

STARTABILITY: AN OBVIOUS SNAG FOR
A) METHANOL-FUELED ENGINE IN A METHANOL ECONOMY ?

by

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I- INTRODUCTION

The idea of using alcohol as a fuel for internal combustion engines (ICE) is so old that it seems that alcohol was used for this purpose even before gasoline.

Due to their inherent physical properties only few members of the alcohol family are of interest as motor fuels: methanol, ethanol, isopropanol and tertiary-butyl alcohol.

Early in this century before an abundance of cheap crude oil swept aside all competition, pure or gasoline-blended ethanol — also called "power-alcohol", was seriously considered as a motor fuel since it could be obtained relatively cheap by fermentation. Much data were obtained during its use in the United States, England, Germany and France. But since 1939 its usefulness has been virtually lost except in France and some tropical countries where vegetation for its production is plentiful and supplies of petroleum are difficult to obtain. But even in the countries where vegetation is favorable one must keep in mind a much more serious crisis that will require almost all available soil: the food crisis.

Now, when petroleum supplies are dwindling and reaching higher prices than ever before, methanol the first member of the family is appearing as a promising fuel. This alcohol alone or in blends with ethanol has been widely used as a racing fuel for automobiles since power output is increased. Its importance has been greatly enhanced

since methanol can now be made economically from natural gas, coal, wood and garbage and can be burned with relatively lower emissions.

The purpose of this work is to present a survey of pure or blended methanol as a fuel for internal combustion engines and study one of the most relevant problems that could deter its wide normal use: the engine starting at low temperatures. It should be seen as a first step of methanol studies at KSU.

Also brief comments on energy use for transportation and the place of the internal combustion engine among other means of transportation are presented.

"Energy Crisis": a forerunner to the ultimate exhaustion of fossil-fuel.

Obviously the actual world energy situation is not surprising at all. When man began using petroleum products he was wondering if this energy source that seemed abundant could be renewed. When he found out that it took millions of years to create the final products of decay of prolific animal and vegetable life existing at that time, and worse, that the conditions that created them no longer exist, man kept searching for other energy sources.

On the other hand, when the forecasts indicated more good years ahead due to new well discoveries, oil consumption increased as never before and the shadow of the pollution caused by its use followed the same trend. The bat-

tle against this actual cancer began but a real cure was expected to appear in the future. Of course other energy sources like nuclear or hydroelectric, with their own problems and limited use, were economically developed during the years, mainly due to technological level achieved with oil-propelled tools. Nevertheless petroleum (oil and natural gas) is still responsible for nearly 3/4 of the USA energy market (Figure 1).

Now the Mid East affair has brought the future menace much closer, that is, the long-distant petroleum shortage is right here. The price of the barrel went to US\$11.73 in February 74 from US\$3.38 in September 73 without mentioning the possibility of no supplies at all again, for some countries due to political positions (1)*.

Even if the Arabian-Israeli question comes to an end the price of the barrel in USA would never go back to the September 73's according to the secretary of state Henry Kissinger, mainly as a motivation to the alternative energy sources.

At any rate there is no doubt that now is the time to not only seriously talk about, but really do something like a efficient energy conservation, to look for new --- or "old" energy sources, to improve all the energy-consuming systems in use; but, of course, not forgetting or putting aside the question of clean environment. It is desirable to do this rapidly, otherwise in the very near future the

*numbers in parentheses refer to references after Chapter XI

world is going to see a lack of energy not only to move automobiles, but also to produce basic items like food, even within the rich nations. In order to evidence how energy has been used by these so-called rich nations, consisting of 30% of the world's population, we can simply verify that these countries consume 92% of the total energy market; the USA alone is responsible for 36% of the world's energy with 6% of the world's population (2).

Thus, innumerable things to smooth the whole energy problem like using more thermal insulation and storm windows in residences, making fewer processed foods and reducing packaging costs would have to be done.

"All unnecessary use of energy would have to be avoid". But the whole subject is not that simple to be resumed in one phrase.

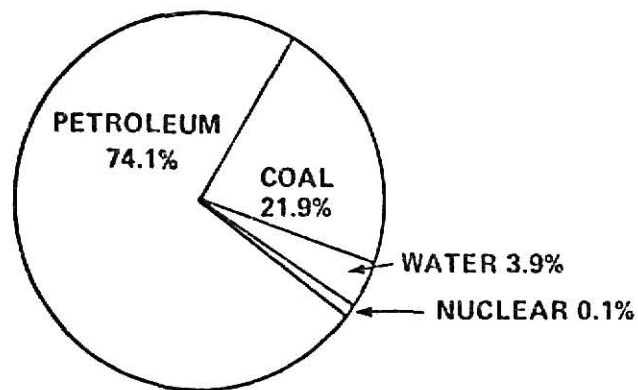
Basically the recent USA Project Independence commitment to reduce energy consumption, utilize energy more efficiently and move toward the use of domestic energy resources looks like a good position (3) to begin solving national energy problems and should be followed by other nations under their specific situations.

Of the areas which show promise for modifications leading to improvements of energy use, the transportation area is the most visible one, particularly automobile utilization. Several works about automobile fuel economy have recently been completed in Universities, Government Agencies, auto and fuel-related industries and good results were obtained. Various improvements on this subject were

done on normal engines in the 1975 models but they were partially masked by new emission devices.

On the other hand due to environmental cleanliness the idea of using fuels other than gasoline for the common engines, or even new engines other than Otto and Diesel, was recently investigated and some forecasts concerning these changes were ventured after the recent so-called "Energy-Crisis".

Figure 1 - USA Energy Market



Source - (14)

II- ENERGY USE AND TRANSPORTATION

In order to see where the energy was going before the energy-crisis, flow patterns for the USA in 1970 are given in Figure 2. We can easily point out that about half of the energy consumed by the USA became waste heat and that the most visible of the energy users, the transportation area, only efficiently used a quarter of the energy supplied to it. If we examine a forecast for 1985 in Figure 3 where only about 40% of the energy in the market would become really useful and the petroleum imports would be increased by an amount just large enough to take care of the energy wasted by the transportation, one has to conclude that the actual energy use trend is not efficient at all.

The enormous rise in private ownership of automobiles in the USA, with all its ease and convenience due to extensive construction of roads and highways, led to declining demand for mass transport causing among other problems further hardship to physically handicapped, elder people and to the poor (1). Analysing the energy efficiency for transportation (Tables I and II) one can easily note that bicycles and public transportation (busses and railroad) offer advantages for inter-city and urban passenger traffic. A good example of bicycles as urban transportation is the case of the Netherlands where 76% of the population own bicycles and special paths and traffic lights were constructed.

Bicycles are less widely used in the USA although there

Figure 2 - USA Energy Flow Patterns, 1970.

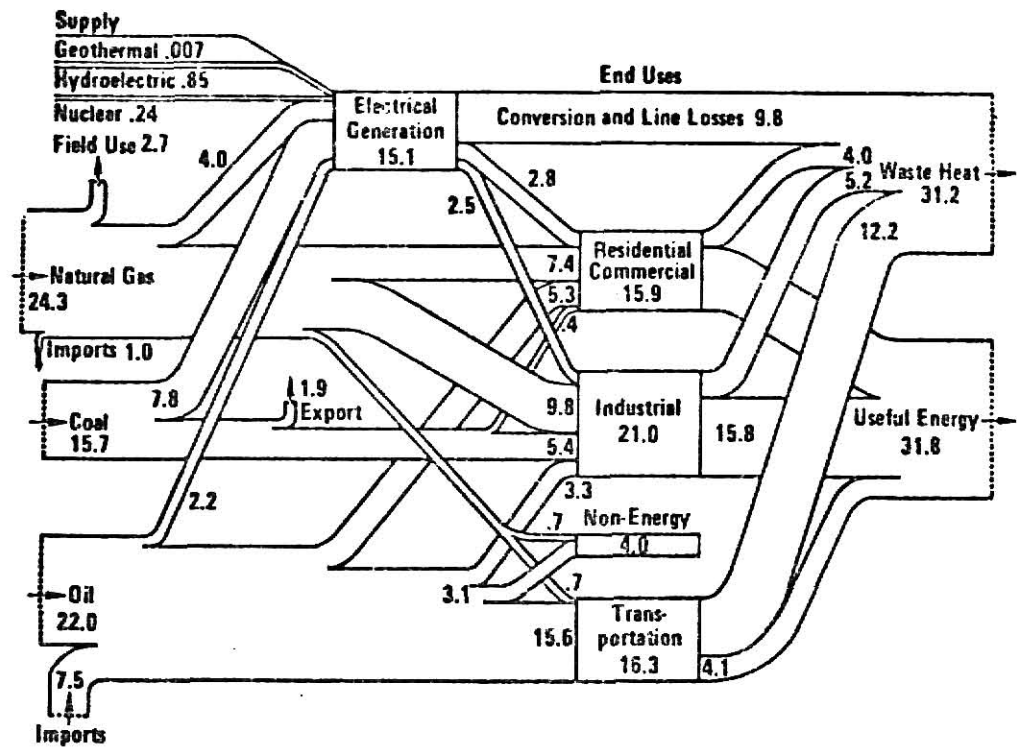
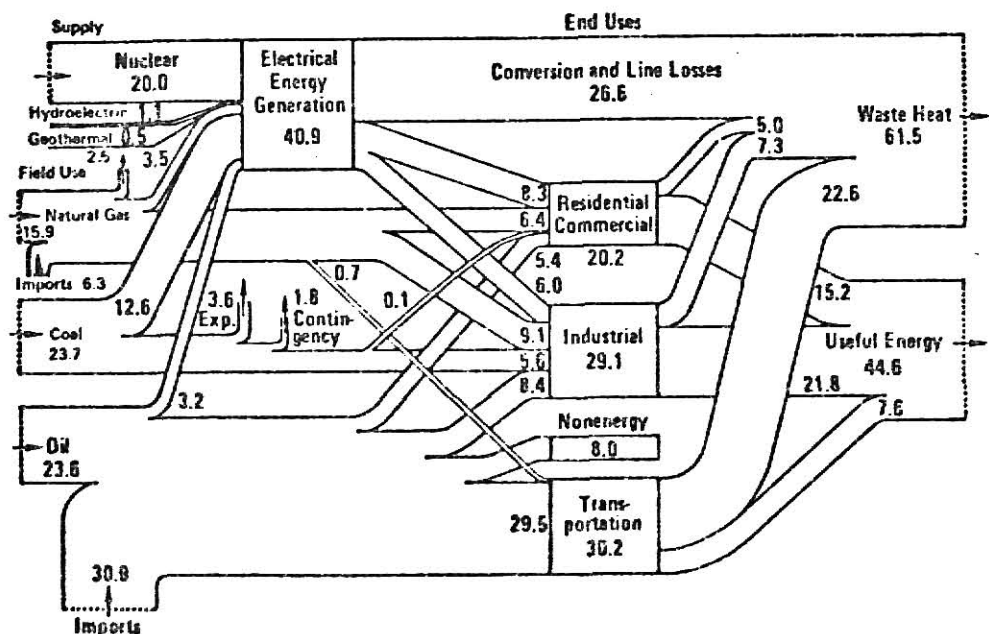


Figure 3 - USA Energy Flow Patterns, 1985.



Source - (14)

are at least 80 million bicycles and its advantages of being quiet, non-polluting, healthy, efficient, inexpensive, less necessary space to park (beats 16:1 the automobile) and less cost for path-way (6:1) are becoming more visible only on the College campus (1).

Table I - Energy Efficiency for
Inter-City Passenger Traffic

Mode	Energy Requirement Btu/passenger-mile
Busses	1090
Railroads	1700
Automobiles	4250
Airplanes	9700

Table II - Energy Efficiency for
Urban Passenger Traffic

Mode	Energy Requirement Btu/passenger-mile
Bicycles	180
Walking	300
Busses	1240
Automobiles	5060

Source - (2)

On the other hand those figures in Tables I and II are based on high-density traffic routes, thus if one happens to have busses operating at low occupancy rates to serve new routes with relatively low densities of origins and destinations

it might lead to less efficient use of fuel: a typical subcompact automobile with an average loading of 1.3 passengers is comparable in Btu/passenger-mile to a diesel bus with an overall load factor of 18%.

Due to the proliferation of highway and airport construction encouraging a decentralized style of living, working and recreation, radical shifts from this particular automobile system are difficult because of the physical facilities now in place, i.e., it would require a transportation system capable of moving a large number of people to a diversity of locations as the housing arrangements place the employed in a widely scattered array. But of course it would be a lot easier to solve this problem in new cities where urban planning is considering the present situation (4).

Several urban mass transportation systems were recently opened in Prague, Seoul and Sao Paulo; the last segment of the automated BART system of San Francisco and a countless number of projects were initiated in Warsaw, Belgrade, Bucharest, Sofia and other places. The USA voters in the November '74 election approved several proposed bond issues to support mass transit.

Despite all these projects, it is going to take a long time before these subway systems really help to solve the urban transportation problem as they are built after the city is settled; in actuality these systems are never completed — they are always behind the city growth.

Today the San Francisco rapid-transit system is only expected to absorb about 2% of the trips in its area; Toronto's

new subway system has absorbed only 3-4% of Toronto's trips (2).

In conclusion we can say that these large-scale concepts undoubtedly have their place but in the long run. If we see how energy consumption by the transportation industry was divided in 1970 (Table III) we can stress the importance of the automobile, responsible for more than a half of the whole consumption, at least in a mid-term basis. Specially when we recall the number of men, tools and industries involved in the whole affair we can conclude that the automobile is going to survive. Other non-energy advantages pointed-out by Adam (5), like privacy or weather conditions, could also help keep the automobile alive.

Table III - Energy Consumption by the
Transportation Industry in 1970

Mode	Energy, %	Principal Fuel
Cars	55	Gasoline
Trucks	21	Gasoline & Diesel
Aircraft	7.5	Jet Fuel
Railroads&Other	16.5	Diesel

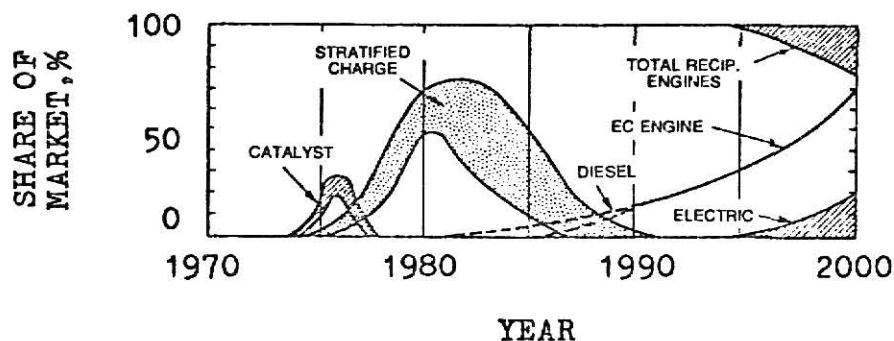
Source- (2)

Assuming that the automobile survives and continues being even a long-run solution it is quite clear that its Otto engine is going to be retired due to its low efficiency comparatively with others internal and external combustion engines. A low ther-

mal efficiency is incompatible to a wise use of energy.

A number of engines for this purpose have been studied to take the Otto's place but all of them seem to be still a long range solution.(Figure 4 and Table IV)

Figure 4 - Range of Expected Market Penetration of Future Engines for Transportation.



Source - (26)

As a short-term solution the Otto engine with stratified charge (6) and a light Diesel (7) have no other competitor to supplant them considering fuel and exhaust problems (8).

On the other hand most automobile trips are like local delivery vehicles: 91% of auto trips are less than 20 miles and represent 53% of vehicle miles. In this way a vehicle with short autonomy could be viable.

Thus, assuming 3 or less 20-mile-trips per day (going to work and coming back) a small electric runabout could be a satisfactory commuter vehicle. Fuel-cells, battery and electric vehicle technology are making this means of transport a desirable

Table IV - Technology Perspective for
Future Automotive Engines

ICE Type	OTTO	OTTO	WANKEL	STRATD. CHARGE	DIESEL
Avg. Life (miles)	50,000	50,000 ⁻	50,000 ⁻	50,000 ⁻	100,000 ⁺
1973 thermal efficiency	.10	.10	.07	.10	.17
Fuel Economy (mpg)	13 ⁻	10	13	13	30
Relative Eng. Cost	1.0	1.6	1.2	1.5	2.0
Multifuel	no	no	no	?	no
Driveability	good	worse	good	good	worse
Capable of Meeting '76 Emissions	no	prob. yes	prob. yes	yes	prob. yes
Critical Elements	none	reactors & converters	reactors , converters & seals	none	none

ECE or Elec. Motor Type	BRAYTON (g. turb.)	RANKINE (turbo)	STIRLING (H ₂)	WARREN (cpc)	BATTERY (or eq.)
Avg. Life (miles)	50,000	100,000	50,000	50,000	100,000
1973 thermal efficiency	.10	.10	.13	.16	.16
Fuel Economy (mpg)	20	15	25	23	(26)
Relative Eng. Cost	2.0	1.8	2.0	1.4	1.8
Multifuel	yes	yes	yes	yes	yes
Driveability	v. good	v. good	v. good	good	
Capable of Meeting '76 Emissions	prob. yes	yes	yes	prob. yes	yes
Critical Elements	high temp. materials & regenerator	none w/ steam new fluids	h.t. alloys head, seals & controls	h.t. valve material	high- density light- weight battery

Source- (26)

one for light-duty vehicles, since there is virtually no local pollution. If a clean fuel such as hydrogen is ultimately used to fuel local power plants a non transportation-related pollution could be achieved with this kind of electrical vehicle. In this way electromechanical way is a good energy carrier that will have applications for short-trip vehicles but it does not seem a short-term solution anyway.

For current vehicles, weight has the most influence on fuel economy (9,10) but probably all kinds of devices and characteristics to improve economy like larger axle ratios, radial tires, tighter torque converters, lighter weight, electronic ignition, overdrive transmission, smaller engines, vacuum gauges and systems like kinetic energy storage (11), special transmission systems designed for optimum fuel economy (12) will be used, in a way that all of them combined will result in great improvements in economy. Some estimations of how much improvement would result from the use of proposed modifications were done (13):

- | | |
|---|--------|
| 1- modifications in carburetion, injection, ignition, air-induction (with the same engine) :- | 5-15% |
| 2- use of an infinitely variable transmission (with the same engine) :- | 10-20% |
| 3- use of a lean mixture engine :- | 15-20% |
| 4- use of radial ply tires :- | 5-10% |
| 5- make the car accessories be driven at constant speed :- | 3-8 % |
| 6- redesign to reduce aero drag (modest one) :- | 3-5 % |

Several of these characteristics can already be seen in the new 1975 american models.

All the other means which are being used to conserve energy in transportation leads to good results: the use of extensive car pooling can affect 20% of the transportation energy use resulting in a 10% savings. A realistic view of work-oriented traffic would expect 30% of the travel by only one person per car, 40% in multiple occupancy auto and 40% by mass transit, causing an 11% fuel savings by 1990 (4). The use of a more economically sized car under way, will be another great improvement in fuel economy leading to 33% savings for auto use.

At any rate nobody can assure that gasoline would be available in a way to keep it as we are now, even for a short-period. Nevertheless, other fuels are becoming economically available and can be used in the Otto engine and future engines (Table IV) as well. Some of these fuels can be used with the so-called gasoline-extender purpose: as a gasoline blend.

III- ALTERNATIVE FUELS FOR TRANSPORTATION

The basic energy resources in the future will be in fact various (Table V) in order to not be so dependent on a few again, with all the risks represented by the situation today.

Some form of nuclear and solar energy and contributions from geothermal, tides, etc, seem likely to be the most important resources in the future. But before that, coal will have to play an important part in the energy panel, specially in the USA, while the full potential of nuclear and solar energy is being developed (4, 14).

Coal is the only indigenous raw material available in sufficient quantities to meet the near-future demands (Figure 3). It is abundant in the USA and other places, presenting known reserves of about 3.2 trillion tons in USA which at the current consumption rate of 600 million tons a year, a 5000 year supply is theoretically available. Although all this coal cannot be recovered at current coal prices, some 5% is and this could supply the present market for 250 years; if this coal is used as an alternate to the imported crude oil demand at projected 1985 levels, even a 75 year extension is estimated. By that time the remaining coal could probably be economically recovered with future technology.

On the other hand none of these future source is

Table V - Future Fuels - Initial List

Energy Sources	Auxiliary Material Sources	Potential Automot. Fuels
Coal	Air (O_2, CO_2, N_2)	Acetylene
Shale oil	Rock (limestone)	Ammonia
Tar sands	Water	Carbon monoxide
Uranium and thorium	Land	Coal
Nuclear fusion		Distillate oils
Solid wastes (garbage)		Ethanol
Animal wastes		Gasoline (C_5-C_{10})
Wind power		Heavy oils
Tidal power		Hydrazine
Hydropower		Hydrogen
Geothermal heat		LPG (synthetic)
Solar radiation		Methanol
		Methyl amines
		Natural gas (C_1-C_2)
		Naphtas
		Vegetable oils

Table VI - Future Fuels - Final List

1. Coal derived fuels:
 - . Gasoline
 - . Middle Distillate
 - . Methanol
 - . Oxygenated Compounds
 - . Hydrogen
2. Shale derived fuels
 - . Gasoline
 - . Middle Distillate
3. Ethanol via fermentation
4. Hydrogen from water by electrolysis

really suitable for direct use in transportation vehicles; thus, many scientists have been examining numerous synthetic fuels that could be made from abundant resources (like air and water) and the energy available from those nuclear and solar sources. (Table V and VI)

An ideal vehicle fuel should have certain basic characteristics which are not essential in a fuel for stationary consumption purposes. The basic requirements for a suitable fuel (not necessarily synthetic) for transportation purpose could be listed as:

- 1- high volumetric energy density.
- 2- high mass energy density.
- 3- high stability at normal conditions.
- 4- ease of transference from stationary storage to on-board storage.
- 5- long storage life.
- 6- relatively inert and non-toxic in handling and use.
- 7- minimal pollution or health hazards from exhaust products.
- 8- economical characteristics.

Present candidates do not meet all these requirements but such a list can help direct the search. Hydrogen produces the most energy on a weight basis, thus it is normally used in rockets where volume and cost are secondary; gasoline produces the most energy on a volume basis hence it is going

to long be preferred for airplanes. Methanol produces the second highest amount of energy on a volume basis of all liquid fuels in Figure 5, which is one of the reasons for the proposed use of this fuel.

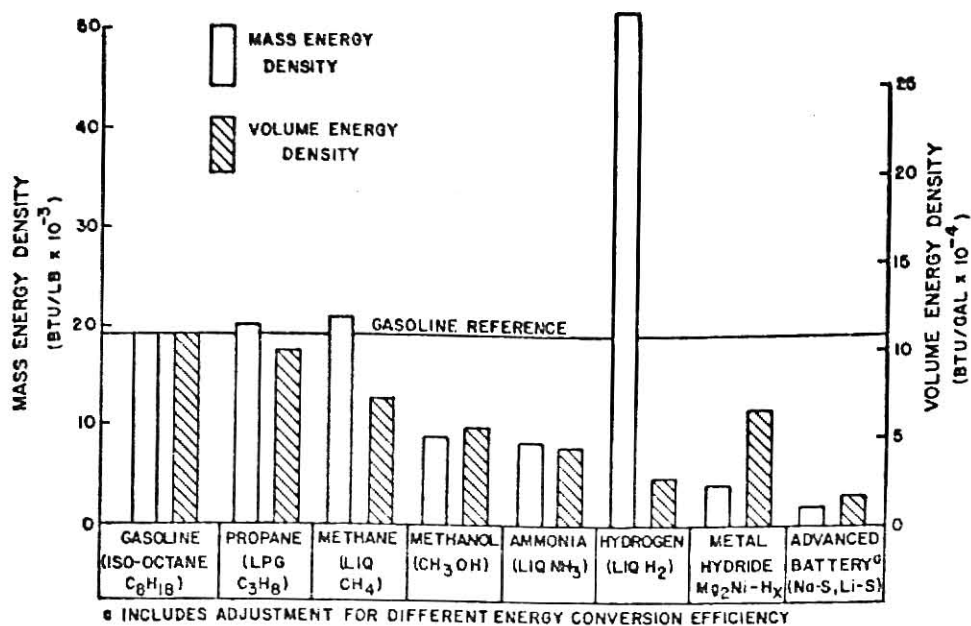
Generally speaking, the desirable properties of an ideal synthetic fuel (not necessarily for transportation) can be summarized as:

- 1- possible to be made from abundant resources.
- 2- "recyclable" characteristics: the fuel consumption should return the components to their original state.
- 3- the fuel consumption should produce minimum health hazards (pollution, etc)
- 4- no sophisticated or dangerous handling should be necessary.
- 5- energy, raw material and catalyst should be the only necessary elements to manufacture the fuel in a plant.
- 6- stability at normal conditions.
- 7- liquid and vapor phases should be relatively inert.

G. Hagey and A. J. Parker (3) and R. T. Johnson (4, 15) discussed some of the possibilities of non-petroleum fuel and predicted future candidates. Data of various possible fuels are given in Tables VII, VIII, IX, X and Figure 5.

