as being the ratio of fuel to air in the actual case to the ratio of fuel to air for the stoichiometric case (in which just enough oxygen is available to react entirely with all of the fuel present).

TERNEPLATE - sheet iron or steel coated with an alloy of tin and lead.

VOLATILITY - a measure of the ease with which a fuel can be vaporized. Volatility is important in determining ease of starting, warm-up, and acceleration. However, if it is too high, vapor lock problems and carburetor icing may arise.

"METHYL-FUEL"® - a tradename of the Vulcan-Cincinnati Co. for its proprietary blend of methanol with controlled amounts of C_2 - C_4 alcohols.

SYNTHESIS GAS - manufactured gas, consisting of carbon monoxide and hydrogen, used for the production of methanol.

IMEP - indicated mean effective pressure is defined by Obert²¹ as that theoretical constant pressure which can be imagined exerted during each power stroke of the engine to produce power (or work) equal to the indicated power (or work).

APPENDIX D

ADDENDUM OF 1974-1975 RESULTS

An update through April, 1975, is given below for Section 3 on methanol-gasoline blends. This includes work done by Hurn of ERDA, by Wigg et al. of Exxon Research and Engineering Co., by Johnson et al. at the University of Missouri at Rolla, by Ingamells and Lindquist of Chevron Co., and by Colucci et al. at General Motors Corp. References are given in the reference section.

Wigg and Lunt^{38,39} tested three cars for fuel economy emissions. They compared results for gasoline alone, and for gasoline with 15% methanol and matched Reid vapor pressure. The 1975 Federal test procedure was used. Since they defined F/A equivalence ratio as the inverse of Obert²⁰ and others, care must be used in analyzing their results. They experimented with three cars: a 1967 car, operating rich on gasoline alone (about 0.9 equivalence ratio); a 1973 car, operating lean (equivalence ratio between 1.0 and 1.1); and a 1973 catalyst-equipped car (1977 emission standards to be met) with carburetion adjusted slightly richer than the 1973 or, with an operating equivalence ratio slightly lean. For the 1967 car, with the use of methanol and the matched RVP, there was an increase in fuel economy of 1% in miles per gallon and 8% in miles per BTU over that with gasoline alone. In the other two cars there was a decrease in miles-per gallon and a slight increase in miles per BTU (1 to 2%).

Changes in the emission levels with methanol addition were also accounted for by Wigg on the basis of the change in equivalence ratio. The 1967 car shows substantial decreases in CO and HC and an increase in NO_x . The 1973 car shows lesser effects for CO and HC and was predicted to show only a small change in NO_x emissions. However, the 1973 car did show a significant decrease in NO_x emission (from 2.6 to 1.7 grams/mile); this may be related to methanol's high latent heat of vaporization, which leads to lower peak flame temperatures in the combustion chamber. Aldehyde

emissions were 30 to 50 percent higher for the methanol blend car. Results are tabulated in Table D-1.

"All three cars performed well during warmed-up operation with the methonal blend, and the 1967 car showed no problems at any time. The leaner-operating 1973 and "1977" cars, however, did experience stalling, hesitation, and backfire during the first few minutes of operation from a cold start. Stalling was also observed with the base blend in the case of the 1973 car, but hesitation and backfire did not occur."³⁹

"A 13-car driveability study indicated that the large increase in fuel volatility which occurs with the addition of methanol to gasoline could pose serious problems."³⁸ The tendency of a fuel to cause driveability problems at high temperature, due to vapor lock and related effects, can be predicted by the Reid vapor pressure and the front-end volatility index of A.J. Blackwood.* Because the addition of 15 percent methanol causes a large increase in both of these, vapor lock problems occur if no modifications in the base fuel are made. The major malfunction found during tests was acceleration vapor lock, defined as hesitation or bucking resulting in at least 25% longer acceleration times, or stalling during accelerations. Difficult hot starting and rough hot idle were encountered infrequently in the tests and could be due to age-related problems since they occurred chiefly in older cars.