The candidates can be separated into 3 categories:

Figure 5 - Energy Density Characteristics of various Transportation Fuels.



Source - (4)

Table VII - Synthetic Transportation Fuels: Properties and Description.

Chemical Formula	Hydrogen Liquid	Methane Liquid	Isooctane	Methanol	Ethanol	Ammonia	Projected Battery
	H ₂	CH ₄	C ₈ H ₁₈	CH ₃ OH	C ₂ H ₅ OH	NH ₃	Na-S or Li-S
Molecular Weight	2	16	114	32	46	17	---
Specific Gravity @ 60°F	Gas (0.07 at boil)	Gas (0.424 at boil)	0.69	0.79	0.79	Gas (0.71 at boil)	---
Melting Point, °F	-435	-296	-162	-144	-179	-108	---
Boiling Point, °F	-423	-260	211	149	173	-28	---
Appearance	Colorless odorless	Colorless odorless	Colorless character-istic odor	Colorless odor	Colorless charac. odor	Colorless pungent odor	Sealed container
Vapor Toxicity	Nontoxic	Nontoxic	Extreme concentr. causes narcosis	Cumulative toxic, irritant	Toxic only in extreme dose, irritant	Toxic, acts like alkali	Possible caustic compounds.
State at normal atmospheric conditions	Gas	Gas	Liquid	Liquid	Liquid	Gas	Solid
Conditions for liquid state.	Cryogenic -423	Cryogenic -260	Normal atmosphere	Normal atmosphere	Normal atmosphere	200 psi at 100°F	Operates as molten salt at 50°F
Handling	Cryogenic small scale commercial	Cryogenic standard commercial	Liquid standard commercial	Liquid small scale commercial	Liquid small scale commercial	Pressurized liquid, standard commrl.	Unknown, known standard operating temperatures with HT casing

Source - (4)

Table VIII - Synthetic Transportation Fuels: Fuel Characteristics.

	H ₂	CH ₄	C ₈ H ₁₈	CH ₃ OH	C ₂ H ₅ OH	NH ₃	Projected Battery
<u>Volumetric density</u> lb/gal	0.59	3.53	5.75	6.60	6.60	5.93	11.4
<u>Mass Energy Density</u> lb/ft ³	4.37	26.4	43.0	49.3	49.3	44.3	85
<u>Volum. Energy Density</u> x10 ³ Btu/lb	51.60	21.50	19.00	8.60	11.60	8.00	1.23
<u>Combustion Air req.</u> x10 ⁴ Btu/gal	3.0	7.6	11.1	5.7	7.6	4.7	1.3
<u>Exhaust water</u> x10 ⁶ Btu/ft ³	0.23	0.57	0.82	0.43	0.57	0.35	0.1
<u>Exhaust nitrogen</u> x10 ⁻⁴ lb/Btu	6.7	8.0	7.9	7.5	7.8	7.6	29
<u>Exhaust CO₂</u> x10 ⁻⁴ lb/Btu	1.74	1.05	0.74	1.31	1.02	1.98	3.0
<u>Exhaust NO</u> x10 ⁻⁶ lb/Btu	5.1	6.1	6.0	5.8	6.0	6.9	22
<u>Exhaust HC</u> x10 ⁻⁶ lb/Btu	0	1.27	1.62	1.60	1.66	0	5.9
<u>Manufacturing eff.</u> Btu fuel/Btu raw mat.	6.7	8.1	7.0	7.1	6.7	7.5	7.7
<u>Vehicle efficiency</u> (wheels Btu/tank Btu)x10 ²	0	18.7	20.6	17.3	18.9	0	0.68
<u>Total system eff.</u> (man. eff. x veh. eff.)	0	0.6	1.0	---	---	0	0.13x10 ⁻²
	0.5	0.5	0.5/0.8	0.66	0.75	0.4	0.3
	9.9	9.4	9.4	12.1	10.3	9.4	40
	5.1	5.0	4.7/7.8	8.0	7.7	3.8	12.0
		(from coal/oil)					

Source - (4)

Table IX - Fuel Characteristics related to Combustion Behaviour.

Fuel Property	H ₂	CH ₄	Ammonia	Hydrze.	Methanol	Ethanol	Petrol.Gas.
Volatility (Bg.Point)							
IBP °F	--	--	--	--	--	--	100
50% D @ °F	-423	-259	-28	236	149	173	210
90% D @ °F	--	--	--	--	--	--	330
FFP @ °F	--	--	--	--	--	--	400
Vapor Press.@ 100°F, psi			212	0.28(a)	4.6	0.28(b)	8-12
Heat of Vap. BTU/Lb @ NFP	194	219	591	540	474	360	(150)
Heat of Combustion (Net) BTU/Lb							
(Net) BTU/gal	51,600	21,500	8,060	7,294	8,640	11,550	18,650
Stoichiometric Mix	30,600	80,000	31,000	61,000	57,370	76,000	113,500
#Air/#Fuel	34.6	17.3	6.1	4.3	6.5	9.0	(14.8)
BTU/ft ³ @ STP	85.2	90.9	83.5	104	95	97	100
Vol.air/Vol.fuel	2.38	9.53	3.57	4.76	7.14	14.3	57
Octane No.(no Add.)							
Research		130	130		106	106	86-93
Motor		105			92	89	77-84
Flammable Limits							
Upper, Vol%	74	15.4	25	100	37	19	8
Lower, Vol%	4.1	5.0	15	4.7	6.0	3.5	1
Kinematic Vis., 77°F							
cs.				0.89	0.64	1.39	0.5
Auto Ignition Temp., °F	1085	1004	1204		878	738	800-950
Max.Flame Speed,ft/sec	8.7	1.12	0.034		1.6	(1.1)	(1.1)
Cetane No.		0	0		(10)	(15)	(0-5)

Note: (a) @ 77°F
(b) @ 68°F

Blank indicate absence of desirable data.
Dash indicates data inconsequential.
() indicates estimated values.

Source - (3)

Table X - Fuel Properties related to Handling and Storage.

Fuel Property	H ₂	CH ₄	Ammonia	Hydrze.	Methanol	Ethanol	Petrol.Gas.
<u>Density (liquid)</u> @ 60°F, lb/ft ³	4.43 (a)	27.9 (a)	48.1 (a)	62.6	49.7	49.3	46.0
<u>Freezing or Pour Pt.</u> °F	-435	-296	-108	35.6	-142	-179	-40.0
<u>Flash Point (open cup)</u> °F	--	--	--	126	52	65	-40 (b)
<u>Sol.in water</u> @ 68°F, Wt%			33.1	00	00	00	Nil
<u>Sol.for water</u> @ 68°F, ppm				00	00	00	0.02
<u>Emulsion tendency</u>	(np)	(np)	(np)				can be contr by careful refining & additives.
<u>Static Charge</u>				D	ld	ld	D
<u>Toxicity</u> vapor	none (c)	none (c)	Hi	Hi	Mod.	Low	(Sig)
ingestion				Mod.	Mod.	Mod.	(Low)
skin				Hi	Low	Low	(Low)
<u>Lubricity</u>		np					np
<u>Corrosivity</u>			(d)	(e)	(f)		

Note: (a) at NBP
 (b) closed cup
 (c) asphixiant
 (d) corrodes copper, brass and zinc.
 (e) avoid cobalt, copper, pure iron,
 lead, manganese, magnesium, tin&zinc.
 (f) see Chapter V.

Code: np - no problem
 D - danger
 ld - less D than
 petroleum HC.

Source - (3)

- 1- hydrocarbons (alcohols included)
- 2- hydrogen
- 3- inorganic hydrogen compounds (primarily ammonia)

Hydrocarbons--

The light hydrocarbons (methane and propane) present better emission characteristics but are considerably more difficult to handle and store than gasoline-type fuels. The available processes to convert coal to these gaseous fuels appear to have thermal efficiencies of approximately 50%. Thus to obtain 1 Btu of fuel to use in vehicles with the present conversion technology requires 2 Btu of raw material; this is an inefficient way of using coal but facing the time factor it might be a compulsory solution.

Another more likely synthetic fuel that can be made from coal to replace gasoline is methanol, with an overall thermal efficiency for the conversion between 60-70%. Methanol can be made also from natural gas (methane) and other sources (see Chapter IV). This fuel presents a volume energy density that is roughly half that of gasoline but is liquid at normal conditions. References indicate that methanol is suitable to use directly or mixed with gasoline in the present Otto engine, with reasonable economy and emissions. In the 1970 Clean Air Race a methanol-fueled Gremlin run by some Stanford students surpassed the 1976 CO and NO_x specifications. Its use as a source of hydrogen, as a fuel for fuel-cells, as a fuel for boilers with less NO_x, as a source of city gas, and as raw material for the synthesis of protein were

also studied with promising results. Methanol (also called methyl-alcohol) will be discussed in detail later on this work. (4, 15, 16, 17)

Hydrogen-

During the last 10 years the environmental pollution problem has led to reexamining the use of hydrogen as a vehicle fuel, which is not a new idea since before World War II it was being considered. Hydrogen likewise presents interesting characteristics concerning its use as a full-scale energy source not only for vehicles, but for home and industry also. It can be produced from a wide variety of other fuels by chemical means or can be generated by electrolysis of water, which appears as the most feasible procedure for the near future. Several projects like the one being developed here at KSU using wind power to obtain H_2 use electrolysis of water. (18, 19)

However the problems of distribution of hydrogen and carrying it on board have not been satisfactorily solved; the cryogenical or interstitial ways are presenting some problems concerning mass and volume energy density. The technical, economical and safety questions limit the direct use of hydrogen as a fuel to a select few transportation media (or farm use) in the foreseeable future. Some work has been done about gasoline-enrichment with H_2 but it has also been shown that this will not be a solution compatible with

the time factor as it cannot be applied to normal engines without great modifications. Nevertheless, as a 10% methanol-gasoline blend by volume becomes 40% hydrogen, methanol blends may be a simplest way of operating a car with a high proportion of hydrogen. (4, 15, 16, 20, 21, 22, 23)

Inorganic hydrogen compounds-

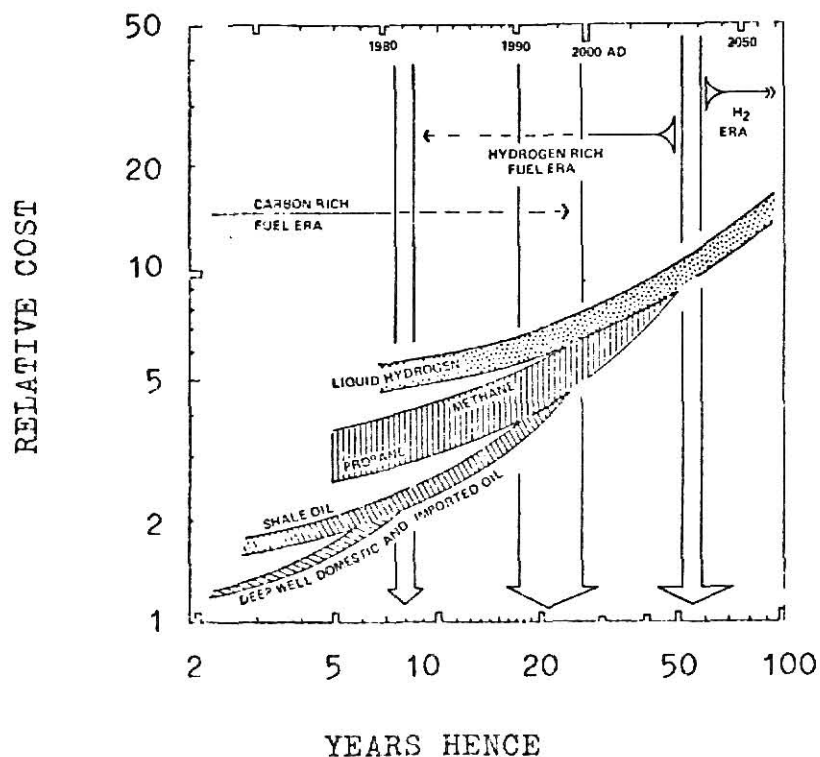
Of the hydrides of non-carbons (NH_3 , SiH_4 , etc) ammonia is the most promising for a synthetic. Although it is toxic and gaseous at standard temperature and pressure it can be easily liquefied and stored with standard equipment and procedures. The University of Tennessee's ammonia-fueled urban vehicle competed in the 1972 Urban Vehicle Design Competition and finished 5th in 65 entries.

A good reason to study ammonia as a candidate is that if energy and hydrogen are available, ammonia may prove to be an important fuel for surface vehicles. The reason for this is that ammonia can be dissociated into hydrogen and nitrogen, the hydrogen burned as a fuel with the nitrogen as a diluent gas, i.e., ammonia would be just a hydrogen carrier. (4, 15, 24)

G.A. Hoffman (25) by dividing the "future" fuels in 3 major chronological eras predicted their period of utilization based on the current technology. The 3 major eras: carbon-rich, hydrogen-rich and hydrogen era would be as shown in Figure 6; in this way the future cost of carbon-rich fuels

are predicted to be four times current prices by 1990, when they would begin to be supplanted by hydrogen-rich fuels. About 50 years later cryogenic hydrogen would become the most economic fuel for transportation vehicles. Price estimates of the carbon-rich and hydrogen-rich fuels and electricity are shown in Tables XI and XII.

Figure 6 - Cost of Fossil, Synthetic and Electrolytic Automotive Fuels.



Source - (25)

Table XI - Current Price Estimates of Carbon-rich
Automotive Fuels for Heat Engines

Fuel	Source	Price (\$/GJ)	Reserves (years)
Domestic crude oil	Deep wells	1.0	20
Domestic kerogen	Shale oils	1.5	50
Imported oil	1973 suppliers	1.3	50
Imported oil	All global sources	1.4	100
Liquefied coal	Strip mines	2.0	50
Liquefied coal	Deep mines	2.5	150

Table XII - Current Price Estimates of Hydrogen-rich
Automotive Fuels and Electricity

Butane	Oil or coal	2.0-2.2	100
Propane	Oil or coal	2.2-2.5	200
Ethane	Coal	2.5-3.0	400
Ethanol	Cellulose fibers	3.0-3.5	500
Methane	Coal	3.0-4.0	600
Methanol	H ₂ + CO	4.0-5.0	800
Ammonia	Air, electricity	5.0-6.0	1,000's
Liquid H ₂	Electrolysis	4.0-5.0	1,000's
Electricity	Geothermal	1.8	large
(1972 Calif. costs at the plant)	Nuclear	2.6	large
	Coal	2.9	200
	Gas and oil	3.2	20

Source- (25)

IV- METHANOL: USES AND PRODUCTION

There is not much doubt that the use of synthetic or alternate fuels will play a great role in the near future. We have selected some of the possible candidates for the major position, but every day unexpected new technologies appear and since social events, national and international political positions are deeply involved, a precise forecast is completely impractical.

"When and which fuel?" seems to be a difficult question. The most likely answer could be: several. Nevertheless this may not be a vague answer at least for vehicle use: instead of choosing between regular, premium, or unleaded one would have to choose between methyl-fuel, ammonia, hydrogen or even an electrical plug at the "gas" station.

At any rate methanol or methyl alcohol appears as the nearest solution as not much modification in the normal gasoline engine and fuel distribution system would have to be done. If a gasoline-methanol blend is used the engine will not require great modification in the current practice. Even a "methanol-economy" is nearly possible.

If higher alcohols are tolerated in the product of a methanol production plant, its output can be increased by 50%. This final product contains more energy than pure methanol and it is cheaper. "Methyl-fuel" a name given by Vulcan-Cincinatti has been used to denote this product, and

has been sometimes considered as synonymous of methanol (27).

Methanol can be made from natural gas (methane) for a short term period, it is a good way to use coal and could be made from wood and biomass forever (23). Also the resulting emission in gasoline engines seems to be much lower than when gasoline is used.

Back in 1925 an interesting article published in Industrial and Engineering Chemistry (April issue) reported: "... we publish an article from our French correspondent on the subject of synthetic methanol, at a cost far below that of the natural product ... We do not predict that it will necessarily be the fuel to supplement our diminishing petroleum resources, but who shall say that synthesis will not prove the key to our liquid fuel problem? Water gas may be produced cheaply and it would seem that so long as we have coal it may be possible ... The field is new and the opportunities are correspondingly great." --- This prediction could really come true now.

Methanol has many uses besides the use for ICE that would support construction of new plants to produce methanol.

How to use Methanol

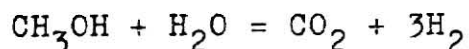
Methanol has been in common use for many years. In the mid-1800's it was burned in household lamps replacing fish and whale oils before kerosene by its turn put methanol aside. Nowadays it has been of limited use as an oc-

casional fuel for chafing dish or a camp stove. In the US industry methanol is consumed at the rate of about a billion gallons per year as a raw material for chemical industries.

Nevertheless there are several other uses for methanol justifying the construction of more plants for its production. It can be used as:

1- A raw material for the production of hydrogen.

Methanol has already been used to produce hydrogen, although at a small-scale production rate, but one which has proven economical. The reaction is represented by:



2- A fuel for generating electricity in fuel-cells.

Fuel-cells are portable generators of electrical power and have received much effort toward their development, mostly due to the Apollo space ship program. The size of a fuel-cell which generates several kilowatts of electricity is now the same as a domestic refrigerator.

As the best efficiencies of actual ICE's are in the range of 25-30% and fuel-cells can reach 70-80%, the use of the cells is really advantageous for nowadays, especially to generate electricity. From the point of view of cost and efficiency the hydrogen-fueled cells with an aqueous solution of potassium hydroxide as electrolyte have been considered the most practical. If the hydrogen is produced from methanol

an overall efficiency of 50% or higher could be expected, including H_2 generation, fuel-cell efficiency and DC to AC conversion. Virtually no pollution results and a small amount of cooling water are likely to be required.

Studies to develop small-capacity fuel-cells to be installed in homes eliminating the transmission of electricity or at least, as a means for peak-shaving, have been conducted by United Aircraft Corporation, Pratt & Whitney Aircraft Division, Tokyo Gas Co. and Osaka Gas Co.

3- A fuel for steam boilers.

Since in some boilers a large part of the heat is transferred by radiation from flames (and from heated refractory walls) and only a small portion is transferred by convection, methanol is not suitable as a fuel for boilers that operate in this way. This is due to the fact that about 50% of a methanol molecule is formed of oxygen, thus carbon particles deposited in the flame which are responsible for that radiation would not be formed as they are when oil fuels are used.

On the other hand methanol is more easily used for the operation of combustion units where a fluidized catalytic bed* is employed. The use of methanol reduces the NO_x emission from this type of boiler.

* Fluidized catalytic bed is used to prevent the formation of the boundary layer by the stagnant gas located close to the solid wall; this layer constitutes the principal resistance to the transfer of heat to the wall of boilers. The use of this kind of bed can reduce the combustion temperature to inhibit the NO_x formation in the furnace.

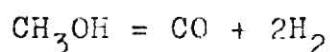
4- A source of city gas

Methanol by itself cannot be used as substitute for city gas, but it is easily converted to methane. Methane-rich gas has been produced in US from naphta and steam for city gas --- so-called SNG (synthetic natural gas), as a way to substitute for the natural gas which is in short supply (31). According to Cambridge Institute of Technology if the present NG consumption rate is maintained a 30% shortage in 5 years is estimated.

Methanol may also be converted to a methane-rich gas by a similar process, with the advantage that it is not necessary to use the desulfurization process, which is required when naphta is used, to prevent decay of the catalyst. Predictions indicate that the utility market for methanol could be so big that its demand in 1985 would be twice as much the demand for the gasoline-extender purpose (10% blending for Otto engine).

5- A source of reducing gas

The substitution of reducing gases for coke for the purpose of reduction of metalic in the metallurgical and steel industries has been suggested when the procurement of coal become difficult as has happened in Japan. The catalytic decomposition of methanol may be used to produce reducing gas (synthesis gas):



6- A raw material for the synthesis of protein.

It is predicted that the food shortage is going to increase, thus the production of synthetic protein from sources of carbon may be a partial solution. Synthetic proteins are prepared by cultivating micro-organisms which digest n-paraffins as a source of carbon. These micro-organism cells are used as food or as a source of protein. The synthetic protein must be economically competitive with degreased soybean (which is used for food stuffs) to be used nowadays and may be compulsory solution to help world hunger.

Methanol may be used as a substitute for n-paraffins with several advantages:

1. as methanol is soluble in water (n-paraffins are insoluble), less power is consumed for cultivation - vessel agitation to form a uniform suspension and produce air bubbles.
2. as about 50% of the methanol molecule consists of O_2 , the oxygen concentration in the cultivation vessel is easier to maintain and very little air need be supplied during the course of the cultivation (the O_2 concentration controls the cell propagation rate).
3. as less heat would be generated in the cultivation vessel when using methanol, the control of the vessel temperature is easier (optimum - 30 C).
4. no washing of the final product is needed when methanol is used, which has to be done when using n-paraff-

fins to remove unconsumed material.

Nowadays the price of methanol compared to n-paraffins is not low enough to be feasible for the production of synthetic protein. This can happen if "Jumbo" plants which are already projected were constructed.

7- A means of sewage denitrification.

The Environmental Protection Agency (EPA) has told a major company interested in methanol plants that if large quantities of methanol become economically available, a significant demand for its use in municipal and industrial waste water treatment is certain.

The reason is that methanol can be used in tertiary treatment of waste waters for denitrification: methanol is oxidized to carbon dioxide while it reduces nitrates to nitrogen.

8- A fuel for internal combustion engines (ICE).

Otto engines are usually operated under conditions where insufficient oxygen is present for the complete oxidation of the usual fuel --- gasoline. The methanol molecule presents about 50% of its weight of oxygen and its calorific value is about 50% less than iso-octane, which is commonly taken as representative of gasoline. However that fact leads to the alcohol "leaning effect" when methanol is added to gasoline, causing a reduction in CO emissions. Other information about emission will be given in Chapter V. If we use pure methanol that lower heat value is compensated by the fact that the stoichiometric ratio is half of the stoi-

chiometric ratio of gasoline. In this way approximately the same amount of energy would be burned per cycle.

Other advantages of using pure or blended methanol as ICE fuel are due to its high latent heat of vaporization (higher volumetric efficiency), higher octane rating compared to gasoline and some properties like less crank case oil dilution, cooler engine operation, less carbon deposit inside the engine, and the fact that alcohol fire can be put out with water sprays. Also a small amount of water could be added to the fuel without reasonable loss in efficiency.

Some disadvantages like low mileage per gallon (though not necessarily per dollar) and a bigger tank, difficulty in cold starting (for pure methanol), vapor lock (for blends), and stability of fuel at low temperatures will be discussed later in this study.

The use of methanol for gas turbines for electricity generation where clean combustion gives high efficiency is also promising. This would provide the possibility to divert the fuel oil and natural gas currently burned in these turbines to other uses. If 100% alcohol is used a lower blade erosion and deposit build-up are expected. Again the lower combustion flame temperature leads to less NO_x formation and some 40,000 hours of run between maintenance can be achieved. Conventional jet fuels require 15,000 hours between regular maintenance.

More information about use of methanol can be found in the following references: 14, 17, 28, 29 and 30.

How To Produce Methanol.

The range of sources to produce methanol is great as the basic reactions in its production are:



Any combustible substance containing carbon and hydrogen will produce synthesis gas as well as ethanol and other alcohols, ammonia and synthetic gasoline. In such a way the most likely sources within the present technology could be selected as: natural gas ($\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$), petroleum (not an answer to the problem), coal, oil shale, wood, and farm and municipal waste products.

Union Carbide now produces synthesis gas from waste at a demonstration plant in West Virginia. Seattle is studying the production of alcohol from municipal waste and about January 1975, Maine energy officials proposed the use of some timber threatened by disease to produce methanol. The production of methanol from this Maine timber would be enough to be used in state vehicles and to heat state buildings.

Economic studies of methyl-fuel (crude methanol) vs. liquefied natural gas (LNG) conclude that the idea of converting the currently flared natural gas in the Middle East to crude methanol deserves serious consideration. Last year federal energy officials were discussing a methanol plant using coal.

In such a way the production of methanol is flexible as it can be made from many sources depending on the situation. As near-future sources, natural gas and coal are the most probable ones but the major source for a long range answer would be waste materials as these would always be available: "where the automobile are, the people are".

Nowadays the major source of methanol is natural gas, despite the fact that natural gas itself is in great demand for other purposes and it is in short supply in the USA (31).

The production sites of natural gas are usually far from the sites where the gas is used, hence pipelines are usually constructed on continents to transport natural gas. Recently liquefied natural gas (LNG) has been shipped from the Middle East in special refrigerated tankers. These tankers are a really delicate matter as few shipyards have the necessary technology and their cost is so high that even studies about a pipeline under Mediterranean Sea were made.

Instead of shipping this LNG, the mentioned idea of converting the natural gas to methanol on the Persian Gulf and North Africa, and then shipping it to the consumer country, in common tankers, has been proved economical. The break-even point for the distance between source and consumer is around 3,500 miles. This could be expected since a ton of LNG carries roughly twice as much energy as a ton of methanol, but tanker cost per unit weight of LNG is 4 times as much. On the other hand roughly twice the amount of methane is consum-

ed to produce 1 million BTU of methanol as to produce 1 million of LNG.

Despite the fact that methanol could be used as a substitute for natural gas a large portion could be directly used as a fuel.

Farm wastes such as pig and chicken manure and sewage can be used to biologically produce methane by the waste decomposition. This also would help about 50% in the problem of disposal of such wastes. The conversion of methane to methanol is convenient despite the fact that methane could be used as a fuel for internal combustion engines. This is because methane-fueled vehicles would require too much space and weight to carry compressed methane. Some methanol plants using natural gas as raw material have been constructed and several studies about them were done by Davy Powergas Inc., Houston Natural Gas Corp., Vulcan-Cincinnati Inc., and M.W. Kellogg (27,33,34,35,36,37,38,39).

Although coal is the most abundant fuel in the USA it is also the most polluting one; but a relatively non-polluting fuel can be made from coal by gasification or liquefaction. Methanol, as said before, is one of these fuels. However some competing fuels such as methane, hydrogen and synthetic gasoline can also be made from coal.

As methane and hydrogen are gaseous fuels, the switch to them would involve the mentioned major changes in on-board fuel storage, stationary storage, handling and consumption.

Gasoline cannot be made more cheaply from coal than methanol can and does not present good emissions compared to methanol.

No new technology beyond coal gasification is required to produce methanol from coal, as the only difference compared to the already commercial Lurgi process is the CO/H_2 ratio in the shift reaction. The coal gasification development has increased mostly because of the idea to produce SNG, and many processes have been developed like the Lurgi's low pressure methanol technology. This process will have its first American tryout with natural gas as source of synthesis gas at Celanese Chemical's Bishop, Texas complex --- a 1,000 ton day plant is scheduled for completion in late 1976 (32).

The gasifier designs for the production of methanol would probably be similar to those used on a commercial scale by the US Bureau of Mines and major chemical companies to produce synthesis gas.

In the last century the principal energy source for the USA was the capture of solar energy by the forests. Nowadays not less than 23% of the area of this country is covered by commercial forests. Even with an efficiency of 1% which can be achieved by improved forest management, the USA present annual energy needs would be provided by these "energy-plantations". Between 5 and 20% of these commercial forests

could supply all USA electrical demand and of course this is a renewable source of energy.

Methanol can be seen also as a way to use hydrogen when for example the coal supply becomes exhausted: methanol could continue to be synthesized from nuclear-generated electrolytic H_2 and naturally occurring CO_2 . In this way, in comparison with hydrogen, methanol would present a much lower cost of transportation and all the advantages of being liquid fuel in the normal automotive engine concept.

Further information about methanol production are available in the references 14, 29, 40, 41 and 42.

V- METHANOL AS A FUEL FOR INTERNAL COMBUSTION ENGINES.

Several authors defend methanol as a really good short term solution for an alternate fuel for internal combustion engines. The reason for this is its suitability for Otto engines and several other properties of methanol concerning production, emission etc, some of them discussed in the preceedings chapters.

The term "short-term" means that the use of methanol could begin in 5 years with significant impact within 10-12 years. Oil importation requirements would be reduced by developing an automobile fuel derived from coal like methanol requiring simpler and cheaper plants to meet the new demand.

The reason to wait a few years to begin using methanol as an normal ICE fuel (even in blends with gasoline) is that although its price per gallon is lower than that of the gasoline, the total USA production is only about 1% of that of gasoline, and it is used already for other purposes.

In this way the use of methanol to fuel automobiles cannot be done as a drastic change but as methanol added to gasoline as an additive. This would not require even a change in carburetor jets with a 5% in volume blend gradually supplied. Depending of the improvements in other energy sources a 10% or 15% blend could be used, or even 100% methanol. However, for the use of pure methanol some carburetor modifications

have to be done, being US\$ 100.00 an estimative cost of the conversion in December 1973 (27).

Historic.

Alcohols became a popular fuel for lighting in about 1830 replacing the bad-smelling oils derived from fish. Especially in France, where a partial methanol economy was occurring, alcohol use as fuel for various purposes was extremely popular: wood was distilled in the provinces to give alcohol to be burned in Paris for heating, lighting and cooking. It was much more suitable to use alcohol than transport wood to the capital.

But in their turn kerosene replaced the alcohols, especially for lighting purposes by 1880. By this time a great invention attributed to Otto was announced: a heat machine that happened to be possible to run with alcohol as a fuel. Some authors reported that alcohols were probably used in that kind of engine even before gasoline (43).

In 1890 a high-compression tractor engine was designed to use ethyl alcohol, considerably more efficient than contemporary engines operating on kerosene (43). Ernest Sorel in his book "Carbureting and Combustion in Alcohol Engines", translated from the French and published in 1907 by John Wiley and Son, New York (44), discussed the use of alcohol in the earlier engines, with brief comments on the work of Lebon in 1801, Lenoir in 1860 and Beau de Rochas (4 stroke). Sorel commented also the old international competitions organized

by the French Minister of Agriculture in 1902 as a means to compare results of various fuels. Since those days the controversy of alcohol use as a fuel for engines was extremely rough with heated partisans and opponents (44).

Ethanol was of particular value then because of its wide universal availability from several crops as shown in Table XIII. But the low cost of gasoline put aside the alcohol use and a number of years elapsed before there was again a reconsideration of it as a fuel for engines. This happened during the World Wars I and II when gasoline shortages occurred, especially in Germany and France.

Table XIII - Alcohol Production From Various Crops.

	imperial gal/ton	imperial gal/acre
Molasses (beet)	66	---
Molasses (cane)	73	---
Sugar Mangolds	11	220
Sugar Cane	18	255
Sugar Beet	21	240
Artichokes	28	500
Mangolds	8	150
Potatoes	22	220
Grain	78	50
Grapes	18	
Bananas	13	
Wood (dry)	up to 75	

Source- (45,46,47)

Soon after the First World War an Empire Fuels Committee in England was set up to investigate the use of alcohol, mainly ethanol 90-95% pure, in ICE and notable works were presented by Ricardo, Tizard, Pye, Ormandy and others (48).

In 1920 the methanol production in the USA began but for use as a solvent, for plastic manufacture and fuel injection in piston aircraft. In 1921 a book written by Carleton Ellis and Joseph V. Meigs called "Gasoline and Other Motor Fuels" was published in New York (49), presenting a good survey of alcohol as a fuel with 54 references. In London, 1922, "Power Alcohol: Its Production and Utilization" by G.W. Monier-Williams was published, treating yet more extensively the subject (45).

Prior to the Second World War an American Chemical Foundation was set up to discover means of utilizing farm surpluses. Leo M. Christensen, author of "Power Alcohol and Farm Relief" among other books and articles (50,51,52), appeared as the leading partisan of ethanol-gasoline blends in the USA, as a way to help farm industry, creating more jobs or briefly expanding agriculture. Others publications like the Miscellaneous Publication No. 327 from the US Department of Agriculture in December 1938 ("Motor Fuels From Farm Products") presented further studies about ethanol use as a fuel in a neutral position.

On the other side there was the "Anti-Alcohol School" group leaded by G. Egloff, who stressed the danger of phase separation and other questions like the fact that the drinking-kind alcohol --- ethanol, could be obtained from ethanol-

gasoline blends by simply shaking the blend with the addition of water.. In this way the "automobile bar" would have to be prevented by denaturants as is usually done nowadays where ethanol is used. Egloff claimed that those blends led to blindness and death if the denaturant separation was not done properly. In fact it is really difficult to remove a common denaturant at home --- methanol. Other denaturants like nitrogen-base substances and oxidized petroleum distillates were easier to separate (53).

France with a vast wine surpluses has also encouraged alcohol fuels. However too high percentages of alcohol were used (sometimes around 50% alcohol) causing unbalanced blends giving alcohol a bad name in some places.

The use and production of alcohol all over the world was briefly presented in a book published in 1938 in England, written by A.W. Nash and D.A. Howes, who presented also a good survey of alcohol fuel subject till that date (46).

During the Second World War with the loss of Malayan rubber the necessity of synthetic rubber turned out to be another cause of ethanol production from grain. Books like "Food for Thought" by H.F. Willkie and P.J. Kolachov published by the Indiana Farm Bureau in 1942 were defending utilization of farm products for producing farm motor fuels to solve the agriculture fuel problems (54).

In 1949 another major partisan of alcohol cause --- S.J. Pleeth wrote "Alcohol A Fuel For Internal Combustion Engines", a good comprehensive work with up to date results and some re-

search done by himself (43).

As a conclusion for this half of this century we can quote Pleeth: "unfavourable reports appear to emanate consistently from sources inimical to the production of alcohol." At that time countries with considerable oil deposits or who controlled oil deposits in other lands (like Holland, USA, etc) tended to produce reports against the use of alternative fuels to gasoline. On the other hand countries with little "oil power" tended to produce favorable results of alcohol use.

Of course some destructive criticism was constructive, leading to solutions of the problem, like the old problem of tendency of gum formation when cracked gasoline was used. In this way the alcohol opponents could help solving the problems for alcohol use which exist today.

In 1964 four separate SAE papers from the University of Michigan, the University of California, the Nebraska Department of Agriculture and Inspection, General Motors Corporation and from the Southwest Research Institute were grouped in a special publication, the so-called SP-254 (55, 56, 57, 58). These papers brought the whole subject up to date once again, with more emphasis on the relatively new importance of emissions, i.e., EPA.

The farm-derived alcohol price was much higher than gasoline with some exceptions concerning locations. This is the case of tropical countries with suitable climatic conditions and soil like Brazil. This country is the largest sugar pro-

ducer after USSR, with sugar-cane derived alcohol surplus and the necessity to import 75% of its oil consumption (1). Ethanol-gasoline blends up to 15% in volume have been used there for a long time, but due to the diverse range of percentages depending of the city and season some operating problems appeared. This was the only problem and one that could be easily overcome with a fixed percentage. Other troubles concerning vapor-lock also were encountered but only in certain makes cars.

Thinking emission-wise, several studies in the USA on straight methanol as a fuel were developed before the so-called energy-crisis, like one sponsored by EPA and conducted by Consolidated Engineering Technology Corporation (CETEC) (59) in a Dodge Dart model 1969. It has been claimed that a municipal vehicle converted to methanol has been satisfactorily operated in Santa Clara, California (27). Other published works about methanol as a fuel for ICE prior to the 1973 oil embargo can be encountered such as one done at the Stanford University (60). It consisted of modifying an American Motor Company Gremlin to be fueled by pure methanol to enter the 1970 Clean Air Race, whose good emissions results will be discussed in the next section. Very interesting results with blends of toluene, iso-octane, n-heptane and methanol as fuels were obtained from experiments carried at Ford Motor Company by J.S. Ninomyia, A.Golovoy and S.S. Labana (61). Some theoretical predictions about performance with various fuels in-

cluding methanol were developed at the University of California, Berkeley, by Starkman et al (62). Experiments in a CFR engine were done by G.D. Ebersole and F.S. Manning from Phillips Petroleum and the University of Tulsa (63), with an objective of comparing performance and emission characteristics of methanol vs. iso-octane, which is usually considered as a typical gasoline in most works. This particular work turned out to be one "of the most thorough investigation" about the subject (64).

When the search for additives to be used in un-leaded gasolines instead of lead anti-knocks, alcohol was considered and it was reported that 3% iso-propanol and 10% tertiary-butyl alcohol have been used in few commercial gasolines (65) for other purposes. A 25% tertiary-butyl alcohol, 3% water and 72% gasoline blend has been reported as a successful mix by two Goodyear scientists (66).

However the main importance of alcohol fuel arose with the energy crisis which caused the gasoline price to be higher at the same time that new commercial methods of methanol production were developed. In less industrialized countries the other member of the family --- ethanol, may be still an attractive fuel as it can be produced forever from agricultural products by fermentation, as mentioned before. Actually, in the USA ethanol has been studied again at the University of Nebraska (81).

In a recent visit to Brazil, Dr. Melvin Calvin, 1961 Nobel Prize in Chemistry declared (67) that that country is

the only one in the world with a capacity to develop an energetic project of sugar-cane utilization leading to ethanol production to be used as an additive to gasoline, or even in the pure form, in 100 years. Evidently some improvements, especially in extraction techniques, have to be done to increase the production gradually. This particular position is due mainly to the fact that while the USA and the Philipines have reached the maximum sugar production and Cuba has been decreasing its production, Brazil has just begun to increase its production and has enough land area available. As a result of the actual energy situation a work about optimization of alcohol use for fueling automobile engines directed by Umberto E. Stumpf (68) was initiated in the middle of 1974 by the Centro Tecnico Aeroespacial, Brazil, with great results (69). This research has been supported with funds from the Secretaria de Tecnologia Industrial (STI-Ministerio da Industria e Comercio). The STI has also supported some research on alcohol from manioc (70) which can be cultivated during the whole year (86).

However the ethanol availability is not that easy in other places and even in Brazil, ethanol alone would not be available so soon. So the idea of producing methanol appears as a good help to a mixture with ethanol to be used as an additive for the short-term, or just using straight methanol as an additive depending of the country.

In Germany a recent increasing interest in methanol as

a fuel is felt (Volkswagen and German Ministry for Research) and some work has been published (30,71,72,72), as well as in other parts of the world (74).

Nowadays a similar situation to that described by Pleeth 25 years ago concerning the controversial alcohol use as a fuel can also be seen. One of the most relevant partisans of methanol as a gasoline-extender has been Thomas B. Reed from Massachusetts Institute of Technology, who has published several articles about the subject (23,27,30). Reed's next step will be collecting data from the use of methanol blends in 200 MIT vehicles.

An article in the Wichita Eagle last January (82) indicates several California scientists who believe that "methanol is one of the most promising things to surface.". Among those scientists are J. Frautschy and W. Nieremberg (Scripps Institution of Oceanography) and B. Golding (San Diego University).

There are other defendant groups, some of them interested in the methanol production like the ones connected to Houston Natural Gas Corporation, Davy Powergas Inc., Vulcan-Cincinnati, M.W. Kellogg and Celanese, Corp. T.O. Wentworth from Vulcan-Cincinnati, R.G. Jackson from Continental Oil Co., T. Yamamoto from Catalysis and Chemical Industries Co., Ltd., W.D. Harris and R.R. Davison from Texas A&M University and G. Alex Mills and B.M. Harvey from the US Bureau of Mines are among the defendant people (14,17,29,33,34,35,36,37,38,39,40,42).

In the anti-methanol group E.E. Wigg and R.S. Lunt from Exxon Research Company and J.C. Ingamells and R.H. Lindquist from Chevron Research Company are among the major opponents and according to Reed (30) "there are many in Detroit and in the petroleum industry" (28,42,64,75,76).

In the following sections a tentative of showing the most relevant advantages and disadvantages claimed by the two groups concerning methanol use as a fuel for ICE, straight or in gasoline blends, will be given.

Other unpublished papers like the SAE papers 750118, 750120, 750121 and 750124 (77,78,79,80) could give more information on the matter but unfortunately they are not available yet.

Use of Pure Methanol for ICE.

There are several important aspects concerning the specific use of straight methanol as a fuel for internal combustion engines, that could be summarized as follows.

1- Exhaust Emissions.

HC and CO:- First considering the results of the Stanford University emission tests with an AMC Gremlin vehicle (60) as tabulated in Table XIV. These tests were made at two different Environmental Protection Agency laboratories: in Ypsilanti, Michigan where methanol was used of unknown purity, and in Cincinnati, Ohio where technical grade alcohol (99.9%) was employed. All these tests were a result of one contract awarded for further testing of this vehicle, which was the only liquid-fueled

entry to surpass the then-proposed 1975 Federal Emissions Standards at the 1970 Clean Air Race.

The experimental results show (Table XIV) that when a catalytic muffler was used, the HC (hydrocarbons) and CO emissions were below the 1975-76 Federal Standards. But when no catalyst for oxidation of unburned HC and CO was employed, these emissions were not always below such standards.

Table XIV - Emissions from Methanol-Fueled Gremlin, g/mile.

Cars	HC	CO	NO _x	%NO ₂	No. of Tests	Comments
1975-1976 Federal Standards (before revision)	0.46	4.70	0.40	--	-	Cold Start
Gremlin-Ypsilanti	0.34	3.83	0.28	--	4	Cold Start
Gremlin-Ypsilanti	0.06	0.40	0.29	--	3	Hot Start
Gremlin-Cincinnati	0.18	3.25	0.44	16	3	Cold Start
Gremlin-Cincinnati	0.02	0.62	0.38	12	3	Hot Start
Gremlin-Cincinnati	1.33	10.76	0.37	48	1	No Catalyst
Gremlin-Cincinnati	0.77	2.58	0.35	53	1	No Catalyst

Source- (60)

Theoretically (62) the CO emissions when using methanol would be less than for gasoline, assuming iso-octane as a good representative, presenting even better behavior with richer mixtures.

An air-injection system was used to provide extra oxygen for oxidation of HC and CO in the catalytic muffler. This

system was standard on all 1966-68 AMC engines. It was necessary especially on cold starts tests when a richer mixture was used. In all other seven modes (Table XV), the low lean misfire limit of methanol permitted successful operation at a stoichiometric equivalence ratio* of 1.33. This lean operation furnishes enough oxygen to reduce HC and CO emissions while maintaining adequate performance.

Compared to gasoline, most authors agree that methanol can go leaner (without operating problems), in order to lower the CO levels. But as far as HC this is not so clear: Ebersole and Manning (63) examining methanol versus iso-octane in a CFR single-cylinder, found that at the same power output and equivalence ratios, the unburned fuel (included in the HC emissions) was 10-30% of that with iso-octane. On the other hand Ingamells (64) disagreed saying that methanol showed a "slightly higher unburned fuel levels even in the lean regions where cars will be operating."

In another publication Ingamells (76) reported larger concentrations of unburned fuel (as well as for CO levels) when using methanol in relation of those of gasoline, if using standard exhaust system. When using catalyst and air-injection, Ingamells recognized that methanol "performed better relative to gasoline" with respect to CO levels, but the unburned fuel was about the same as gasoline.

* Equivalence Ratio is defined as the weight ratio of air to fuel, with the stoichiometrically correct ratio set at 1.0. Thus, fuel-rich carburetion is typified by equivalence ratios less than 1.0 and lean carburetion greater than 1.0.

When the lean misfire limits of methanol (0.2 equivalence ratios leaner than with gasoline) was explored, better results were obtained: from Table XVI the 14% lean methanol vs. 5% gasoline showed clear advantages for methanol concerning CO emissions and unburned fuel emissions in hot starts. For cold starts, again, due to a longer period of warm-up, the unburned fuel emission was higher. This was a result of the poor vaporization of the fuel when the engine is cold.

The above results concerning emission tests from cold starts were obtained in the Stanford experiments also. This was attributed in the same manner to the fact that when methanol was employed it was necessary to use 3 minutes of choked operation while only 25 seconds was necessary for gasoline. This behavior was due to the utilization of exhaust-heated intake manifold (necessary for methanol) for gasoline also. Probably it took longer to reach the catalytic operating temperature when using methanol, causing the higher HC levels. The CO levels for gasoline were higher despite the fact that operating temperature could be reached in a shorter period of time. Maybe an electric heater for the muffler and an improved fuel vaporization in the carburetor could solve the problem.

NO_x :- Considering the same Stanford Gremlin tests, the authors stressed that "while a catalytic muffler was partly responsible for the low HC and CO emissions, no control devices were used for NO_x reduction, and it is quite surprising that such

Table XV - Air-Fuel Ratio for Typical Operating Conditions
as Deduced from 1970 Federal 7-Mode Cycle Test
Procedure.

Mode	A/F	$1/\phi^*$	ϕ^*
Idle	7.4	0.88	1.13
0-25 mph	8.6	0.75	1.33
30 mph cruise	8.4	0.76	1.32
30-15 mph	7.6	0.85	1.18
15 mph cruise	8.6	0.75	1.33
15-30 mph	8.8	0.73	1.37
50-20 mph	7.6	0.85	1.18

* ϕ ... Equivalence Ratio (actual AF/stoichiometric AF)

Source- (60)

Table XVI - Lean Operation Comparisons.

	Gasoline 5% Lean	Methanol 14% Lean	Methanol 18% Lean
COLD START TESTS			
C.S. Driveability Demerits	5	0	1
Cycling Thermal Efficiency, Miles/ 10^6 BTU	138	157	--
Unburned Fuel,g/mile	3.0	4.2	--
Carbon Monoxide,g/mile	20	14	--
Nitrogen Oxides,g/mile	8.3	3.1	--
HOT START TESTS			
Cruising Thermal Efficiency, Miles/ 10^6 BTU	236	252	263
Cycling Thermal Efficiency, Miles/ 10^6 BTU	146	180	167
Unburned Fuel,g/mile	2.7	0.3	3.1
Carbon Monoxide,g/mile	18	8	6
Nitrogen Oxides,g/mile	6.9	2.0	3.7

Source- (76)

low NO_x emissions were observed."

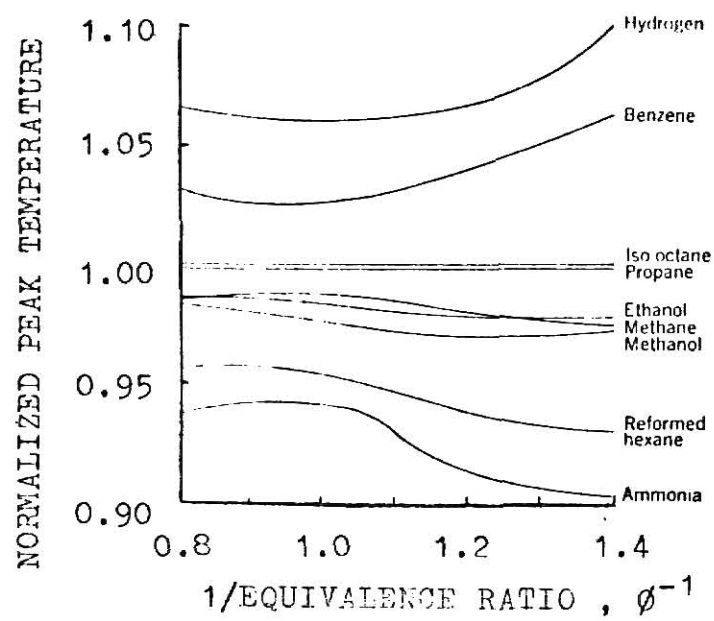
In actuality we should expect a little lower NO_x formation as a result of the lower theoretical peak temperature for the Otto cycle when using methanol. Starkman et al. (62) calculated the Figure 7, comparing these peak temperatures with the one of iso-octane. This lower temperature slows the rate of NO formation reducing NO_x levels.

Ingamells (76) obtained the same good results (around 50% less NO_x) for methanol against gasoline, even when the leaner limit of methanol was not explored (Table XVI). The same occurred in the tests reported by Ebersole and Manning (63) in a CFR for equivalence ratios.

Methanol seemed to behave like gasoline with respect to NO_x emissions versus equivalence ratios and spark timing (60), i.e., earlier spark yields more NO_x and the behavior described by Figure 8 concerning equivalence ratios. In this way as the higher flame speed of methanol permits spark retardation and if the leaner limit of methanol is explored we could really expect low NO_x levels.

As a conclusion to this brief resume of pure methanol as a fuel for ICE with respect to emissions of HC, CO and NO_x we can partially quote Gregory and Rosenberg (16): "the non-polluting potential of methanol fuels has not been fully explored". But it is possible to foresee even better emission results for methanol in comparison to gasoline especially if special devices to attain a better fuel vaporization in the carburetor were employed. Thus, a shorter warming-up period

Figure 7 - Otto Cycle Peak Temperature Compared
To That For Iso-Octane.



Source- (62)

note: ϕ = actual AF/stoichiometric AF

would be possible (this problem will be discussed later in this study).

Aldehyde measurements are recommended since formaldehyde may be formed in the methanol combustion. However, according to Ingamells (76), these levels were the same as for gasoline even when the standard exhaust system was used.

2- Fuel Economy and Power Output.

From the summarized physical properties of iso-octane and methanol in Table XVII, methanol has less than half the heating value of iso-octane and about half the stoichiometric air-fuel ratio. Thus, approximately the same energy per gaseous stoichiometric mixture. That means that the same power output could be expected if the other physical properties were similar. However, the methanol heat of vaporization is more than four times higher than for iso-octane.

In this way methanol cools the air entering the engine much more than gasoline, i.e., better volumetric efficiency. Moreover the octane number of methanol is higher than the 100 octane number of iso-octane. This means that a higher compression ratio could be used for methanol, i.e., better thermal efficiency. In such a way better power output and fuel economy on an energy basis would be the result.

Nevertheless, 75-100% more fuel in a volume basis would be needed by the same car with the same engine. However methanol would be less-polluting, thus it is possible to eliminate much of the equipment (not all) now employed to cope

with the gasoline-related pollution, yielding an even lower ratio of consumption increase.

On the other hand, measurements with the same mentioned Stanford Gremlin made mostly under high-speed cruise (70 mph) indicated about 18 miles/gal for gasoline versus 9-10 miles/gal for methanol. This lowered methanol mileage was attributed to the use of the catalytic muffler and air pump that in this case were not employed when running with gasoline. It is important also to stress that the compression ratio was optimum for gasoline, i.e., too low for methanol. In any event larger amounts of fuel must be employed, meaning that straight methanol-fueled cars need larger fuel tanks to keep the same autonomy as gasoline. However the cost of filling up this larger tank with methanol could be less than filling up the actual tank with gasoline.