The above problems require further study. One solution is to back out some of the low-molecular-weight hydrocarbon components of gasoline, such as butane and pentane. The result of such actions would cause methanol to be a substitute component of gasoline instead of an extender, and thus its chief usefulness would be negated. "Stretchiness"³⁸ (a lack of expected response to

*Front-end volatility index = Reid vapor pressure + 0.13 (percent evaporated or distilled at 158°F ASTM).²¹

TABLE D-1. COMPARATIVE FUEL ECONOMY AND EMISSIONS

Investigator	Percent Methanol	Single-Cylinder CFR or Multi-Cylinder Tests	Vehicles used and Driving Cycle	Fuel Economy (Miles per Gallon)	Fuel Economy (Miles per BTU)	CO Emissions	HC Emissions	NO _x Emissions
Wigg and Lunt 38, 39	15%	Multi-Cylinder or Dynamometer	3 cars, 1967, 1973, 1973 with catalyst 1975 FTP	1967 cars: + 1% 1973 cars: slight decrease	1967 car: + 8% 1973 cars: +1 to 2%	50% decrease or greater except for catalyst car	25% decrease for 1967 car; almost no change for 1973 cars	25% increase for 1967 car; 12% average decrease for 1973 cars

Note: Comparisons are for engines using methanol-gasoline blends against the engines using gasoline alone.

throttle movement) is a problem with methanol-gasoline blends. This problem, being related to excessively lean carburetion, was much more pronounced with the newer cars tested."

Hurn⁴⁰ has reported results, up to May, 1975, on four vehicles, on both fuel economy and emissions for base fuel, base fuel with 5% methanol, and base fuel with 10% methanol (See Table 3-1). Two base fuels were used, indolene and commercial gasoline. Also, results were given for ambient temperatures of 20°F, 75°F, and 100°F. Fuel economy was measured for both highway and FTP driving. Fuel economy expressed in miles/BTU appeared fairly constant for the two compact vehicles and for the two intermediate cars for FTP driving. It increased slightly (averages about 7%) for one intermediate car and decreased slightly (average about 4%) for the other intermediate car in highway driving. Emissions were lowest for 75°F ambient conditions (compared to 20°F and 100°F). Changes in emissions between gasoline and methanol blends were minimal: very small changes in CO and HC emissions, decreased NO_x emissions (about 4% average) and increased aldehyde emissions (about 20% average) in comparing results for 10% methanol blends and straight indolene or commercial gasoline. The data are not sufficient to be conclusive, but appear to run counter to other more optimistic data that fuel economy and emissions are much improved for methanol blends over gasoline. More extensive results (including fleet tests with 40 vehicles) are expected from Hurn by the fall of 1975.

A set of graphical data⁴⁰ is also provided by Hurn on methanol/gasoline/water phase separation for five weight-percent methanol and different components of gasoline for temperatures between 0° and 80°F. For most of the gasoline components, phase separation at 80°F occurs for about twice the weight percent of water as at 0°F. The limit on water content for representative gasoline constituents at 75°F is as follows:

Isooctane	- .02 water weight percent
n-Heptane	- .03 water weight percent
Triethylenebenzene	- .13 water weight percent

Toluene - .30 water weight percent
Benzene - .36 water weight percent.

Extrapolation to other methanol concentrations is indicated by Hurn as well. Other related data are expected to be completed by the autumn of 1975.

Johnson et al.⁴¹ have performed recent experiments on the improvement of both research octane number and motor octane number of methanol over typical gasoline fuels (including summer blends of regular and premium gasoline, and indolene). They define two new parameters, in addition to using BOV as referred to in the main text. One of these parameters is characteristic of the maximum possible effect that methanol will have on a given base fuel. The other parameter indicates how sensitive the octane value of the fuel is to small amounts of methanol. The first parameter can be correlated with the research octane number, and this remains fairly high, even for high octane base fuels. However, the parameter which describes the sensitivity to the addition of small amounts of methanol is correlated with the motor octane number (more significant for newer vehicles now coming out) and shows progressively less improvement as the octane number increases, leveling off at a motor octane number of 86. Thus the smaller dependence on base fuel of this parameter, as well as its smaller variations compared with the BOV, make it appear a better measure of the improvements in anti-knock achievable by methanol in blends with gasoline. Johnson's results suggest that the octane boosting property previously ascribed to methanol in results that were not so carefully analyzed should be reconsidered and that the BOV is less significant than has been thought. Johnson is continuing his work on Federal test procedure simulation as well as on engine parameter studies, and these results will soon be available.

Work at Chevron Research Co.^{42,43} has been reported, with emphasis on problems of materials compatibility, cold start driveability, vapor lock, and water separation. Use of a 40% methanol/60% gasoline blend resulted in large currents between the fuel pump and the gasoline tank, leading to a new fuel tank being effectively stripped of itsterneplate coating in two days' exposure.