Table XVII - Physical Properties of
Iso-octane and Methanol.

Property	Iso-octane	Methanol
Chemical Formula	C_8H_{18}	CH_3OH
Molecular weight	114.22	32.02
Specific gravity (68°F)	0.692	0.792
Stoichiometric A/F	15.1	6.4
Latent heat of vaporization at B.P., BTU/lb (MJ/kg)	117 (0.490)	502 (2.101)
Heating value, BTU/lb (MJ/kg)		
Higher	20,556 (86.047)	9770 (40.90)
Lower	19,065 (79.806)	8644 (36.18)
Octane No., Research	100	106
Octane No., Motor	100	92
Energy, BTU/ft ³ of stoich. mixture (1 atm, 60°F, LHV, gaseous fuel) (MJ/m ³)	95.5 (3.559)	90.0 (3.354)

Source- (60)

According to the Ebersole and Manning experiments (63), the power output was the same for methanol as for iso-octane. However, the experiments by Harris and Davison (40) and others (43,55,76) show that methanol produces 10% more power with the same test conditions (displacement and compression ratio). The increase in power is due to the higher volumetric efficiency when methanol is used. Use of methanol as a fuel also allows the use of higher compression ratio engines and therefore more power. That was the reason for the use of methanol for automobile speed records (43). Of course, for this latter purpose the race drivers used compression ratios as high as possible to get most of the fuel without considering emissions or fuel economy.

3- Carburetion and Intake Manifold.

According to Table XVII the stoichiometric ratio for methanol is less than half for gasoline. Thus, it is necessary to rejet stock carburetors. A factor averaging 2.5 proved to be a good ratio of increase of jet areas (idle and mainjets) in order to obtain lowest emissions but still enough power for good driveability.

Now, due to the mentioned higher latent heat of vaporization a greater amount of heat should be provided to methanol to keep enough vaporized after leaving the carburetor. To have an idea of how much more heat is needed for methanol, we can simply repeat that the latent heat of meth-

anol is about 4 times higher than gasoline and as we have about the double of fuel because the stoichiometric is roughly half, about 8 times more heat will be necessary. The Stanford tests indicated about 9 times more heat, despite the fact that for an acceptable distribution and good power at WOT (wide open throttle) significantly less vaporization is necessary for methanol in comparison with gasoline.

We can summarize the methanol manifold characteristics as follows:

- Vaporize all of the fuel at idle and low speed where power is important and good distribution is critical for low emissions.

- Vaporize an as yet undetermined portion of the fuel at part throttle where both power and distribution are desired.

- Vaporize the minimum percentage of fuel necessary at full throttle to ensure good power.

These conditions have been approached in the manifold described by Adelman (60).

A good intake manifold should also provide enough heat, right after the starting, in order to attain a relatively short warm up period. This warm up period is related to emissions from cold start, cylinder wear and of course is

another parameter that is commonly taken by the average driver to judge the fuel and the car. This is usually considered as a fuel quality, but apparently methanol cannot attain a short warm up period by itself (see Chapter VI). Thus, special devices would have to be employed to counter this disadvantage. The new Early Fuel Evaporation System (EFE) that is already designed into the new 1975 Chevrolet engines (83) to provide quicker engine warm up with un-leaded gasoline could be recalibrated for methanol use.

On the other hand methanol seems to present better behavior when fuel injection systems are employed (60,64) since less problems of manifold heating are encountered.

A new kind of carburetor — Dresserator (84,85) presents also great characteristics to be applied for methanol-fueled engines, due to its vaporization devices.

4- Cold Start

This particular aspect of methanol use seems to be the major problem associated with the use of straight methanol as a motor fuel according to most researchers. Below 40-60°F the cars would not start unless special additives or devices are employed. More details are given in Chapters VI and VIII.

Other advantages of straight methanol for ICE can be listed:

- 1) Being immiscible with oil, it will not dilute the crankcase oil.
- 2) Being miscible with water, alcohol fires can be put out by water sprays; this means a higher degree of safety and thus can minimize the storage, handling and transport restrictions which could affect insurance rates.
- 3) Due to its lower volatility methanol turns out to be a convenient fuel for hot climates since it is free of vapor lock, while some kinds of gasoline sometimes cannot be used. This lower volatility is also responsible for better safety concerning inflammable vapors.
- 4) Due to its cooler-running, a longer life for the methanol-fueled engines can be expected. However a redesign of current cooling systems is needed.
- 5) Its high solvent power would produce less gum formation, longer life for spark plugs, less need for decarbonization, or in brief, less maintainance cost.
- 6) Since water can be added to methanol in certain amounts without reducing power and efficiency (40,41), the economic consequences can be enor-

mous. And of course this will give lower combustion temperatures, leading to lower NO_x levels, permitting higher compression ratios, i.e., wise energy use; and of course without the need for Exhaust Gas Recirculation systems (EGR).

The other methanol disadvantages are said to be:

- 1) Its vapors are somewhat more toxic than those of gasoline but its low volatility prevents high evaporation.
- 2) Since it does not mix with oil, it can cause lubrication troubles in the upper parts of the cylinder; thus special additives might be necessary.
- 3) As it has a high solvent power, it can transfer gum from the tank when used in old cars; however it will then keep the system clean.
- 4) As formaldehyde is formed in the methanol combustion, formic acid can appear and cause corrosion of valves, etc.... However, this is a result of running too cool. When leaner mixtures are employed the aldehyde formation would be prevented, and in the case of rich mixtures small amounts of basic volatile bodies, concentrated ammonia, nicotine or others, can

be used to neutralize the acid (47).

- 5) According to one reference (76) methanol is said to cause troubles concerning for instance terneplate lining corrosion in the conventional fuel tank, leading to the need of developing a low cost corrosion inhibitor. However, all other references have not mentioned any problem of that sort, even when straight or blended methanol were used for more than 10,000 miles (23) or even 23,000 on unmodified cars (30).

In such a way methanol-fueled automobiles might have their place under the sun, especially when all the advantages of such a fuel are fully explored. Methanol seems to behave even better when fuel injection systems are employed (60,64) allowing the use of even leaner mixtures. The reason is the more precise control of fuel metering as well as the obviously great improvement concerning mixture distribution attained by the injection system.

The major drawback of the fuel injection system is the high price tag carried with it, as a system similar to the Volkswagen (VW) sells for approximately US\$ 125.00 (88). On the other hand new kinds of fuel injection systems are available (87,89) at lower costs, allowing methanol to show its better properties. It would also cover its disadvantages

like the somewhat expensive intake manifold (that is not needed when injection is used) and problems with cold starts (see Chapter VIII).

Another good reason for methanol use is that this will be a way to fight automotive pollution at its main source: imperfect combustion. From more complete combustion we should expect better fuel economy, less pollution, and thus a wiser use of energy in ICE. Nowadays most automotive anti-pollution approaches (except CVCC and few others) are dealing with the pollution after the combustion. This is leading to an increase in waste of fuel. If we deal with the combustion itself, that waste could not occur.

The majority of pollution problems could be solved in this way (90) leading to an energy saving instead of a waste.

Use of Methanol-Gasoline Blends for ICE.

Here again we can summarize as follows the most important aspects of methanol blends for the specific use of fueling internal combustion engines, based on experiments carried out recently in the USA. The notation suggested by Reed (23) will be used: M-5 (for example) for 5% by volume methanol in gasoline.

1- Exhaust Emissions.

HC and CO:- Changes in the HC, CO and NO_x emission levels with methanol addition can be considered on the basis of the change in equivalence ratio in the same way as for gasoline (Figure 8). As for example the M-5 fuel results in about

10% increase in equivalence ratio ϕ relative to the base fuel (Figure 9 — the so-called "alcohol leaning effect"). The Figure 8 can be used to show the influence of such an addition.

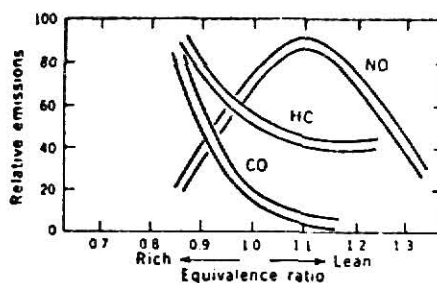
This leaning effect is explained by the fact that the stoichiometric ratio of methanol is about half that of gasoline (Table XVII), around 50% in weight of its molecule being formed by oxygen. In this way when methanol is added to gasoline and used in the original gasoline carburetor a lower CO and HC concentration can be expected.

Experiments by Ninomyia et al. (61) in a laboratory single cylinder engine with up to 25% methanol, maintaining the Research Octane Number at 93, showed no influence of the percent of methanol in CO levels. However several others tests in vehicles indicated that CO levels do decrease with the increase of methanol percentages as shown on Figure 10. It has been reported (17) that these CO levels can even become zero if M-30 is used, and a range of 14-72% for CO level reduction has been claimed (27,30), depending on the year and make of the car.

This wide range of variation can be explained by the fact that the older cars, which usually operate on the base fuel at an equivalence ratio of 0.9, would show substantial decreases in CO levels. On the other hand a lean operating car (as the new ones) which present an average equivalence ratio of 1.05 would show lesser effects on CO decrease.

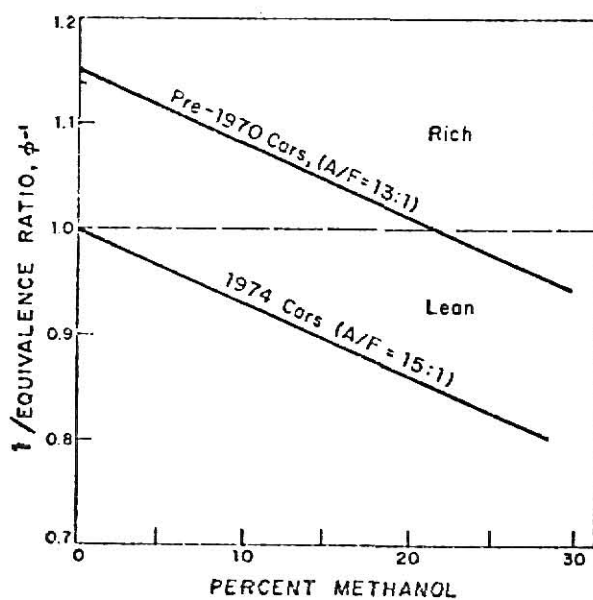
Tests carried out by Wigg (28) using M-15 on three rep-

Figure 8 - Relationship Between Equivalence Ratio and Exhaust Emissions.



Source- (28)

Figure 9 - Chemical Leaning Produced By Addition Of Methanol To Gasoline.



Source- (23)

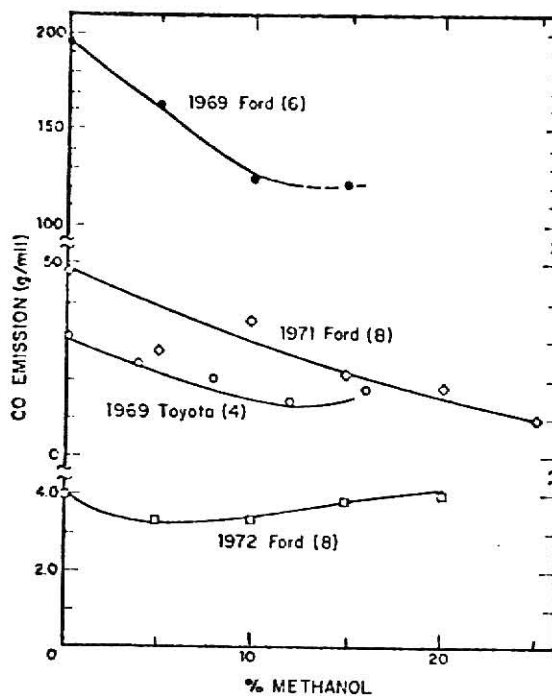
representative V-8 vehicles, confirmed that behavior (Figure 11): a rich operating 1967 model (equivalence ratio of approximately 0.94) without any emission control obtained a 50% CO reduction, a 1973 model (equivalence ratio of approximately 1.06) showed 40% CO reduction and a prototype "1977" model somewhat richer operating than the 1973 model, but employing an oxidation catalyst, showed the same CO levels as for gasoline. The CO levels for the latter were well below 3.4 grams per mile, the most stringent standards proposed for this pollutant.

In respect to HC emissions it has been predicted that the amount of unburned hydrocarbons decreases in the automobile exhaust with the addition of methanol (17). Those experiments by Ninomiya et al. (61) showed no effect on the HC emissions when methanol is added, except under fuel-rich conditions when an increase in methanol concentration caused an increase of unburned fuel. This was explained by the fact that the presence of formaldehyde inhibits the combustion of the hydrocarbons in the fuel.

Considering those M-15 tests by Wigg (28) with the three representative cars, as shown in Figure 12, again good results for HC levels were obtained for the 1967 car. The 1973 and "1977" cars showed no difference in comparison to gasoline.

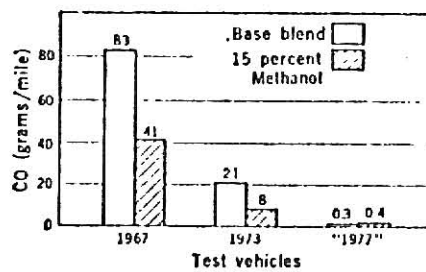
Here again, as more aldehydes may be formed with a methanol blend use, these levels should be measured even though they are not currently regulated by law. The need for that is because aldehydes are about as photochemically reactive in

Figure 10 - CO Emissions with M-0/30.



Source- (23)

Figure 11 - CO Emissions with M-0 and M-15.



Source- (28)

the atmosphere as olefins (the most reactive of HC emissions) and formaldehyde is a known eye irritant. Results of M-15 on the three cars according to Figure 13 showed an increase of aldehyde levels (up to 50%) for the 1967 and 1973 cars but no difference for the "1977" car.

NO_x :- Once more the high latent heat of vaporization of methanol can play a big role: if a large portion of the methanol is not vaporized, leaving droplets that will tend to vaporize in the cylinders, a temperature decrease can be expected. Methanol dissociation into $\text{CO} + \text{H}_2$, leading also to a temperature drop at the end of compression, could occur too (23, 27). As NO_x is greatly dependent on combustion temperatures a NO_x level decrease can be expected.

The mentioned tests conducted by Ninomiya et al. (61) showed no difference in the NO_x levels and in the temperature of exhaust when up to 25% methanol was added. This may indicate the occurrence of a good fuel vaporization in the carburetor and manifold and no change in the engine combustion temperature in those tests.

On the other hand Reed and Lerner (27) experiments indicated an exhaust temperature decrease of 1-9%. Wigg's representative cars in Figure 14 indicated lower NO_x emissions for the 1973 and "1977" cars and a somewhat higher NO_x level for the 1967 car when M-15 was used in comparison with gasoline. Such results could not be expected on the basis of the leaning effect of methanol using Figure 8 and were attributed

Figure 12 - HC Emissions with M-0
and M-15.

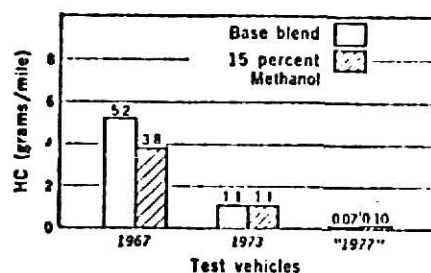


Figure 13 - Aldehyde Emissions with
M-0 and M-15.

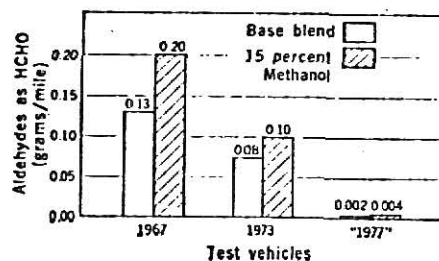
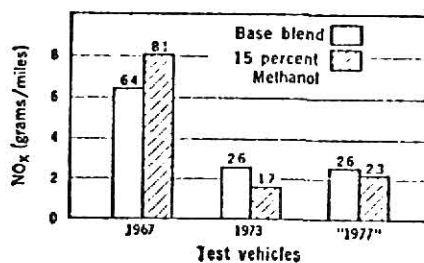


Figure 14 - NO_x Emissions with M-0
and M-15.



Source- (28)

to the cooling effect of methanol. Tests about changes in spark timing as a way to decrease NO_x levels for methanol blends have not been reported.

As a conclusion of current emission experiments with methanol blends we can say that no great improvements on exhaust emissions can be expected with such a fuel in comparison with gasoline. However the pros and cons of this factor seem to balance and the final decision should be based on other characteristics of the fuel.

2- Fuel Economy and Power Output.

Results of some fuel economy tests conducted by Reed et al. (23) in a number of unmodified private cars (year models 1966-1974) are shown on Figure 15 as a function of methanol concentration. The conclusion was a fuel economy increase of 5-13% on a volume basis.

Although two gallons of methanol would be required to replace the energy of one gallon of gasoline, sometimes less than one gallon of methanol was enough to replace the gallon of gasoline that would be saved (Figure 16). In any event the major economy will be on an energy basis. The better efficiency can be seen, even if no modification were made concerning compression ratios. In this way that improvement was due just to the high latent heat of methanol yielding better volumetric efficiency.

Fuel economy tests were also conducted by Wigg (28,75)

Figure 15 - Fuel Economy with M-0/30.

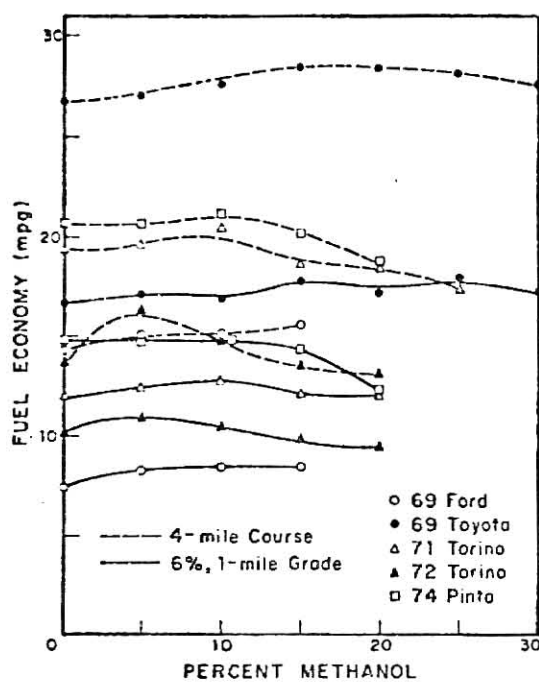
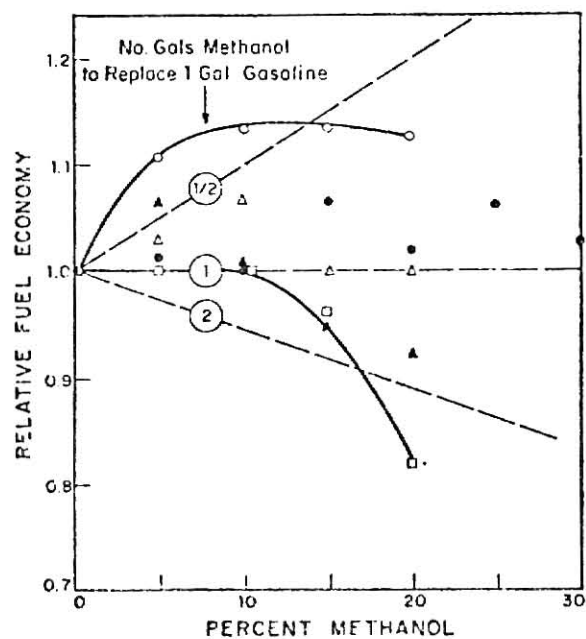


Figure 16 - Fuel Economy Relative to Gasoline for Methyl-Blend.



with those three representative cars using M-15. The relationship between fuel economy and equivalence ratio for gasoline could be shown as in Figure 17, where optimum fuel economy occurs at an equivalence ratio of 1.10. In such a way a fair improvement in fuel savings on a volume basis would be expected for the 1967 car (equivalence ratio of 0.94), a small difference should be expected for the 1973 car (equivalence ratio of 1.06) and an intermediate effect should occur for the "1977" car as it operates in a slightly richer range than the 1973 car. These were indeed found as shown in Table XVIII, meaning that significant reductions in fuel consumption with methanol blends would be expected only on an energy basis for vehicles operating at equivalence ratios greater than 1.0. The leaning effect of methanol would cause a fuel economy decrease on a volume basis for equivalence ratios greater than the unity. However for rich operating cars the economy was up to 8% on an energy basis and 1% on a volume basis.

Other tests conducted by Ingamells and Lindquist (76) using M-10 also showed no improvement on a volume basis, but the improvement on an energy basis was up to 4.4% (Tables XIX and XX).

As the M-10 has 5% less heat of combustion than the base gasoline and the measured losses in fuel economy on a volume basis were less than 5%, the improvement in thermal efficiency with methanol is evident. The same occurred for Wigg's tests with M-15.

Concerning power output, the time required to reach

Figure 17 - Relative Fuel Economy as a Function of Carburetion.

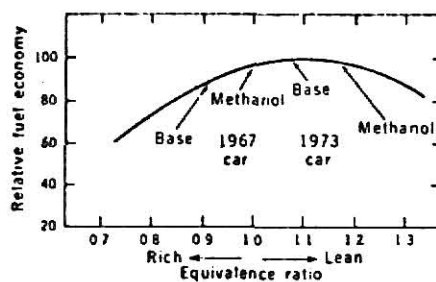


Table XVIII - Fuel Economy for Three Representative Cars.

Car	Fuel Economy (mpg)		Effect of Methanol (%)	
	Base Fuel	Methanol Blend	Volume Basis	Energy Basis
1967	14.3	14.4	+ 1	+ 8
1973	11.2	10.5	- 6	+ 1
"1977"	11.5	10.9	- 5	+ 2

Source- (28)

Table XIX - Fuel Economy with M-0 and M-10
on a Volume Basis.

1971			Fuel Economy, mpg		
Car Make	Car Size	Engine	M-0	M-10	Increase, %
A	Intermediate	V-8	14.82	-	-
A	Full	V-8	12.99	12.44	- 4.2
B	Intermediate	V-8	14.99	14.87	- 0.8
B	Full	V-8	10.84	10.41	- 4.0
C	Compact	6	20.37	19.95	- 2.7
C	Intermediate	V-8	15.49	14.71	- 5.0
Average	--	--	14.94	14.46	- 3.2
			(5 cars)		

Table XX - Fuel Economy with M-0 and M-10
on an Energy Basis.

1971			Fuel Economy, miles/10 ⁶ BTU		
Car Make	Car Size	Engine	M-0	M-10	Increase, %
A	Intermediate	V-8	130.0	-	-
A	Full	V-8	113.9	114.9	+ 0.9
B	Intermediate	V-8	131.5	137.3	+ 4.4
B	Full	V-8	95.1	96.1	+ 1.05
C	Compact	6	178.7	183.3	+ 2.6
C	Intermediate	V-8	135.9	135.8	- 0.1
Average	--	--	131.05	133.5	+ 1.9

Source- (76)

60 mph from 0 mph has decreased 7% (27). However the compression ratio was the same as for gasoline, so that the ability of methanol to "boost" gasoline octane quality was not fully explored.

Although methanol rates 106-120 octane number by the Research Method and 88-92 by the Motor Method, when it is added to gasoline its behavior is equivalent to a fuel of 130-135 octane number. This is due to its high blending octane value (BOV) shown in Figure 18. This fact can be explained (23,27) by the methanol dissociation into $\text{CO} + \text{H}_2$, causing a decrease in temperature after compression. The presence of CO and H_2 after ignition could increase the burning velocity of the gasoline mixture when it ignites, yielding better combustion and making leaner mixtures more combustible.

$$\text{BOV} = \frac{O - (1 - M) F}{M}$$

Where:

O ... observed octane number

F ... base octane of the fuel

M ... fraction of methanol in the blend

The use of supercharging is also recommended with alcohol fuels, since their cooling ability and high anti knock values help the usual problems connected to the increase in the inlet temperature. This usually increases the tendency of a fuel to knock. Ricardo's racing fuels (43) containing

water in addition to alcohol, ensured large reductions in the charge temperature and high power output with supercharging.

3- Phase Separation.

One of the most serious problems associated with the use of methanol-gasoline mixtures is the phase separation question, i.e., fuel stability. Methanol and water can be mixed in all proportions but the mutual solubility of gasoline and methanol is lower. In this way an homogenous transparent mixture of gasoline and methanol can easily separate into two layers with water addition or decrease in temperature.

The reason for this low gasoline-methanol solubility is methanol's polar character, explaining why its solubility in non-polar gasoline is limited. This solubility would be greater in fuels with higher concentrations of aromatic hydrocarbons, but for typical gasolines the maximum blending concentration is about 15%, i.e., M-15, for anhydrous conditions. At 32°F (0°C) even less than 10% could be the maximum for some gasolines, despite the fact that some additives like the volatile constituents added to gasoline in winter increases the solubility.

However the major problem is concerned to water addition which exists inside the tank and fuel lines of the vehicle.

When the air temperature in the tank becomes lower,

water drops can be produced from the moist air and a water layer forms in the bottom of the tank. As gasoline dissolves only about 0.01% of water, the only problem related to this fact is some corrosion or stoppage when running with almost empty tank, if using 100% gasoline. But as M-10 will dissolve ten times as much water, proprietary gas-tank drying agents generally contain methanol. However if the solubility limit is exceeded, which can easily occur with moderate quantities of water and with high-percentages of methanol in gasoline, the alcohol will separate into the water phase and settle to the bottom of the tank. This will require the use of a different AF, or driveability troubles may occur.

In this way Reed (23) suggested the use of M-5 from the first tank full, or the addition of some additives to increase solubility when using methanol blends for the first time or under low temperatures conditions.

Phase separation problems could be diminished by addition of substances like isopropanol and tertiary butyl alcohol since for example, at 70°F (21°C) the mixture of 5% t-b-alcohol, 15% methanol and 80% gasoline tolerates 4000 ppm water while a 15% methanol, 85% gasoline blend tolerates only 1500 ppm water. Also a small amount of diethyl ether, butanol, acetone or cyclo hexanol decreases the separation temperature of the water layer to reduce the effect caused by the water. Some of these compounds are

too expensive to use as an additive to gasoline. More than 150 other additives have been tested without great success.

The effect of temperature on anhydrous methanol-gasoline blends is shown in Figure 19. The higher alcohol mixture, the so-called methyl-fuel as mentioned in Chapter IV page 29, presents much better solubility characteristics. Even with addition of water its behavior is really better than that of methanol as shown in Figure 20 where a mixture of 10% methyl-fuel can dissolve ten times more water than a mixture of 10% methanol.

Of course this is not an impossible problem to solve but this particular aspect shows more need of improvement.

Several ideas, like using drier filters in the venting of fuel tanks and carburetor bowls, can minimize moist air intrusion but will cause obviously higher costs.

Undoubtely the best solution is to feed the cylinders with two separate injections systems, resulting in no problems concerning solubility, and then M-80 could be used with any water level desired. As was briefly said in previous pages the fuel injection system prices are getting lower and with large production and the need for new fuels this idea may be a really useful one (17, 23, 28, 30,75).

4- Vapor Lock

Methanol is less volatile than gasoline but a mixture

Figure 18 - Research Octane Number
of M-0/30.

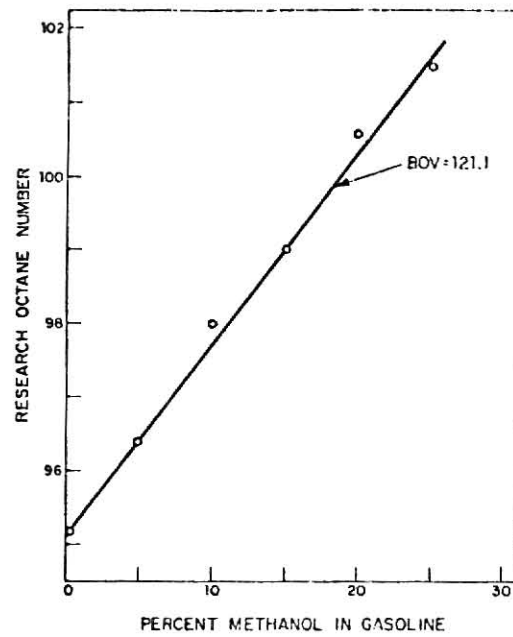
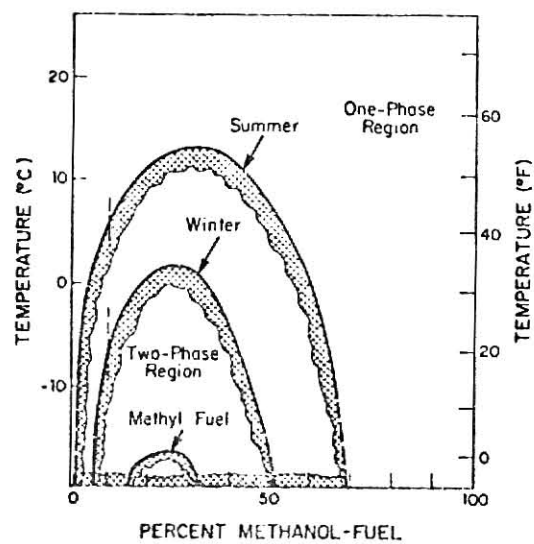
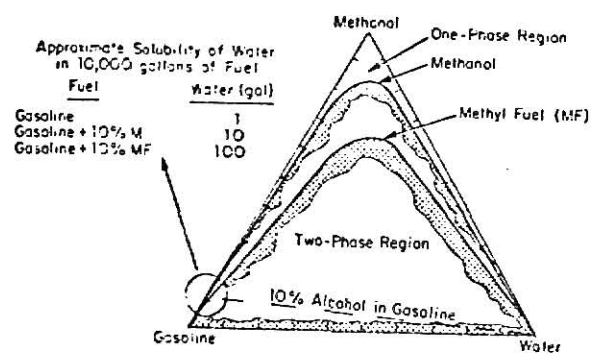


Figure 19 - Temperature Separation
of Methyl-Blends.



Source- (23)

Figure 20 - Water Solubility and Separation
with Methyl-Blend Fuel.



Source- (23)

of methanol and gasoline turns out to be more volatile than either of its constituents. Volatility is related to starting and vapor lock characteristics and is usually graded by a distillation curve (% of evaporated vs. temperature) and the Reid vapor pressure (pressure reading at a given temperature in a special device after agitation). These tests follow specific procedures: ASTM D 86 and ASTM D 323 respectively.

For good starting it is necessary to have a minimum quantity of evaporated fuel in order to provide an ignitable mixture, i.e., more volatile fuels would present better startability. However a too volatile fuel would cause hot start problems and vapor lock due to fuel boiling in the fuel line or in the fuel pump inlet, limiting the flow to the carburetor.

In such a way there should be a compromise between starting and vapor lock characteristics of a given fuel based on distillation curves and RVP. Fortunately most vapor lock problems occur in summer while most starting problems occur in winter. Thus, if different volatility blends were used specifically for use in each season, as is usually done for normal gasolines, that problem can be minimized.

Innumerable attempts have been made since the early days in order to define a precise relationship between data from laboratory tests and the actual use in the vehicle.

More details about this subject are presented on Chapter VI, but we can say that nowadays a vapor lock index (VLI) seems to reasonably correlate the actual and the laboratory characteristics concerning vapor lock tendencies:

$$\text{VLI} = \text{RVP} + 0.13\% \text{ distilled at } 158^{\circ}\text{F} (70^{\circ}\text{C})$$

Thus the higher the VLI the greater the high temperature driveability problems.

If methanol is added to a typical gasoline, a 2.5 psi increase in RVP and a 22°F decrease in the 10% point of the distillation curve would occur. This is followed by the fact that vapor lock would occur at $15\text{--}20^{\circ}\text{F}$ lower ambient temperatures relative to the base gasoline. In such a way if methanol is added to gasoline without regard to volatility, vapor lock problems would be encountered. However if the mixture were done on a less volatile gasoline, no problems at all would be encountered concerning vapor lock. On the other hand the cold starting problems should be reviewed.

Tests conducted by Wigg and Lunt (75) on 4 different fuels with matched VLI, matched RVP or no matching at all, indicated acceleration vapor lock troubles, i.e., hesitations or bucking which resulted in at least 25% longer acceleration times, or stalling during accelerations.

On the other hand Reed (30) has not noticed any vapor

lock problems on his tests.

In order to eliminate that difficulty completely, the solution of feeding separately each fuel by two injection systems would be the best one.

Some tests with ethanol blends in the 250 CID Chevrolet engine indicated that the use of an electric fuel pump (not as close to the engine as the original pump) would solve the problem, even under high ambient temperatures. However for M-40, currents of 40 microamperes have been measured between the fuel pump and the gas tank leading to cases where a new fuel tank could be effectively stripped of theterneplate coating to the liquid level of the blend and severe corrosion develop in the exposed sheet metal. This would not occur when straight gasoline is used as it is an effective isulator. Thus, leakage current from the fuel pump's commutator to the ground fuel tank is not a problem for gasoline (76). In the methanol blend case an insulation of the tank may solve this electric pump problem if high concentrations of methanol are desired.

In this way vapor lock may be another serious problem only if methanol would be added in high concentrations to gasoline without any modification on the base gasoline or in the engine (such as the fuel pump).

In this way the best solution would be to prepare a less volatile base at the refinery, suited for later addition of methanol, by omitting light blending stocks. How-

ever markets should be found for these light stocks to avoid an inefficient petroleum usage.

5- Carburetion and Driveability.

As it was pointed out a few pages before, new cars present leaner operating carburetors to give minimum exhaust emissions with a still reasonable driveability. With the addition of methanol its leaning effect may lead to stalling, to hesitation on opening the throttle and to surge under some conditions. An unleaded gasoline and a M-10 on the same base gasoline were tested by Ingamells and Lindquist (76) in 1971 cars with six different drivers. Every car showed a higher driveability demerit level for M-10 in comparison with the base gasoline, although driveability was still acceptable in two cars. This indicates that the air-fuel ratio (AF) should be modified in the newer cars to compensate for the leaning effect of methanol: an enrichment of about 6% under all operating conditions seems enough to provide good driveability without considerable engine modifications. A carburetor tune up would be enough.

Other tests conducted by Wigg (28) on M-15 using the mentioned 1967, 1973 and "1977" cars, indicated that the 1967 richer car showed no driveability problems at any time. The leaner operating 1973 and "1977" cars did experience stalling, hesitation and backfire during the first few minutes of operation from a cold start for the same leaning reason. If the

carburetor "were provided with a richer fuel-air mixture during start-up one would expect the performance problems associated with cold start to be reduced."

This enrichment in new cars could lead to an increase in emissions but as some unburned fuel emissions were attributed to misfires due to excess lean mixtures (76) maybe the new levels would be still comparable to the base gasoline.

On the other hand these tests conducted by Reed and Lerner (23,27) showed no problems concerning driveability even with 1974 cars when using up to M-20. Some hesitation was noted for M-30 and M-50 under idling conditions due to lean misfire even with a rich operating 1969 car. It was also observed that a 1971 Ford ceased to show "Diesel" operation (continue to run after the ignition is turned off), when M-5 or more were used.

As a conclusion of the most important aspects of using methanol-gasoline blends for ICE based on recent experiments carried out in the USA, we can say that the blends show less advantage than straight methanol. This would be the case if the idea of no modifications at all on engines is to be applied. These aspects are mostly related to "degree of customer satisfaction" as mentioned by Wigg (28), as driveability problems may occur for newer cars if a modification of the carburetor is not done. However, the price of this "new" fuel could provide compensation, and if methanol really helps to diminish the dependency on foreign oil the user might tol-

erate few driveability problems. In any event, it would be good to recall that these operating problems were not noticed by some researchers.

Anyway the use of these blends may cause such problems but since methanol is not available yet to be used without gasoline, it might be a solution for a transition period.

However, to assure the same levels of driveability as provided by gasoline and with no problems of fuel stability and vapor lock, from using cheaper fuel mixture of higher methanol percentages, the idea of feeding methanol separately is undoubtedly a brilliant one. And as the cost of fuel injection systems is going down even for low production, it may be the best solution of all for the transportation energy problem.

The gasoline could be metered by conventional carburetors, and methanol could be injected. After some decades with gradual methanol percentages increase, a 100% methyl fuel could be used and the carburetors abandoned. In this case it will be necessary to have two fuel tanks. The increase of volumetric efficiency due to the cooling of the air provided by methanol would not be so evident if direct injection would be used.

The other advantages and disadvantages of methanol use, such as crankcase oil dilution, solvent power and corrosion, are similar to those resulting from use of straight methanol. Vapor lock and starting characteristics are not similar as volatility is completely different for blends and straight methanol.

VI- STARTABILITY

One of the most important properties of a fuel is the ease with which it will enable a cold engine to start. This is a common parameter for the average car driver to judge the gasoline (or whatever fuel) he is using (91); particularly on cold early mornings or when he is late for any schedule or even during an emergency.

Starting a cold engine on any fuel may be regarded as consisting of two stages (92):

- 1) cranking the engine for a few revolutions by external devices till the first explosion.

- 2) keeping the engine running after this by itself in order to reach its operating temperature.

The first and most important stage representing the readiness which a fuel will fire in a given engine is normally referred to as "ease of starting".

The second stage, usually referred to as the "warming-up period", ends at the moment that a wide open throttle would not cause any backfire or stall. It essentially shows the ease of acceleration of the fuel in a specified engine under the worst temperature conditions.

"Ease of Starting" depends upon many factors besides the fuel and temperature such as the several physical and mechanical variables involved in an Internal Combustion Engine. Some of these are bearing play, the relative tight-

ness of the piston within the cylinder, the viscosity of the lubricating oil and the condition of the ignition system, battery and starting motor.

Since we are concerned with the fuel itself we will assume all other factors have been eliminated apart from temperature. Thus the engine and battery will be assumed to be in perfect order, the spark plug and carburetor properly adjusted and the lubricating oil of suitable viscosity and condition.

Experimental tests back in 1925 (91) established that startability for a given engine, fuel and temperature depends upon the actual number of engine revolutions and not upon its speed, provided the same air-fuel ratio is supplied by the carburetor in the speed range used. This is due to the fact that initially the induction system is filled with air alone, causing a dilution of the "convenient mixture" supplied by the carburetor (91). Since this dilution decreases with succeeding revolutions, regardless of cranking speed, it is expected that the number of revolutions required to obtain an explosive mixture in the cylinder would be independent of the speed, if the air-fuel ratio is constant.

Then after the first explosion, if the conditions are favorable for a reasonable warming-up, the engine could reach its idle velocity and complete the warm-up period properly.

The number of revolutions considered to indicate a good cold start is not fixed. However, Obert (93) assumed less than 10 turns as a good start.

The Figure 21 was obtained (91) for several fuels (non alcohol) and various temperatures, showing how that "convient" mixture performs. The abcissa, air-fuel ratio (AF) given by the carburetor, is defined as follows:

$$AF = \frac{\text{mass air}}{\text{mass fuel}}$$

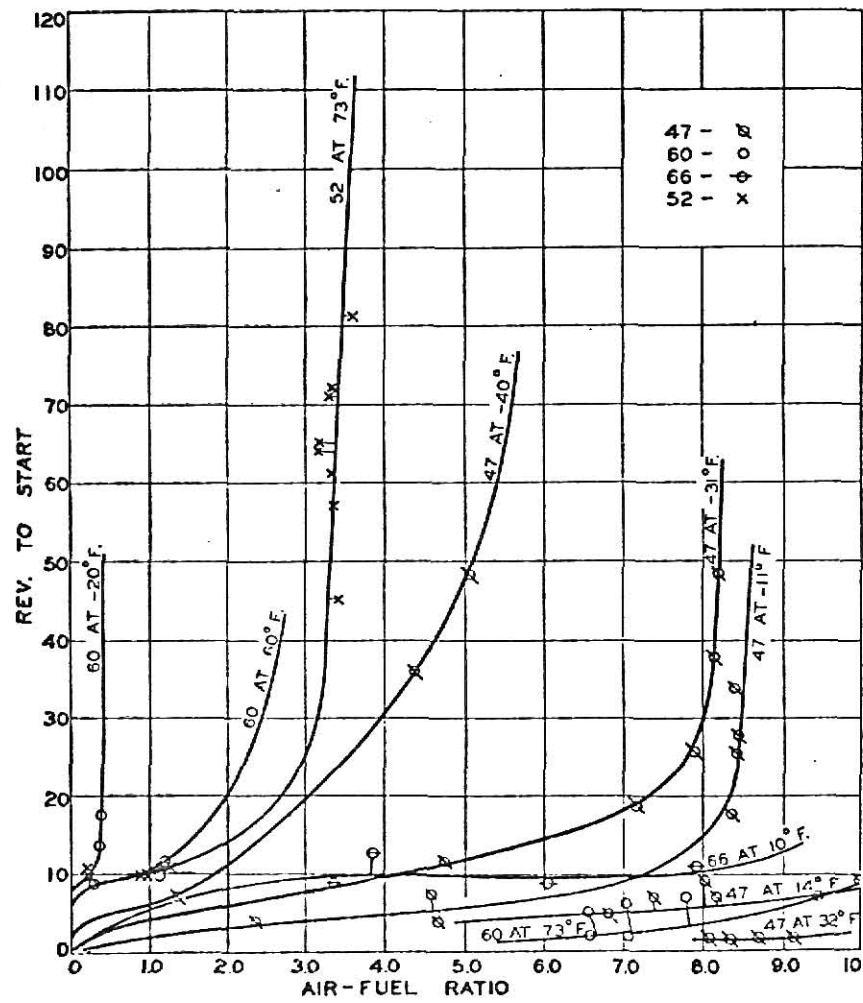
When the fuel is liquid the air-vapor ratio (AV) can be more important than AF (60), particularly from the starting ability point of view.

$$AV = \frac{\text{mass air}}{\text{mass vapor}} = \frac{AF \times 100}{\text{percent fuel vaporized}}$$

This fact was verified (91) when no practical difference in the necessary number of revolutions to start was observed, whether one or all spark plugs of the engine being tested were connected to the ignition coil. It clearly indicates that the distribution of the mixture under starting conditions is extremely uniform, as would be the case if only the vapor phase were effective in starting the engine. In order to confirm this statement a collector jar placed between the carburetor and manifold to collect the unvaporized fuel made no perceptible difference during a cold start.

For gasoline-powered vehicles 60% vaporization in the manifold at wide open throttle (WOT) is assumed optimum for

Figure 21 - Startability Diagram



Source- (91)

acceptable distribution and good power (60), but for methanol (not blended with gasoline) this situation may be significantly less than 60% (43).

To enable an engine to start with any fuel, a sufficient amount must be converted into vapor to produce a "convenient mixture", i.e., an explosive mixture within the cylinders. At low temperatures only a comparatively small amount of fuel will vaporize under carburation conditions and no heat due to combustion of the fuel is available to assist in its vaporization. This is the reason for the very rich air-fuel mixture at the carburetor in order to provide an ignitable air-vapor mixture at the spark plug. Depending upon the fuel properties, an AF of 1:1 at the carburetor is necessary to obtain an AV of 10:1 at the spark plug on a weight/weight basis.

The fuel property called Volatility shows this ability to pass from the liquid to the vapor state. Volatility of a given fuel is usually determined from its distillation curve, vapor pressure, surface tension and heat of vaporization. The first two parameters are normally the most important ones. Thus, in the next pages, we will see in brief what is commonly understood by them.

Distillation Curves.

A characteristic of every pure liquid is its boiling point. Thus pure water, irrespective of its source will always boil at 212°F (100°C) as methanol will at 149°F (65°C)

under standard conditions. The boiling point is indeed one means of identifying a pure substance.

When two liquids are mixed their respective boiling points are obscured and a boiling range is obtained. Mixtures of some liquids give boiling range curves that vary continuously from the boiling point of one to that of the other. Other mixtures will boil at a fixed temperature like a pure substance, water and ethanol mixtures being an example. Such mixtures are known as azeotropes, and it is sometimes hard to distinguish between an azeotrope and a pure substance.

Complex mixtures such as petroleum yield on distillation a smoothly-flowing curve from the lowest temperature at which the distillate can be collected to the highest temperature at which products will distill.

Generally speaking such curves can be determined by heating the fuel in a special device and consecutively removing the fractions that boil away within a definite temperature range.

This distillation range depends upon the method of determination (43). In order to avoid confusion, the standard method, ASTM D86-XX, was defined to which most of the petroleum and related industries adhere. "XX" is a notation meaning the year of the latest modification or revision, e.g., D86-67 of 1967 revision (94).

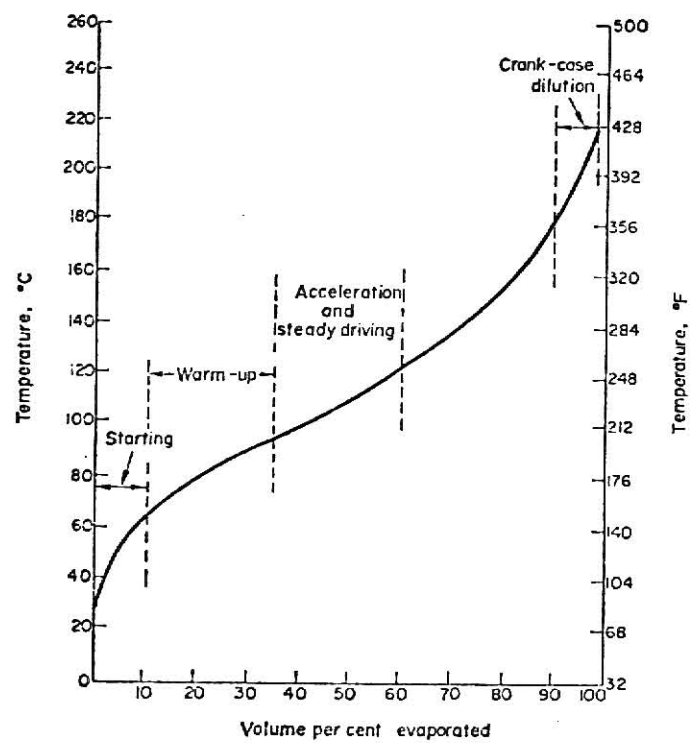
Based on gasoline some points of the normal distillation curve are usually taken as parameters of volatility of the fuel. A typical graph is presented in Figure 22 and the points defining ranges of the curve which influence performance features are indicated.

Similar interpretations are encountered such as some Canadian gasoline requirements (96) based on the 10%, 50% and 90% points and in a Russian reference (97):

- 1) The boil-away point of 10% describing the starting properties of the fuel.
- 2) The 50% point showing how the gasoline is adapted to a change in engine duty — transition from low to full load without drops in power and misfiring in engine operation.
- 3) The 90% point delimiting the working fraction — bulk of fuel which boils away between 10% and 90%, ensuring the formation of the mixture in a warmed-up engine.
- 4) The end of boiling away, characterizing the poorly evaporating fractions of the gasoline and their influence on the wear of elements in the piston group.

Sometimes the temperature at the beginning of distillation is also rated for some grades of petrol. Very light fractions are not desirable in gasoline as despite yielding a

Figure 22 - A Distillation Curve for
a Typical Gasoline.



Source- (95)

better start, they may evaporate in the fuel pipe causing vapor lock.

Based upon normal gasolines an empirical relationship between startability and the 10% evaporation temperature has been obtained (43) when the fuel is distilled by the standard ASTM method; in order to obtain a start this temperature should be less than a figure expressed by:

$$(125 + 5/4(\text{air temperature})) \text{ } ^\circ\text{F}$$

The Figure 23 shows the relation between number of revolutions to start and the 10% evaporated point at 10⁰F air temperature.

Therefore, it is generally considered that front end volatility is the most important from the point of view of engine performance. The term "front end volatility" used here is the level of the front end of the ASTM distillation curve, namely up to one third evaporated.

Other attempts included even the 10% point slope (98) but were criticized because of the argument that the ASTM distillation test may be far out of date nowadays (99).

Other processes to anticipate the behavior of the fuel in such situations have appeared, such as the ASTM distillation test, which despite being well-accepted is

run under different conditions than those of the actual engine manifold. Test apparatus were devised to simulate engine conditions such as the process called Equilibrium Air Distillation (EAD) (93) and many others (91).

Thus, additives such as alcohol affect the distillations curves and startability, but that relationship cannot be applied since it was obtained from normal gasolines(43). No comparable attempts have been made for methanol such as to find a relation between startability and the 10% evaporated points.

In order to see how the addition of alcohols to gasoline affects the distillation curve, also called fractional distillation curve, some of them are given in Figures 24 and 25.

Observing these curves we conclude that when a methanol or ethanol-containing fuel is distilled a considerable quantity of material is found to boil at low temperatures.

The characteristic "alcohol flat" may also be seen. This flat is due to formation of a succession of low-boiling azeotropes between the alcohol and a number of the lower hydrocarbons present in the gasoline (46). These constant boiling-point mixtures have vapor pressures (see next pages) usually greater than either two constituents and thus boil at a lower temperature than either.

Particulary we can see from the 10% ethanol curve (II) that the proportion of material boiling over at 140°F (60°C) has increased from 6% to 10% in comparison with the 0% ethanol curve (I), although pure ethyl-alcohol boils at 172°F (78°C). Data concerning azeotropes of methanol and hydrocarbons are given at Table XXI.