Also magnesium and magnesium/aluminum alloys were found susceptible to methanol corrosion. An additional problem was increased swelling of gaskets, seal materials, and fuel pump housing. Problems with smaller percentages of methanol in the blend should not be so severe, but can be expected to occur.

Cold start driveability tests⁴³ using 10% methanol in a blend were conducted by six drivers commuting between their homes and the Chevron Research Laboratory. Driveability demerits were recorded based on the number of malfunction occurrences and the severity of each occurrence for the commute trips. Every car showed a higher demerit level for the 10% methanol blend than for the base unleaded gasoline which was used on alternate trips.

"Driveability tests⁴³ were also conducted with three of the cars on an all-weather chassis dynamometer at 25°F. The methanol effects were even larger under these conditions. Average demerits were tripled with the addition of 10% methanol."

Vapor lock problems were also studied, and the results are similar to those of Wigg and Lunt, discussed earlier in this section.

Water sensitivity⁴³ of methanol-gasoline blends was studied and results with the 40% methanol/60% gasoline blend indicate several cases of engine stall that were attributed to methanol separation in the carburetor. Whenever the carburetor bowl was examined during the test, it was usually possible to see haze formation during exposure to ambient air. At lower concentrations of methanol, problems of water haze are often more severe. A number of additives were tried to minimize the water-solubilizing effect. A mixture of 5% tertiary butyl alcohol/15% methanol/80% gasoline was found to tolerate 4,000 parts per million water at 70°F, whereas a 15% methanol/85% gasoline blend only tolerates 1,500 ppm, water. The cost of the higher alcohols may be rather high (although the use of "methyl-fuel"[®] is indicated as a possible solution by the author of this report).

Colucci et al.^{44,45} have reported quantitative results on the 14 vehicles tested as referred to in Section 3 of this

report. Results on fuel economy and emissions have been discussed.

Driveability of the 14 cars was evaluated using a demerit system. On the average, there were about twice as many demerits indicated when 10% methanol was added as there were for the base fuel. Performance was also reduced for the 10% methanol blends.

"For 1975 model year cars⁴⁵ with catalytic converter systems, the results of using methanol-gasoline blends instead of gasoline are expected to be similar to those for pre-1975 cars. Possibly the carbon monoxide reduction may not be as substantial. Wigg has presented data which agree with this."

Colucci et al. emphasize the leaning effects of the addition of methanol to gasoline. They state that carburetion changes would become necessary if methanol is to be extensively used. If methanol-gasoline blends were marketed, future cars could be designed, with small modifications, to accommodate the new fuel. Richer carburetion would be provided to obtain acceptable and safe driveability and performance. The effects of such a move on hydrocarbon and nitrogen oxide emissions would depend on the ultimate equivalence ratio of the new vehicles. The advantage of methanol for carbon monoxide emissions would [possibly] be eliminated."

THE HISTORY OF

THE CITY OF BOSTON

FROM THE FIRST SETTLEMENT TO THE PRESENT TIME
BY SAMUEL JOHNSON
OF THE BOSTON BAR

IN TWO VOLUMES
THE FIRST VOLUME
CONTAINING THE HISTORY FROM THE FIRST SETTLEMENT TO THE YEAR 1780
LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD, 1780

THE SECOND VOLUME
CONTAINING THE HISTORY FROM THE YEAR 1780 TO THE PRESENT TIME
LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD, 1780

THE HISTORY OF THE CITY OF BOSTON
FROM THE FIRST SETTLEMENT TO THE PRESENT TIME
BY SAMUEL JOHNSON
OF THE BOSTON BAR

IN TWO VOLUMES
THE FIRST VOLUME
CONTAINING THE HISTORY FROM THE FIRST SETTLEMENT TO THE YEAR 1780
LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD, 1780

THE SECOND VOLUME
CONTAINING THE HISTORY FROM THE YEAR 1780 TO THE PRESENT TIME
LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD, 1780

THE HISTORY OF THE CITY OF BOSTON
FROM THE FIRST SETTLEMENT TO THE PRESENT TIME
BY SAMUEL JOHNSON
OF THE BOSTON BAR

IN TWO VOLUMES
THE FIRST VOLUME
CONTAINING THE HISTORY FROM THE FIRST SETTLEMENT TO THE YEAR 1780
LONDON: PRINTED BY J. JOHNSON, ST. PAULS CHURCH-YARD, 1780