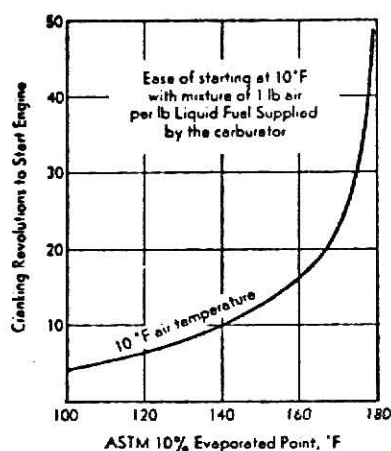
Some considerations about the future of gasoline (66) predict that significant distillation range modifications --- not related with alcohol additions --- cannot be tolerated with the present foreseeable energy supply, but the 90% point declining to approximately 300°F (150°C) from the present 330°F (165°C). However it is reported, in the same reference, that in a separate development K.J. French and J.J.Tazuma have combined alcohol with gasoline to achieve brilliant results. They claim that the most successful mix is a blend of 25% t-butyl alcohol, 3% water and 72% gasoline.

Vapor Pressure

All substance, liquid or solid presents a characteristic vapor pressure at any given temperature, representing its tendency to escape to the gas phase.

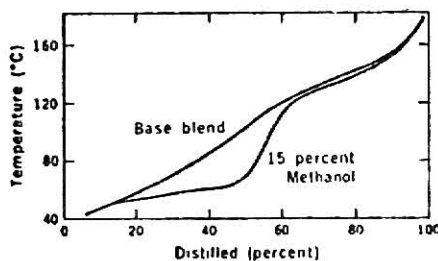
Fuel vapor pressure is closely related to its startability, governing its ability to form easily inflammable air-vapor mixtures, its tendency to vapor lock and the

Figure 23 - Effect of the 10 Percent ASTM Temperature on Starting Effort.



Source- (93)

Figure 24 - Effect of Methanol on Fuel Distillation Characteristics.



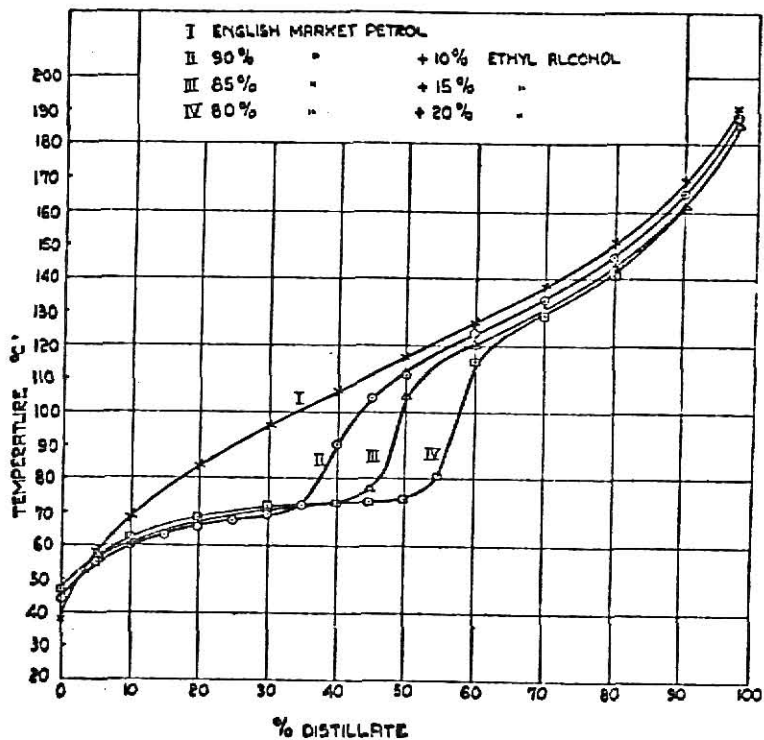
Source- (28)

Table XXI - Constant Boiling-Point Mixtures of Methanol and Hydrocarbons.

Substances in the Mixture C		Boiling Points, °C			% by Weight of Methanol
A	B	A	B	C	
Methanol	Isopentane	64.7	27.9	24.5	4.0
Methanol	Trimethyl-ethylene	64.7	37.2	31.8	7.0
Methanol	n-Hexane	64.7	69.0	50.0	26.4
Methanol	Benzene	64.7	80.2	58.3	39.6
Methanol	Cyclohexane	64.7	80.8	54.2	37.2
Methanol	n-Heptane	64.7	98.5	60.5	62.0

Source- (46)

Figure 25 - ASTM Distillation Curves for Gasoline-Ethanol Mixtures.



Source- (46)

extent to which the loss of volatile fractions might be anticipated on storage.

Vapor pressure, associated with V/L ratio (volume of vapor V per unit volume of liquid L flowing through the fuel system) is more related (98) to vapor lock than starting ability.

A vapor lock index (VLI) is now used to indicate the vapor lock tendency of a given fuel, based on both vapor pressure and distillation curve.

$$\text{VLI} = \text{RVP} + 0.13\% \text{ distilled} \quad @ \ 158^{\circ}\text{F} \ (70^{\circ}\text{C})$$

when RVP ... Reid vapor pressure

The vapor pressures of pure substances can be determined with great accuracy and are tabulated as functions of temperature as showed in Table XXII or given by an empirical equation such as:

$$\log p = A + B/T + C/T^2$$

where: p ... vapor pressure
 T ... temperature
 A,B,C ... particular values for each substance

Complex mixtures, such as motor spirits, do not require the "tedious academic methods" (43) because "no great degree of exactness is necessary for the startability purpose".

The standardized method devised by Reid and given in detail in ASTM D323-XX, followed by the petroleum industry, is based on this assumption. It consists in agitating a given volume of the fuel with 4 times its volume of air within a closed bomb maintained at 100°F (37.8°C), and the maximum pressure attained. This pressure is the result of the various pressures of the spirit components, the enclosed air and water.

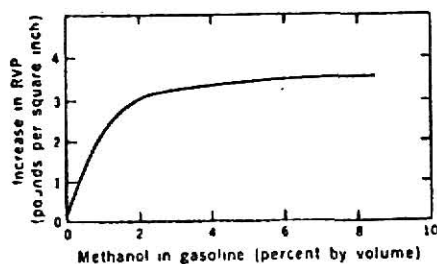
The well-accepted standard Reid test procedure is run with a fixed air to fuel ratio (AF), the air being completely saturated with fuel vapor at the test temperature. Hence, a diverse condition of an actual cold induction pipe. Some attempts, like the process by which Verdier and Hure (43) vaporized the fuel in considerably excess air, were done to get closer to the real condition.

The vapor pressure of a petroleum fraction is approximately the weighted average of its components, with small percentages of the more volatile hydrocarbons affecting the final vapor pressure considerably (43).

There is considerable variation in opinion (66) considering the control of this Reid vapor pressure (RVP). California has legislated a maximum so-called RVP limit of 9 psi in summer and New York City a limit of 7 psi but willing to settle for 9 psi on a variance basis. When butanes are in short supply it may be necessary to reduce RVP leading to poor vehicle startability and warm-up characteristics.

The effect of methanol on gasoline RVP can better be seen in Figure 26 where adding as little as 2% methanol gives a 3 psi increase in RVP although pure methanol is much less volatile than gasoline.

Figure 26 - Effect of Methanol on Gasoline
Reid Vapor Pressure (RVP) .



Source- (28)

Table XXII - Vapor Pressures of Some Fuels.

Substance	Temperature, °F														
	-40	-30	-20	-10	0	10	20	30	40	50	60	70	80	90	100
	Vapor Pressure, psia														
Methyl alcohol.....	0.025	0.048	0.075	0.12	0.18	0.25	0.36	0.54	0.75	1.03	1.41	1.94	2.64	3.47	4.55
Ethyl alcohol.....	0.009	0.012	0.022	0.039	0.06	0.09	0.14	0.21	0.30	0.44	0.62	0.88	1.23	1.68	2.25
Propyl alcohol.....					0.004	0.02	0.03	0.06	0.10	0.16	0.23	0.31	0.42	0.60	0.89
Butyl alcohol.....								0.004	0.02	0.03	0.05	0.07	0.14	0.21	0.33
Benzene.....	0.01	0.022	0.035	0.064	0.11	0.18	0.29	0.44	0.64	0.88	1.18	1.57	2.04	2.63	3.29
2-Methyl butane.....	0.61	0.87	1.30	1.66	2.25	2.90	3.70	4.70	5.94	7.55	9.49	11.75	14.20		
2-3-Dimethyl butane.....	0.12	0.20	0.30	0.41	0.58	0.79	1.06	1.40	1.85	2.42	3.12	3.87	4.92	6.10	7.40
Isooctane.....	0.01	0.02	0.04	0.06	0.085	0.12	0.16	0.23	0.32	0.43	0.58	0.78	1.03	1.35	1.72

Source- (93)

VII- STARTABILITY OF METHANOL BLENDS

Under equilibrium conditions the air-vapor ratio (AV) can be written as:

$$AV = \frac{(p - p_f) M_a}{p_f M_f}$$

where:

p_f ... fuel vapor pressure at equilibrium temperature
 p ... manifold pressure
 M_f ... molecular weight of fuel
 M_a ... molecular weight of air

Using vapor pressures of iso-octane and methanol for representatives p_f we can generate Table XXIII.

Table XXIII - Equilibrium AV and Percentage of Fuel Vaporized versus Temperature.
 (p=14.7 psia, WOT)

Temperature (°F)	0	20	30	40	50	60	70	80
AV Iso-octane	43.0	22.8	15.9	11.4	8.4	6.2	--	--
Iso-octane at AF=14, %	32.0	61.0	88.0	<u>122</u>	--	--		
AV Methanol	72.8	36.0	23.6	16.8	12.0	8.5	5.9	4.1
Methanol at AF=6.4, %	8.8	17.2	7.1	38.0	53.3	75.0	<u>107</u>	--

Source- (60)

From experimental tests it has been found that combustion may occur for standard gasoline in mixtures varying from 8:1 to 20:1 AV, with the 13:1 AV value being optimum for starting (93). Based on methanol tests, run with other objectives, one can assume that the best starting for methanol will be 4.5:1 AV (60).

According to Table XXIII one can see that these values cannot be reached under equilibrium conditions until approximately 35°F (2°C) for isooctane and 77°F (25°C) for methanol. Thus some improvements have to be made to enable the engine to start with these fuels at low temperatures.

Actually gasoline does not contain only isooctane, but many more components not exactly in equilibrium in the manifold as assumed. For use in colder climates it contains more of the most volatile components to give an adequate AV at low temperatures (60).

Startability tests on alcohol blends often showed different results, not always as good as expected, when analyzing the distillation curves and vapor pressures.

Pleeth (43) conducted engine tests on a Morris 12 HP, 4 cylinder engine at 32°F (0°C) where low volatility gasoline gave a start within 20 revolutions at 2:1 AF. Increasing the volatility to that of a winter-grade gasoline (20% casinghead) improved the startability so that a mixture ratio of even 4:1 permitted a start in 20 revolutions. With 10% ethanol added to the basic gasoline startability

improved so that with a mixture of 2:1 only 15 revolutions were required, the same happening for 20% ethanol.

With 10% casing head added to this 10% ethanol mixture only 10 revolutions were needed and with 10% benzole on this 10% ethanol-10% casinghead mixture even better results were obtained.

Nash (46) reported that blended fuels up to 30% of alcohol exhibit very good engine starting characteristics and the high latent heat of the alcohol does not appear to cause any trouble at starting; but some effort had to be made during the warm-up period to keep the engine running. He pointed out that this problem was particularly noticeable with methanol blends.

Howes (43) stated that a 10% ethanol addition improved the startability of gasoline at temperatures down to 0°F (-17.8°C).

Below this temperature the reverse effect would apply. This critical temperature would increase with higher percentages of alcohol until a 40% blend showed difficulty to start at temperatures below 60°F (15.6°C) (43).

Bridgeman (100) concluded from the use of gasoline and the same gasolines with 10% ethanol, that startability was easier with the blends at temperatures above 0°F , but more difficult than gasoline below -10°F , with little difference in the intermediate range, even if both fuels have the same

vapor-locking tendency. Greater difficulties were encountered with 20% or 40% ethanol blends.

Christensen et. al. (50) related that blends containing up to 25% alcohol give as easy or easier starting than gasoline alone. They also reported that it is possible, by proper selection of the gasoline base, to prepare alcohol blends of greater percentages without sacrificing easy starting; even shorter warm-up periods than for gasoline were claimed.

On the other hand, Egloff and Morrel (53) reported harder starting when using alcohol-gasoline blends, with both cold and warm engines. Brame and King (47) also reported that 25% alcohol-blends caused difficulty in starting, but they did not specify the temperature range.

Other results concerning startability of alcohol blends were also reported by Formanek, Hoffert, Claxton, Eisinger, Cragoe, etc...

Most recently, A.M. Burns et.al. (65) reported that addition of alcohol to gasoline increases the tendency for hard starting in hot weather operation.

E.E.Wigg (28) carried out experiments concerning 15% methanol blends with RVP corrected to keep the same value of the basic gasoline. This required removing all the butane and half the pentanes from the base blend before adding methanol. Three types of cars --- 1967, 1973 and "1977",

based on type of carburetion and anti-pollution devices, were used. His objectives were fuel economy, pollution and performance. Wigg reported that the older, rich-operating car of 1967 showed no problems at any time, while the leaner-operating 1973 and "1977" cars did experience stalling, hesitations and backfires during the first few minutes of operation from a cold start. It was pointed out that if a richer AF was provided during start-up "one would expect the performance problems associated with cold start to be reduced".

Reed (30) claims cold starting improvements with 10% methanol in an article written by P.C.Hood in "The National Observer" of February/15/1975.

Reed in another publication (23) also reported improved starting in a Toyota 1969 model. Another reference (76) indicates that cold starting is not a problem with methanol-gasoline blends containing up to 40% methanol.

In this way, we could expect an improvement in startability when using methanol blended with gasoline, but attention should be given to the vapor-lock problem due to the increase in volatility. This could be adjusted at the refinery and if markets were found for these light stocks from gasoline, a good solution might be obtained for the vapor-lock problem. Since vapor lock problems occur in hot weather and startability problems occur in cold weather, a convenient value for volatility is likely to be

encountered to compromise both questions. This would lead to a summer and winter blendings, i.e., possibly different alcohol percentages.

VIII- STARTABILITY OF PURE METHANOL.

Here again we could think about blending methanol with some additive to improve cold starts.

Ingamells (76) found that the addition of volatile gasoline components to the methanol would be impracticable due to the very large quantities required: 10% butane or 20% isopentane.

Monier-Williams reported that starting an alcohol engine from cold is a "difficult matter", especially on methanol, unless special devices are employed. Of the devices employed by him, to overcome the starting difficulty when using alcohol alone, the more important were:

- 1) Heating of the carburetor and induction pipe by means of a spirit lamp or flame.
- 2) Heating the jet locally by mechanical or electrical means.
- 3) Starting the engine on gasoline and gradually changing over to alcohol, involving a separate gasoline tank and probably a more complex carburetor (45).

For whatever method, it is necessary to keep the manifold warm while the engine is running to secure flexibility under varying loads and quick acceleration.

Back in 1906 the United States Department of Agriculture

(101) conducted a series of experiments at the Columbia University laboratories with commercial 94% grain alcohol as a fuel in various types of internal combustion engines then in extensive use. A 15 HP, 2-cylinder, 4-cycle Nash gasoline engine was started with alcohol in the fuel chamber by injecting a few drops of gasoline into the air suction. After the first explosion the engine would run perfectly on the alcohol.

However, the conclusions of the investigation gave starting and proper carburetion (due to different stoichiometric ratio) as the only difficulties likely to be encountered to convert any gasoline engine into alcohol fuel.

Some recent experiments with acetone (60), in an amount equal to that of the methanol, injected into the fuel line at the carburetor allowed easy starting, without choking, at 40-50°F (4-10°C). However, with choking and "not much more difficulty" the engine would start without acetone at the same temperature.

Aldeman et al. (60) has also installed an intake pre-heater and an injection system to inject a small amount of commercial ether starting fluid into the intake manifold prior to cranking. This has enabled starts below 20°F (-7°C) and it was claimed that an 11 oz-ether can allowed 50 cold starts. It was not necessary to use starting fluid above 50°F (10°C) or if the car had been run in the previous four hours.

On the other hand, ether starting, based on Diesel engine tests, has been reported (7) to be considered only in

an emergency due to its inconvenience and possibility of internal damage to the engine.

Aldeman also suggests the use of fuel injection of carburetion, addition of a volatile component to the fuel and pre-vaporization with electric heating.

Ingamells also found that starting is nearly impossible at temperatures below 50°F (10°C) and even difficult at 70°F (21°C). Using a 1971 Volvo automobile with fuel injection, the same author claimed that no manifold heating was necessary but the same problems with starting appeared again. Even after tripling the fuel input for starting, using the cold start valve of the Bosch injection system, "the engine simply would not start below about 50°F". Finally, the author suggested that a different fuel be injected by the starting system independently of the main system, once one is dealing with fuel injection instead of usual carburetion, and concluded with "to sum up we feel that the major problem associated with the use of methanol as a motor fuel is starting."

Mills and Harney (42) also suggested fuel injection, addition of volatile components and pre-vaporization by electric heating as possible solutions for the problem.

Thus, we could expect great problems in starting an engine with pure methanol as a fuel, and the addition of additives seems impracticable due to the great quantities required.

One idea is to use additives only at starting when either fuel injection or the carburetor is used. Electric heating

and other Diesel starting systems like glow plugs (102) could also be used.

IX - TEST APPARATUS AND PROCEDURE

Previous Investigations.

Important tests on startability followed the request for more information regarding the ease of engine starting at the 1926 annual meeting of the American Petroleum Institute. This request was just after the presentation of a report on Fuel Characteristics and Engine Starting by Sligh and Eisinger (103) which was then followed by several other investigations by Brown (91,92), Bridgeman (48), Cragoe and Eisinger again (104,105,106). But these investigations had for their principal object the elucidation of a relationship between ease of starting and standard distillation tests and, moreover, had been confined almost entirely to straight gasoline.

In Eisinger's tests the standard updraft carburetor of the engine employed was replaced by a single jet mounted axially in a pipe flanged at both ends and connected to the intake manifold. A flat plate orifice was mounted on the upper flange to serve as a throttle and another orifice was mounted at the lower end of the pipe to serve as a choke. The jet was supplied with fuel from a constant level float chamber through flexible tubing. The flow of fuel to the jet was controlled by a quick-acting valve located near the jet and the rate of flow was altered by raising and lowering the float-chamber, which was in turn connected to a burette for measuring the fuel used. Eisinger's procedure consisted of driving

the engine by a dynamometer at a constant speed, usually 200 rpm, with the fuel supply shut off. When engine conditions had become constant fuel was turned on and the time required to obtain an audible explosion was taken by a stop watch. The fuel was shut off immediately and the total amount used was determined. His results were firstly given in time-required-for-starting versus rate-of-fuel-flow-per-second curves, but after a series of experiments it was found that a single EAD-fuel-air-ratio versus number-of-revolutions-required-to-start diagram was enough to include all other variables as "the time required to start varied with the fuel used, the temperature, the mixture ratio supplied, the cranking speed, the type of engine and the like." (104). The following equation for the curve was found to be representative of all the results:

$$\log \frac{r_a}{r_e} = \frac{2}{N}$$

where:

N	... Number of revolutions to start
r_a	... The EAD fuel-air ratio
EAD	... Equilibrium air distillation test
r_e	... The fuel-air ratio attained in engine cylinders when firing begins.

Eisinger's conclusions were based entirely upon tests made over a limited temperature range and with the special set-up described above. However, Brown (91) conducted investigations of the ease of starting a cold engine when this

was driven by the standard electric starter supplied from the standard battery and with the standard carburetor mounted on the manifold instead of the special fuel system used in other tests. Brown's results were presented in actual-air-fuel-ratio-at-the-carburetor versus number-of-revolutions-to-start curves for each ambient temperature which could be controlled as the tests were conducted in a cold room. The rate of air-flow was measured by an orifice meter placed before two 5-gallon surge tanks in the air-line to the carburetor. The "actual-air-fuel-ratio-at-the-carburetor" was the quotient mass-rate of air-flow/mass-rate of fuel-flow. The revolution counter was directly connected to the engine and the total revolutions of the engine was recorded since the engine continued to turn for a few moments after the starter button and ignition were turned off. In this way it required extra care from the tester in order to record the reading when the first explosion occurred.

Other works like the one conducted by Hoffert and Claxton (107) in England were done to investigate ease of starting with fuels others than gasoline or mixtures like benzole-gasoline. Hoffert's tests were conducted with the use of a special carburetor similar to Eisinger's but a little bit more complex since the constant level was maintained without the use of a float chamber and small volumes such as 0.5 cc were measured during the tests. The rate of air-flow was measured by an orifice-plate meter using a cy-

lindrical tank for damping the pulsations due to the engine, which was motored over by means of its usual starting motor operating on the flywheel. Hoffert's results were presented in the same way as Brown's, except for the fact that since the fuels did not present the same density, as this varies with the proportion of the components in the mixture (if the components have different densities), the air-fuel ratio had been given in mass-of-air per volume-of-fuel instead of the usual weight-per-weight basis. As the size of the jet governs the volume of fuel supplied rather than the weight, this idea of presenting the air-fuel ratio in mass per volume was employed in this present work also. When the results are compared on this basis it is assumed that the carburetor with a definite jet setting will supply the same air-fuel ratio, in grams of air per cubic centimeter of fuel, for example, irrespective of the nature of the fuel. Actually, with different fuels, owing to differences in their physical properties (specific gravity, viscosity, surface tension, etc) the volume of liquid fuel passed under otherwise identical conditions may vary somewhat. But tests carried out by this author did not show significant differences for 0-25% methanol-gasoline blends in the 10-85°F range.

Anyway the idea of presenting the air-fuel ratios in that manner (mass/volume) for mixtures is suitable since even if the air-fuel ratio varies for a definite setting un

der more precise instrumentation, if available, one would see the results (e.g., number of revolutions to start the engine for a given mass/volume AF ratio for various fuels) as the startability properties of such fuels for the same carburetor setting.

Starting Test Equipment

The general arrangement of the test equipment is shown diagrammatically in Figure 27.

Engine: The engine used for the ease of starting tests at KSU was an air-cooled, single-cylinder, 10 HP Briggs & Stratton model 243434 with the following specification:

bore	3 1/16 "
stroke	3 1/4 "
displ.	23.94 c.i.
HP	10.0 HP @ 3600 rpm
torque	16.75 lb-ft @ 2400 rpm
idle speed	1000 rpm
starter speed	.	660 rpm (12 volt supply)

Carburetor: The standard carburetor was maintained since a wide range of air-fuel ratio could be easily attained with it.

Cold Box: A 2x2x4 ft Webber chamber was employed to obtain a relatively wide range of temperatures for cold starting.