REFERENCES

1. "Outlook Bright for Methyl-Fuel[®]," Environmental Science and Technology 7, 1002 (1973).
2. "Encyclopedia of Chemical Technology," Kirk-Othmer, Second Edition, Vol. 13, John Wiley and Sons, New York NY (1963).
3. Lichty, L.C., and E.J. Ziurys, "Engine Performance with Gasoline and Alcohol," Ind. and Eng. Chemistry 28, 1094 (1936).
4. Reed, T.B., and R.M. Lerner, "Methanol: A Versatile Fuel for Immediate Use, " Science 182, 1299 (1973).
5. Starkman, E.S., H.K. Newhall, and R.D. Sutton, "Comparative Performance of Alcohol and Hydrocarbon Fuels," SAE Conference Paper SP-254, New York NY, pp. 14-33 (June 1964).
6. Ebersole, G.D., and F.S. Manning, "Engine Performance and Exhaust Emissions: Methanol versus Isooctane," SAE Paper 720692 (Aug. 1972).
7. Bolt, Jay A., "A Survey of Alcohol as a Motor Fuel," SAE Conference Paper SP-254, New York NY, pp. 1-13 (June 1964).
8. Lerner, R.M., T.B. Reed, E.D. Hinkley, and R.E. Fahey, "Improved Performance of Internal Combustion Engines Using 5-20% Methanol in Gasoline," SAE Paper 749104, 9th Inter-society Energy Conversion Engineering Conference (1974).
9. Pefley, R.K., M.A. Saad, M.A. Sweeney, and J.D. Kilgroe, "Performance and Emission Characteristics Using Blends of Methanol and Dissociated Methanol as an Automotive Fuel," SAE Paper No. 719008 (1971).
10. Breischer, Peter, and Roberta J. Nichols, Aerospace Corporation, El Segundo CA, Personal Communication, 1974.

REFERENCES (CONTINUED)

11. Stahlman, Larry E., "Performance of Methanol/Unleaded Gasoline Fuels in S.I. Engines," presented at the Automotive Engineering Congress and Exposition, Detroit MI, Feb. 1975.
12. Ninomiya, J.S., A. Golovoy, and S.S. Labana, "Effects of Methanol on Exhaust Composition of a Fuel Containing Toluene, n-Heptane, and Isooctane," J. Air Pollution Control Assoc. 20, 314 (1970).
13. Lindquist, R.H., et al., presentation at 1974 Engineering Foundation Conference on "Methanol as an Alternate Fuel," Henniker NH (1974). Available from Engineering Foundation, New York NY.
14. Appledoorn, J., et al., presentation at 1974 Engineering Foundation Conference on "Methanol as an Alternate Fuel," Henniker NH (1974). Available from Engineering Foundation, New York NY.
15. Colucci, J.M., et al., presentation at 1974 Engineering Foundation Conference on "Methanol as an Alternate Fuel," Henniker NH (1974). Available from Engineering Foundation, New York NY.
16. Hurn, R.W., et al., presentation at 1974 Engineering Foundation Conference on "Methanol as an Alternate Fuel," Henniker NH (1974). Available from Engineering Foundation, New York NY.
17. Heitland, H., W. Bernhardt, and W. Lee, "Comparative Results on Methanol and Gasoline Fueled Passenger Cars," paper by Volkswagen, presented at 2nd Symposium on Low Pollution Power Systems Developments (NATO/CCMS), Nov. 4-8, 1974, Dusseldorf, West Germany.
18. EPA Paper No. 74-24 AW, "Effects on Methanol-Gasoline Blends on Emissions," available from Test and Evaluation Branch, Emission Control Technology Division, EPA (March 1974)

REFERENCES (CONTINUED)

19. "Current Status of Advanced Alternative Automotive Power Systems and Fuels," The Aerospace Corp., El Segundo CA, Report No. EPA-460/3-74-013 (July 1974).
20. Obert, E.F., "Internal Combustion Engines and Air Pollution," Intext Educational Publishers, New York NY (1973).
21. Adelman, H.G., D.G. Andrews, and R.S. Devoto, "Exhaust Emissions from a Methanol-Fueled Automobile," SAE Paper 720693 (Aug. 1972).
22. Ingamells, John C., Discussion after Paper 720692 and 720693 of SAE Paper 720692 of SAE Conf. (Aug. 1972).
23. Fitch, R.E., and J.D. Kilgroe, "Investigation of a Substitute Fuel to Control Automotive Air Pollution," Report prepared by Consolidated Engineering Technology Corp. for National Air Pollution Control Administration (Feb. 1970).
24. "Survey of Alcohol Fuel Technology," Report M74-61, The MITRE Corporation, McLean VA, (July 1974).
25. "Feasibility Study of Alternative Fuels for Automotive Transportation," Exxon Research and Engineering Co., Linden NJ, Report EPA-460/3-74-013 (June 1974).
26. "Feasibility Study of Alternative Fuels for Automotive Transportation," Institute of Gas Technology, Chicago IL, Report for EPA (1974).
27. "Recycling CO₂," Chemical Engineering News, p. 24 (April 15, 1974).
28. Results of Workshops at Engineering Foundation Conference, Henniker NH (July 1974).
29. Blackford, Judith L., Methyl Alcohol, Chemical Economics Handbook, Stanford Research Institute, Menlo Park, CA (May 1971).

REFERENCES (CONTINUED)

30. Hiller, Heinz, and Friedemann Marschner, "Lurgi Makes Low-Pressure Methanol," *Hydrocarbon Processing*, p. 281 (Sept. 1970).
31. Mills, G. Alex, and Brian M. Harney, "Methanol - the 'New Fuel' from Coal," *Chemtech*, p. 26 (Jan., 1974).
32. Grossman, R.P., and R.W. Curtis, "Pulverized Coal-Fired-Gasifier for Production of Carbon Monoxide and Hydrogen," *Trans. ASME* 76, 689 (1954).
33. Pasternak, A., et al., presentation at 1974 Engineering Foundation Conference on "Methanol as an Alternate Fuel," Henniker NH (1974). Available from Engineering Foundation, New York NY.
34. Kenard, R.J., Jr., and N.M. Nimmo, "Methanol Technology and Economics," *Chemical Engineering Progress Symposium Series*, Vol. 66, No. 98 (1970).
35. Michel, John W., "Hydrogen and Synthetic Fuels for the Future," ACS Div. of Fuel Chemistry, presented at Chicago, p. 1 (Aug. 26-31, 1973).
36. Jones, F.L., and K.S. Vorres, "Clean Fuels from Coal - An Alternative to SNG," ACS Div. of Fuel Chemistry, presented at Chicago, p. 100, (Aug. 26-31, 1973).
37. Jackson R.G., et al., presentation at 1974 Engineering Conference on "Methanol as an Alternate Fuel," Henniker NH (1974).
38. Wigg, Eric E., and Robert S. Lunt, "Methanol as a Gasoline Extender - Fuel Economy, Emissions, and High Temperature Driveability," SAE Paper No. 741008 (1974).
39. Wigg, Eric E., "Methanol as a Gasoline Extender: A Critique," *Science* 186, p. 785 (Nov. 1974).

REFERENCES (CONTINUED)

40. Hurn, R.W., "Experimental Work with Methanol/Gasoline Blends," presented at the ERDA/AAPSD Contractors Coordination Meeting, Ann Arbor MI, May 6-8, 1975.
41. Stahlman, L.E., R.K. Riley, and R.T. Johnson, "Octane Characteristics of Various Blends of Methanol and Unleaded Gasoline," presented at the EPA Symposium-Workshop on Alternative Fuels, Ann Arbor MI, Oct. 15, 1974.
42. Lindquist, R.H., presentation at the EPA Symposium-Workshop on Alternative Fuels, Ann Arbor MI, Oct. 15, 1974.
43. Ingamells, J.C., and R.H. Lindquist, "Methanol as a Motor Fuel or a Gasoline Blending Component," SAE Paper No. 750123 (1975).
44. Colucci, Joseph M., "Methanol and Methanol-Gasoline Blends as Automotive Fuels," presented at the EPA Conference on Alternative Fuels Research, Ann Arbor MI, Oct. 15, 1974.
45. Brinkman, N.D., N.E. Gallopoulos, and M.W. Jackson, "Exhaust Emissions, Fuel Economy, and Driveability of Vehicles Fueled with Alcohol-Gasoline Blends," SAE Paper No. 750120 (1975).