Engine Cranking: The engine was provided with a standard

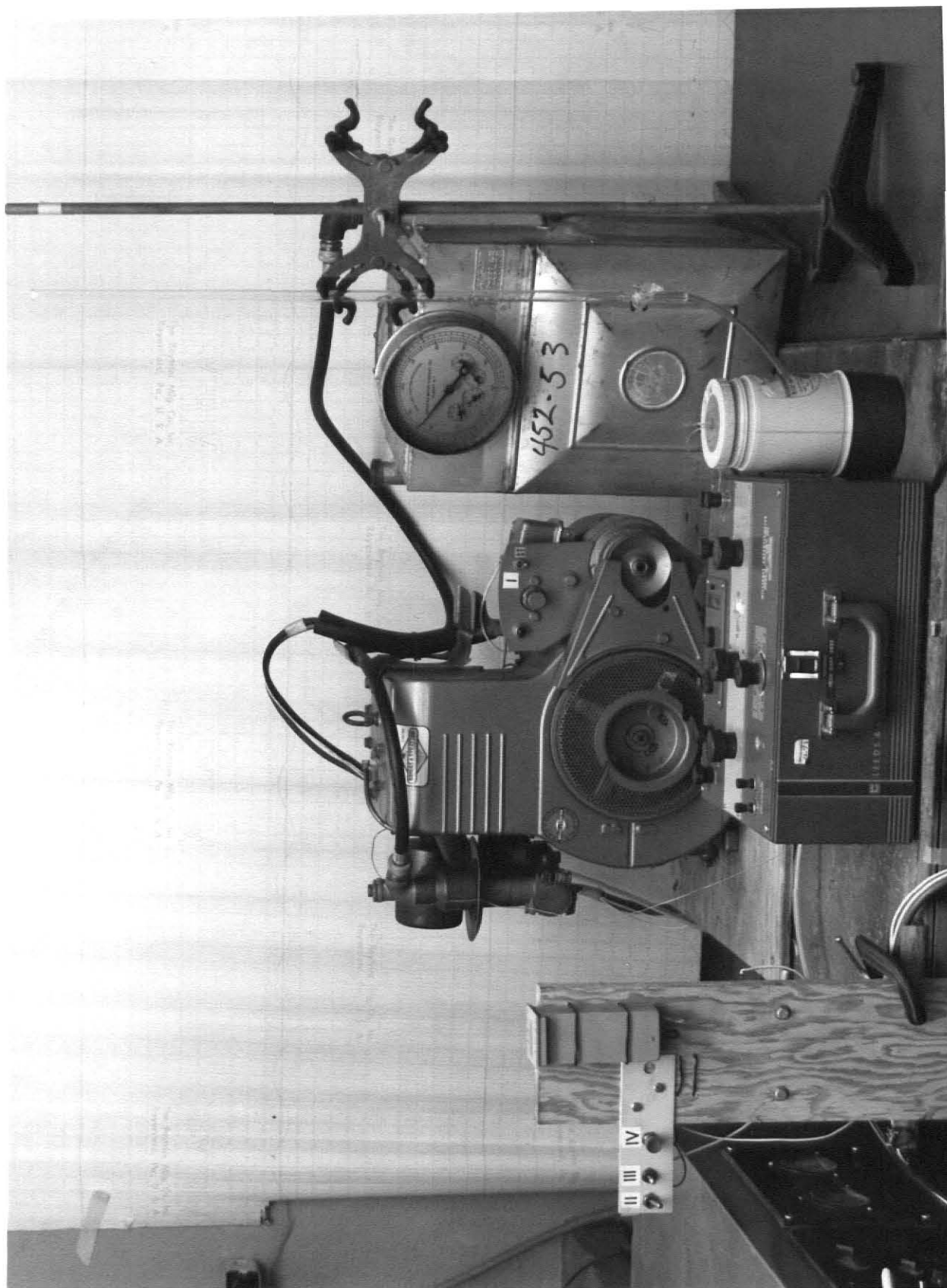


Figure 27 - Test Apparatus

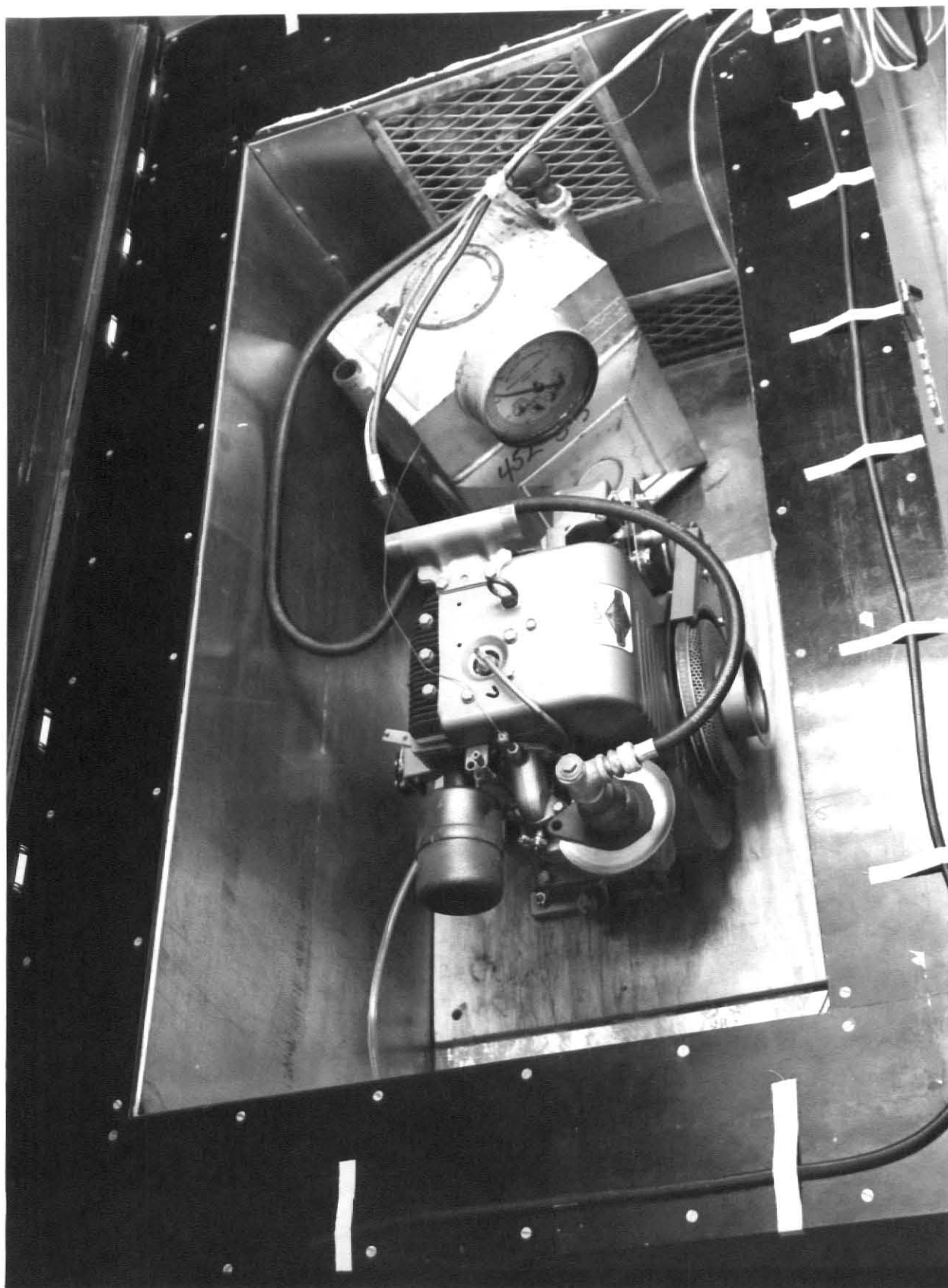


Figure 28 - Test Apparatus (Temperatures below 75°F)

starter and a 12-volt battery placed outside the cold box to prevent temperature influence on the battery. The starting switch was connected to a 24-volt solenoid which activates the starter.

Fuel Measurement: The fuel that was used was measured by a burette (50 ml 20°C) connected to the fuel-line outside the cold box. Enough tubing length was provided to keep the fuel inside the cold box at constant temperature.

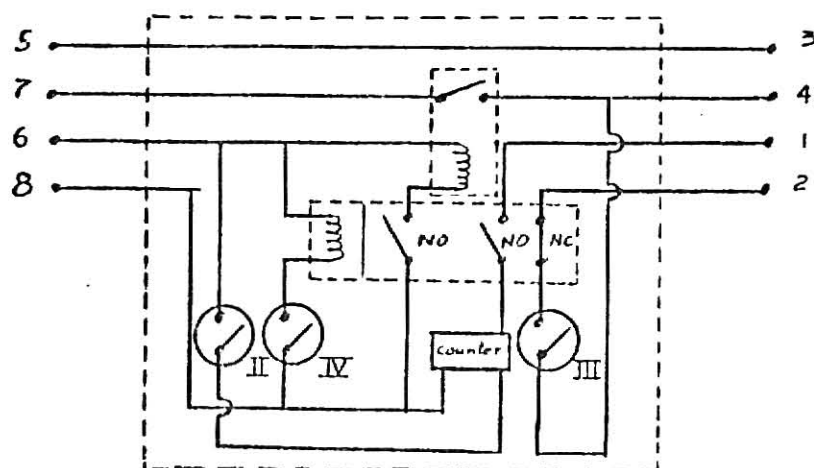
Air Measurement: The amount of air that was supplied to the carburetor was measured by a gas flowmeter 10-300 cubic feet/hour, manufactured by American Meter Company, number 6400008, due to the required compactness (it was not necessary to have surge tanks as one can have an initial and final readings rather than a reading "on the run".).

Instant of Starting: As it was discussed in Chapter VI the instant of starting, i.e., ease of starting or startability, is defined as the moment of the first explosion, which was detected here by the ear. In some Diesel engine test procedures, for instance, this moment is verified by the change in current consumption by the starter, but this was not necessary for these tests.

Number of Revolutions: The starting switch was arranged so that on depression it simultaneously closed the starting battery and ignition circuits and ener-

gized the revolution counter working on the power shaft by means of a magnetic relay. On releasing the starting switch all three circuits were simultaneously broken allowing us to register the number of revolutions to the first explosion even if the engine continued to turn for few more revolutions after the switch was turned off avoiding the problems encountered by Brown. As the counter required a 24 volt supply an extra battery was employed. This same battery was used also to activate the starter solenoid which also operates with 24 volt. The complete circuit is shown schematically in Figure 29.

Figure 29 - Starting Circuit



- | | |
|--------------------------|---------------------------------|
| 1 ... counter signal | 5 ... ⊕ starting battery-high i |
| 2 ... ignition quit wire | 6 ... ⊕ starting battery-low i |
| 3 ... ⊕ starter | 7 ... ⊖ starting battery |
| 4 ... ⊖ starter | 8 ... ⊖ auxillary battery |

Temperature Control: Temperatures above 75°F were obtained at ambient conditions being measured by means of a Hg thermometer (ambient temperature) and a copper-constantan thermocouple placed in the intake manifold. Temperatures below 75°F were obtained by testing the engine inside the cold box which was provided with its own standard control and thermometer, but the thermocouple was used to check the intake manifold temperature.

Procedure.

For each position of the calibrated needle in the main jet the resultant air-fuel ratio was calculated from the initial and final readings of the burette and gas meter after some 800 revolutions at 660 rpm (normal cranking speed) with the ignition off (switch I). The results will be seen in the next Chapter.

The starting tests were carried out by pushing the button IV with switches I and III on, after resetting the counter by means of switch II, until hearing the first explosion. By releasing the button IV, right after this first explosion, the total number of revolutions to obtain the start was registered in the counter. The temperature reading at the thermocouple was recorded immediately before and after the test. The same procedure was repeated for each fuel and jet setting under various temperatures. An average of eight readings

were taken for each condition (jet setting, fuel, temperature) and the range of results are indicated in the next Chapter.

When changing mixtures the carburetor was wiped dry by cranking the engine at high fuel-air ratio (e.g. 1:1) until no fuel was coming out from the exhaust or being accumulated in the manifold; afterwards the engine was cranked up for about 2000 revolutions with no fuel in the carburetor (same procedure of Brown) and the float chamber was filled up with the next fuel and the same procedure to dry the carburetor was repeated to insure that the tests would not be influenced by the fuel used previously. The burette and fuel-line were also cleaned by filling up the burette and tubing with the next fuel after having emptied it of the previous fuel. The same action was taken twice.

Enough time was allowed between tests for cooling the engine down and replacing the fuel vapor in the manifold by air --- about 30 minutes. All tests were made at fixed closed throttle and with the same lubricating oil in the crankcase.

X- EXPERIMENTAL RESULTS

Fuels

Following the procedure indicated in Chapter IX the Startability Tests were conducted for M-0, M-5, M-10, M-15, M-20, M-25 and M-100*. For these mixtures the base gasoline was un-leaded regular (spring) and the methanol was of the reagent kind (99.9% methyl alcohol).

The experimental results for blends and straight gasoline showed that when the engine did not start in less than 12-14 revolutions it would not start at all for any jet setting, temperature or blend. One reason could be the fact that the engine employed was provided with an updraft carburetor and after these 12 revolutions too much fuel was accumulated in the intake tube (before carburetor) causing the engine to "flood".

On the other hand, when using straight methanol the number of revolutions to start reached easily 40 or more. This was probably due to the wider flammability limits of methanol in comparison to gasoline.

The minimum number of revolutions to start the engine in the 10-85°F range was 2-3 for blends and straight gasoline and 3-4 for straight methanol. These values could depend also upon the particular tester.

* Using Reed's notation (see Chapter V): M-XX for XX% by volume methanol in gasoline.

Since the values for the number of revolutions to start varied around 2 or even more revolutions for each condition, an average was taken for some 8 readings at the same condition. These mean values and the range of results can be seen in Table XXIV for each engine situation (fuel, jet setting, temperature).

As indicated in Chapter IX the resultant air-fuel ratio (mass/volume) was measured for each needle position, fuel and temperature and plotted in Figure 30. As mentioned before, the air-fuel ratio in mass/volume did not vary for the fuels and temperature range used for these experiments.

Data Presentation.

Keeping the same needle position and varying the ambient temperature, the number of revolutions to obtain a start was measured (Table XXIV) and curves such as in Figures 31 and 32 (ambient temperature versus number of revolutions) were obtained. This procedure was repeated for various jet settings to see the influence of mixture strength.

From these data the curves in Figures 33 and 34 (number of revolutions versus air-fuel ratio) could be plotted to present the results in the so-called "Startability Diagram" of a given fuel.

In order to compare the relative ease of starting for various methanol blends, curves such as in Figure 35

Table XXIV - Startability Experimental Results.

F Fuel
 T Ambient Temperature ($^{\circ}\text{F}$)
 N Number of Revolutions to Start
 I Interval of Variation for N
 J Jet Setting (Needle Position - Fig.)

F	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0
T	20.0	23.0	28.5	35.5	23.0	28.0	24.5	21.5	64.0	20.0	21.0
N	15.0	6.0	6.2	5.9	6.5	6.6	7.0	7.5	3.1	7.2	7.5
I	14-17	6	6-7	5-6	6-7	6-7	7	7-9	3-4	7-8	7-8
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0	M-0
T	24.0	18.0	20.0	25.0	16.0	23.5	38.0	41.0	45.0	48.0	51.0
N	7.0	8.0	7.0	6.5	--	7.3	5.5	5.3	5.1	4.5	3.7
I	6-8	7-9	7	6-7	--	7-8	5-7	5-6	4-6	4-5	3-4
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-0	M-5	M-5	M-5	M-5	M-5	M-5	M-5	M-5	M-5	M-5
T	55.0	72.0	66.0	59.5	55.0	48.0	43.0	36.0	39.5	32.5	28.0
N	3.8	3.1	3.3	3.5	3.7	4.9	4.4	6.1	5.2	6.1	6.5
I	3-4	3-4	3-4	3-4	3-4	4-5	4-6	5-7	5-6	6-7	6-7
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-5	M-5	M-5	M-5*	M-5*	M-5*	M-10	M-10	M-10	M-10	M-10
T	25.5	19.5	22.0	32.5	28.0	25.5	75.0	60.0	52.0	44.0	41.0
N	7.0	9.0	7.0	7.1	7.7	8.3	2.9	3.3	3.5	5.1	5.5
I	7-8	9	7	7-8	7-9	8-9	2-3	3-4	3-4	4-6	5-6
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	20.0	39.0	35.0	31.0	28.0	25.0	19.0	18.0	74.0	67.5	61.5
N	14.2	5.0	6.0	6.5	6.5	7.4	10.0	--	3.8	3.9	4.5
I	10-18	5-7	5-7	5-7	6-7	6-8	10	--	3-5	3-4	4-6
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.0	3.0	3.0
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	57.5	50.5	41.0	25.0	21.0	74.0	60.0	49.0	41.0	40.0	39.0
N	5.0	5.0	6.1	8.8	--	4.5	5.5	6.0	6.8	6.6	6.9
I	5	4-6	5-7	7-9	--	4-6	5-6	6	6-8	6-7	6-8
J	3.0	3.0	3.0	3.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	35.0	29.0	28.0	25.0	24.5	24.0	74.0	72.0	60.5	49.5	41.0
N	7.5	9.0	9.0	11.5	14.0	--	5.1	5.0	5.9	6.4	7.0
I	7-8	9	8-10	9-14	14	--	4-6	5	5-7	6-7	6-8
J	2.0	2.0	2.0	2.0	2.0	2.0	1.0	1.0	1.0	1.0	1.0
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	34.5	75.0	62.0	59.5	50.5	41.0	40.0	36.0	76.0	64.0	51.0
N	8.0	5.9	6.2	6.5	6.6	7.7	8.2	--	6.5	7.0	7.7
I	7-9	5-6	6-7	6-7	6-7	7-9	7-9	--	5-7	7	7-9
J	1.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.2	0.2	0.2

*M-5 left overnight.

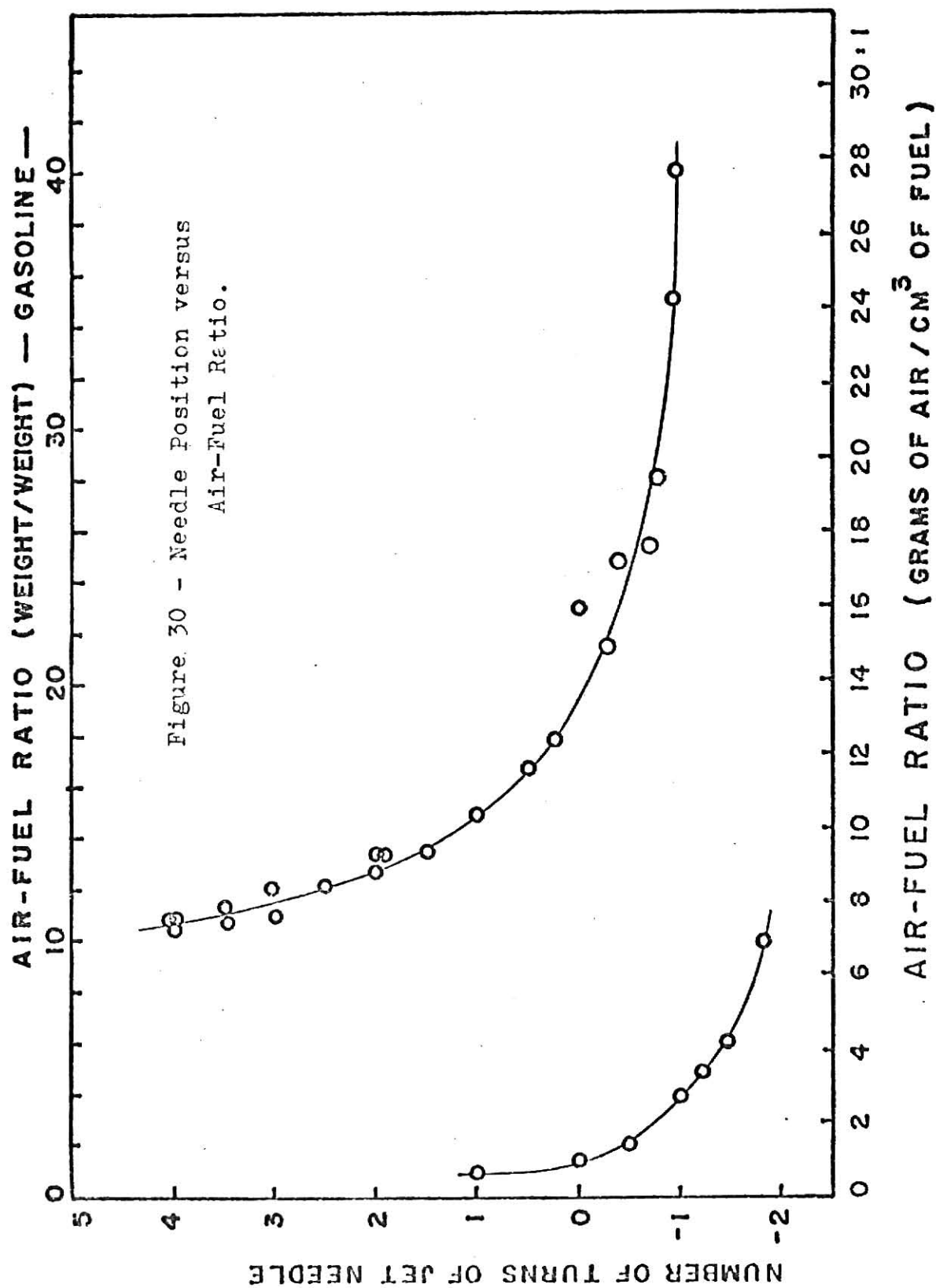
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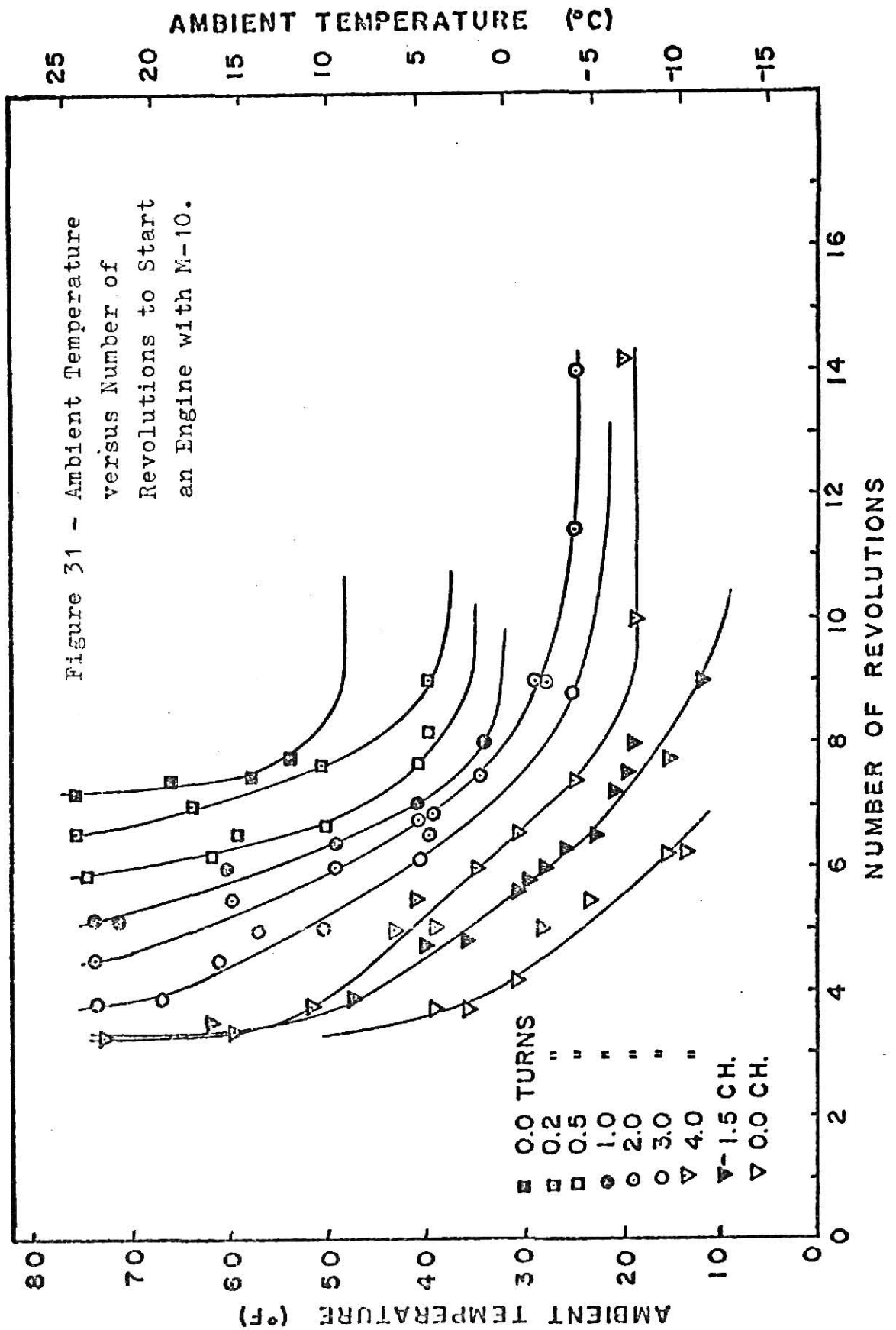
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	40.0	37.0	76.0	66.5	58.0	54.0	47.0	62.0	47.5	39.5
N	9.0	--	7.2	7.4	7.5	7.8	--	3.5	3.9	4.7
I	9	--	7-8	7-8	7-8	7-8	--	3-4	3-5	4-6
J	0.2	0.2	0.0	0.0	0.0	0.0	0.0	-1.5c*	-1.5c	-1.5c
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10
T	36.0	30.5	29.5	28.0	26.0	23.0	21.5	20.0	19.0	16.0
N	4.8	5.6	5.7	6.0	6.3	6.5	7.2	7.5	8.0	7.7
I	4-5	5-6	5-7	5-7	6-7	5-7	7-9	7-9	7-9	7-9
J	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c
F	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-10	M-15	M-15
T	12.0	39.5	36.0	31.0	28.5	23.5	15.5	14.0	75.0	46.0
N	9.0	3.7	3.7	4.1	5.0	5.5	6.2	6.2	3.0	4.3
I	9	3-4	3-4	4-5	4-6	5-6	6-8	5-7	3	4-5
J	-1.5c	0.0c	0.0c	0.0c	0.0c	0.0c	0.0c	0.0c	4.0	4.0
F	M-15	M-15	M-15	M-15	M-15	M-15	M-15	M-15	M-15	M-20
T	39.5	30.0	25.5	22.0	20.0	17.5	16.0	57.5	32.5	62.5
N	4.6	6.0	6.0	6.2	7.3	9.0	--	3.4	5.5	3.5
I	4-5	5-7	6	6-7	6-8	8-10	--	3-4	4-6	3-4
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-20	M-20	M-20	M-20	M-20	M-20	M-20	M-20	M-20	M-20
T	53.5	46.5	40.0	35.0	32.0	27.0	23.0	24.0	22.0	20.5
N	4.0	4.6	5.8	6.1	6.2	6.9	7.4	7.0	9.0	9.3
I	3-5	4-6	5-7	6-7	6-7	6-8	7-9	7	9	8-10
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
F	M-20	M-25	M-25	M-25	M-25	M-25	M-25	M-25	M-100	M-100
T	20.0	30.0	22.0	25.0	26.0	24.0	24.5	43.5	84.0	80.0
N	10.0	6.4	--	6.5	7.4	14.0	10.4	4.8	5.6	5.8
I	9-11	6-7	--	6-7	7-9	14	9-12	4-6	5-6	5-6
J	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.5	3.5
F	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100
T	75.0	71.0	65.0	80.0	71.0	65.0	60.0	55.0	49.0	45.0
N	6.4	6.8	43.0	4.4	4.8	5.4	5.8	6.2	6.4	7.2
I	6-7	6-8	40-50	4-5	4-5	5-6	5-7	6-7	6-7	6-8
J	3.5	3.5	3.5	0.0c	0.0c	0.0c	0.0c	0.0c	0.0c	0.0c
F	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100
T	42.0	40.0	38.0	75.0	64.0	55.0	50.0	47.0	46.0	45.0
N	8.7	21.0	--	5.1	6.0	6.8	7.0	9.0	11.0	20.0
I	7-9	18-24	--	5-6	5-7	6-7	6-8	8-11	10-13	18-25
J	0.0c	0.0c	0.0c	-1.3c	-1.3c	-1.3c	-1.3c	-1.3c	-1.3c	-1.3c
F	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100
T	43.0	66.0	60.0	52.0	48.0	45.0	43.0	71.0	64.0	57.0
N	--	6.2	6.8	7.0	9.0	40.8	--	6.3	7.2	8.5
I	--	5-7	6-7	6-8	9	36-46	--	6-7	6-8	7-9
J	-1.3c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.5c	-1.7c	-1.7c	-1.7c

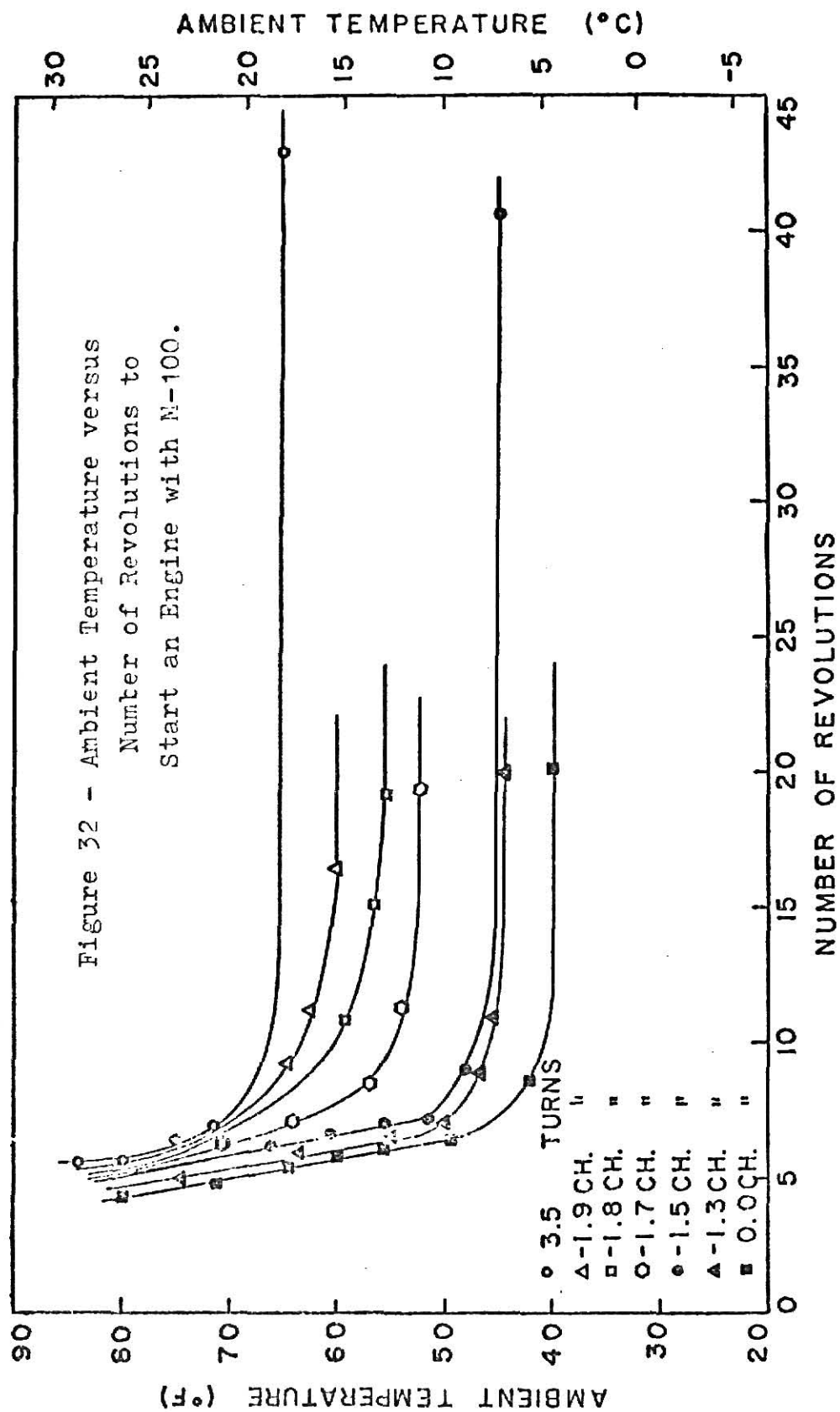
*
c ... choke employed

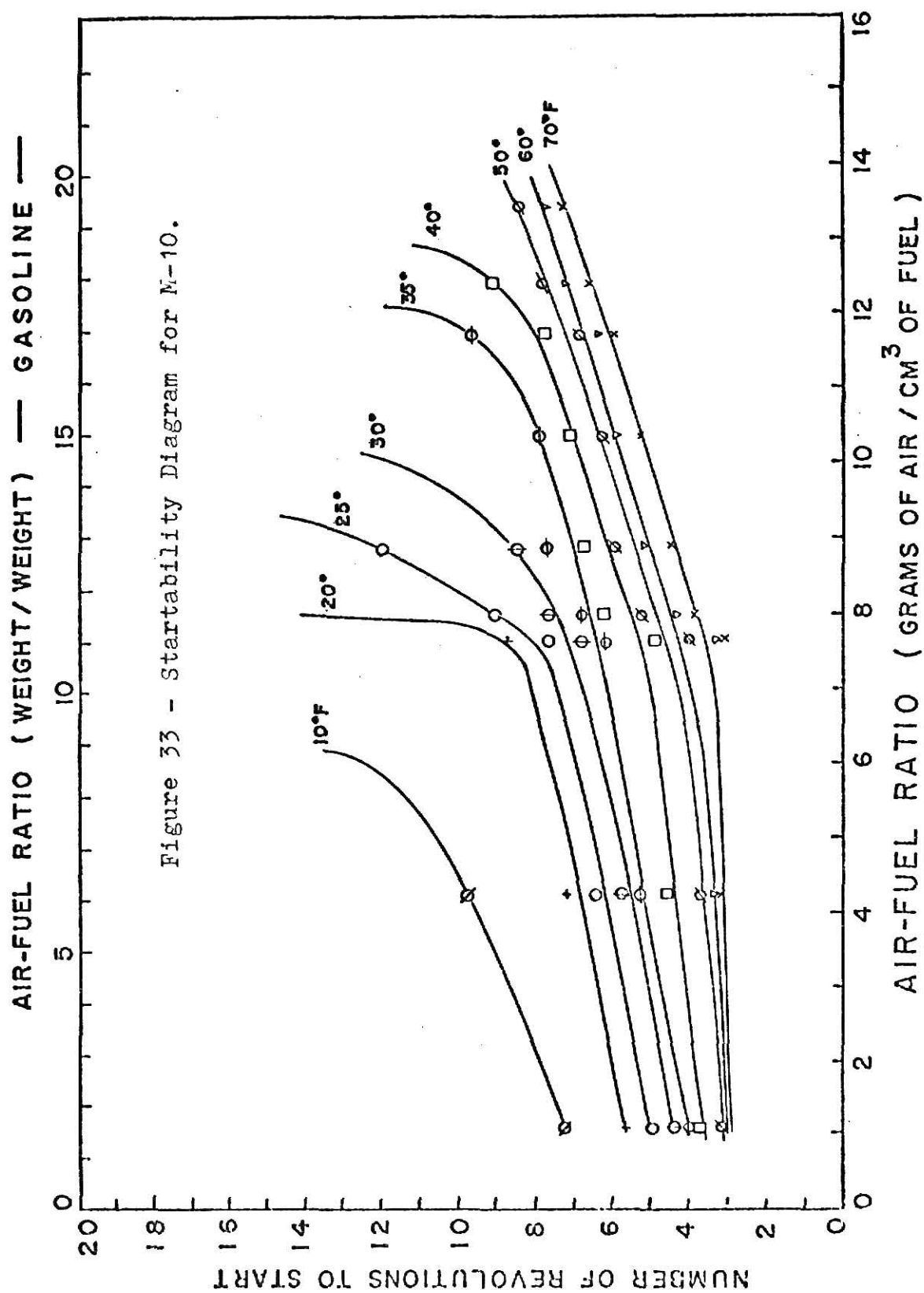
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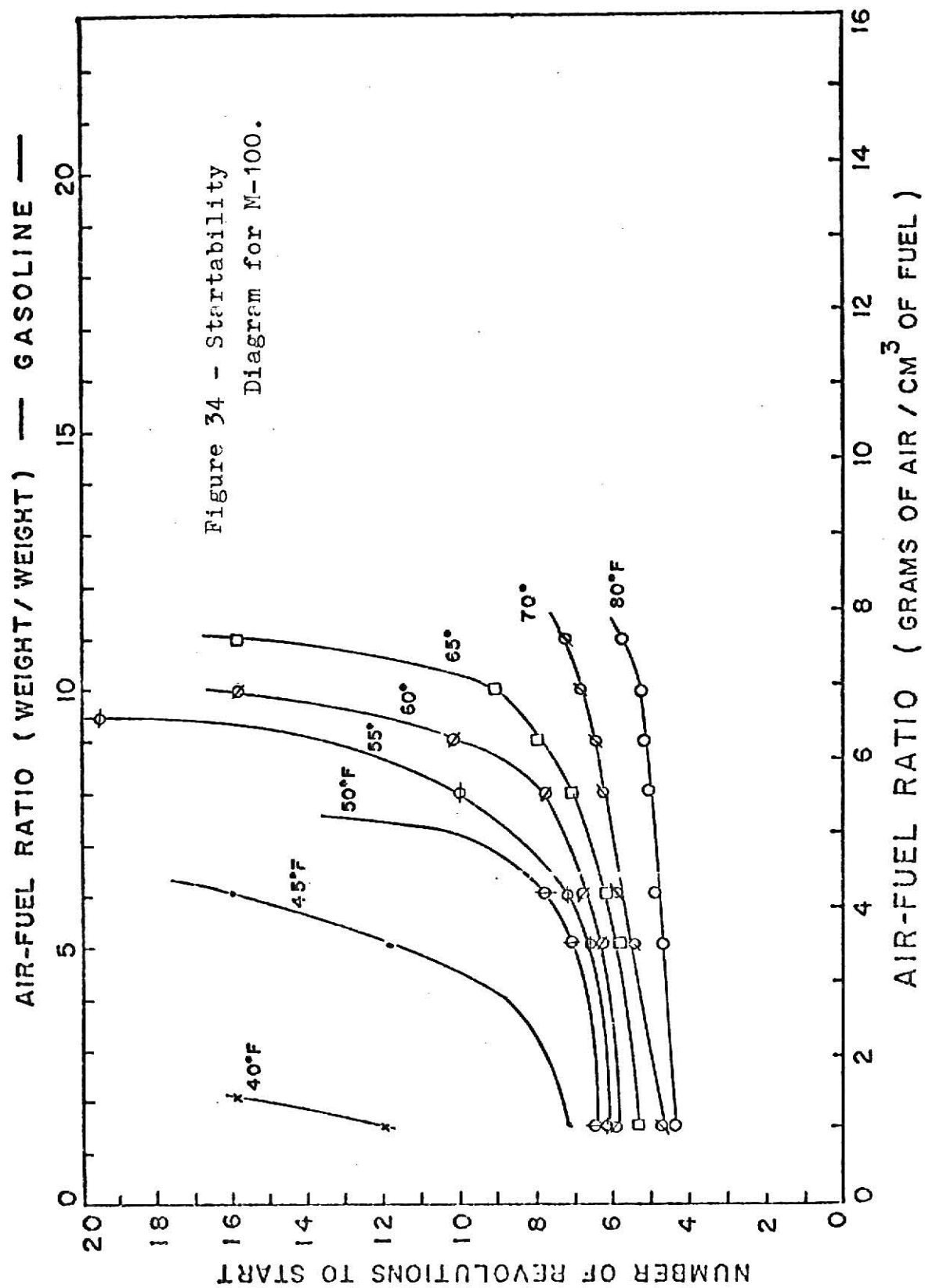
F	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100	M-100
T	54.0	52.0	50.0	59.0	57.0	56.0	54.0	64.0	63.0
N	11.3	19.5	--	10.8	15.0	19.2	--	9.2	11.4
I	10-15	13-22	--	9-12	10-17	13-20	--	8-10	9-15
J	-1.7c	-1.7c	-1.7c	-1.8c	-1.8c	-1.8c	-1.8c	-1.9c	-1.9c
				F	M-100	M-100			
				T	60.0	58.0			
				N	16.5	--			
				I	13-20	--			
				J	-1.9c	-1.9c			







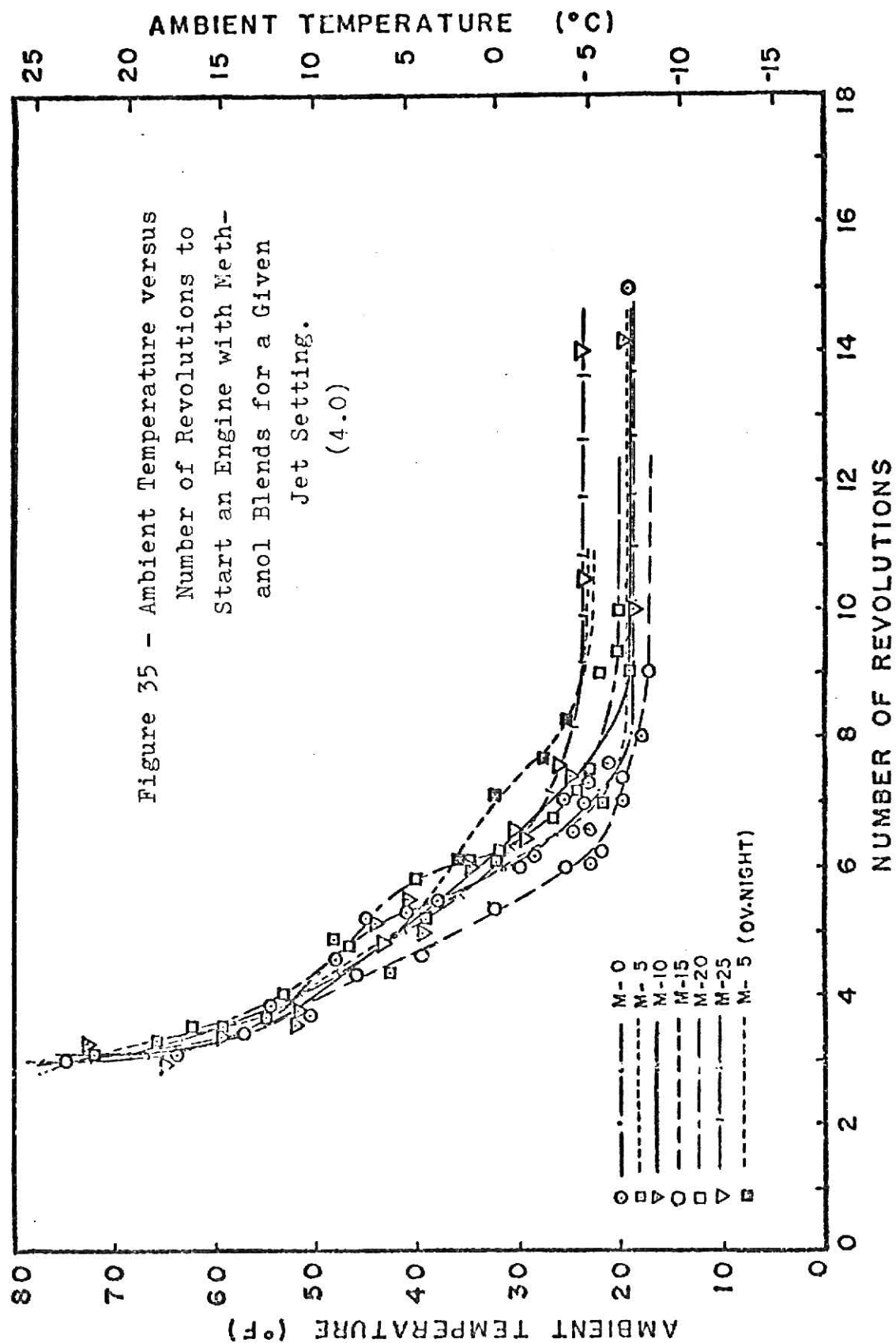


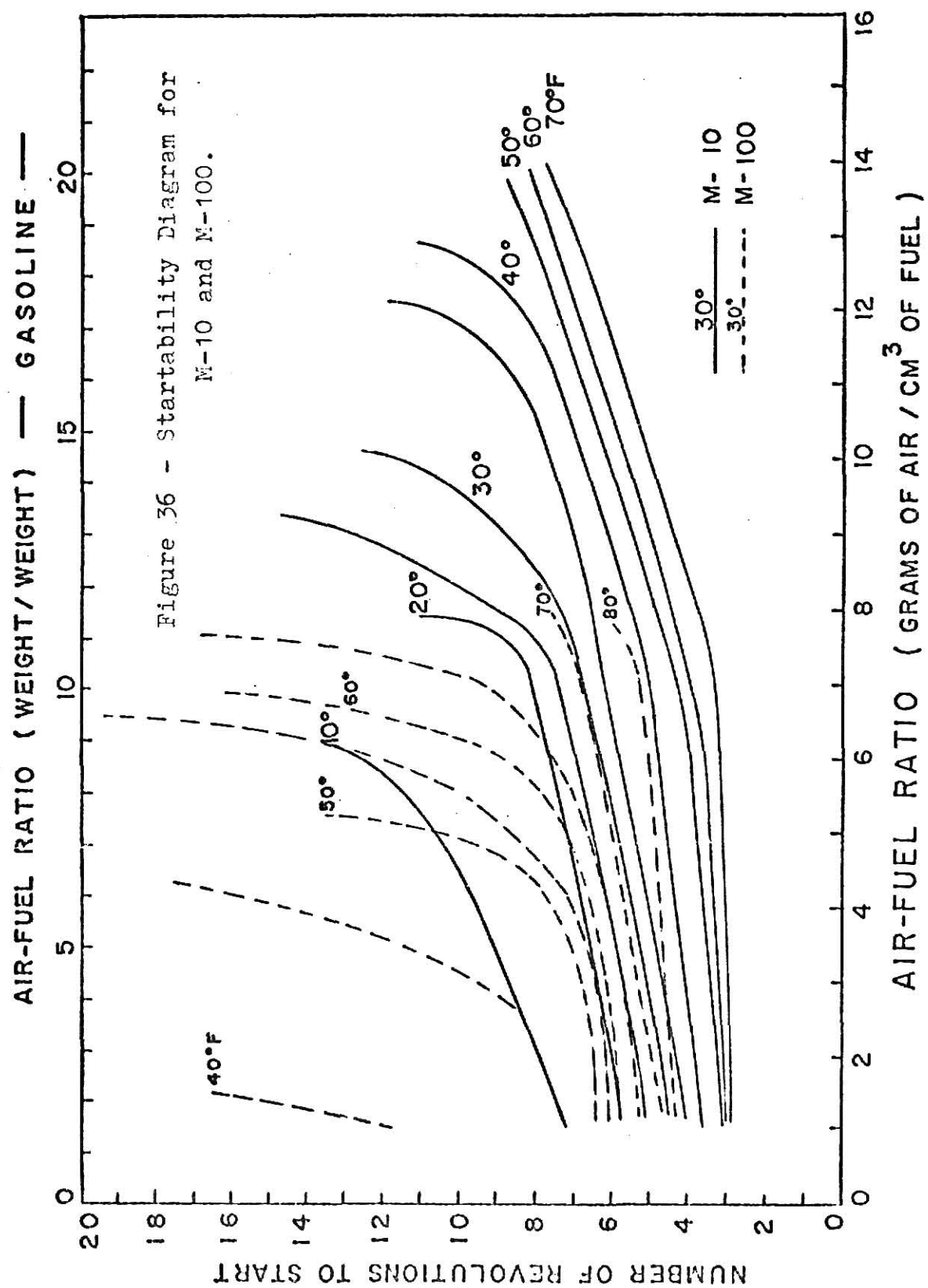


(ambient temperature versus number of revolutions for various fuels) were plotted for the same jet setting. From Figure 34 one can easily notice that little difference concerning ease of starting would be expected between methanol blends and the base gasoline except for M-25. With this fuel the engine would not start below 24°F while M-15 would require only 6 revolutions to start at the same needle position.

This bad behavior of M-25, and slightly less for M-20, is explained if one recalls that at that temperature 25% methanol in gasoline would easily turn to a 2-phase mixture if any appreciable moisture was encountered in the fuel-line. Then, as methanol and water would accumulate at the bottom of the float chamber, we would have after some time almost pure methanol at the chamber, since its level would be increasingly higher with continuous fuel flow. Since methanol tends to be a hard-starting fuel in comparison with gasoline for the same air-fuel ratio (Figure 36) that behavior is explained.

The phase separation problem is really a serious one for methanol blends unless one happens to use methyl-fuel (methanol plus higher alcohols) whose solubility characteristics would be better (Chapter V). This problem was even encountered with M-5 using reagent methanol as a component, when the fuel was left overnight with the upper end of the burette open to the ambient air. The next morning one could easily see drops of methanol-water solution at the lower part of the fuel-line tubing under low temperature conditions (30°F).





The ease of starting of this mixture was much worse than in the previous day as we can see in Figure 35. While 7 revolutions were necessary to start the engine at 32°F with M-5 left overnight, the same 7 revolutions would be required to start it at 22°F with "dry" M-5.

From Figure 36 one can see how a straight methanol-fueled engine is very hard to start as expected (Chapter VIII) in comparison, for instance, with M-10. While a mixture of 4:1 (grams/cm³) would start an M-10 fueled engine at 60°F in about 3 revolutions, this same jet setting would require around 6.5 revolutions to start a straight methanol fueled engine at the same 60°F. This comparison is not really fair as the methanol stoichiometric ratio is roughly half of the gasoline ratio. Thus, comparing each fuel (M-10 and M-100) at their stoichiometric ratios, we can see that for M-10 (11:1 grams/cm³), about the same 6.5 revolutions were necessary to start the engine at 60°F, i.e., same startability as methanol (4:1 grams/cm³).

However for lower temperatures methanol startability gets worse. It will not provide a start at all below 40°F, even at 1:1 which is approximately the richest condition the usual carburetor can provide. In order to compare it with M-10, we can see in Figure 36 that this fuel provides a start, at 40°F and same setting, in less than 4 revolutions.

Therefore, it would be necessary to employ special devices or additives at the moment of starting straight methanol-fueled engines as pointed out in Chapter VIII, if one is

using normal carburetors. When using methanol blends the great improvement expected in startability was not verified, at least for the 10-85⁰F range; but no drawback was encountered concerning starting qualities when phase separation did not occur.

XI- CONCLUSION

The Startability tests conducted in a single cylinder engine confirmed the starting problems when using straight methanol below 40°F: it simply would not start with usual carburetor without additives. Thus, the special devices mentioned in Chapter VIII would have to be employed.

For methanol blends the differences among gasoline and blends for the 10-85°F temperature range were negligible for practical use (less than 2 revolutions) except when phase separation occurred (M-20 up, or under excess moisture in the fuel line).

Concerning the future use of straight methanol, or blends with gasoline, the use of systems like Dresserator (84, 85) and fuel injection seem to be the most promising aspects to be studied, since these systems would help solve starting, emissions, fuel economy, driveability and phase separation problems as mentioned in Chapter V (the latter in the case of individual feed systems).

Individual feed systems would also provide the possibility of higher percentages of methanol in the blends, regardless of moisture and temperature, and even the use of methanol-water blends which promises great results concerning energy use efficiency (see Chapter V).

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STARTABILITY: AN OBVIOUS SNAG FOR
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by

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Mechanical Engineering

KANSAS STATE UNIVERSITY
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Name: Arnaldo V. Carvalho Jr. Date of Degree: October, 1975
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Title of Study: STARTABILITY: AN OBVIOUS SNAG FOR A
METHANOL-FUELED ENGINE IN A METHANOL ECONOMY ?

Pages in Study: 150 Candidate for Degree of Master of Science

Major Field: Mechanical Engineering

Scope and Method of Study: Problems concerning the starting of a cold engine, when using straight methanol or gasoline-methanol blends as a fuel, have been discussed lately as one advantage (or disadvantage) of the use of methanol as a transportation fuel. Use of this alcohol as a fuel has recently become controversial due to the so-called "Energy Crisis", but the important aspects of its use as a fuel for internal combustion engines remain obscure, the results varying from researcher to researcher.

This study involves the basic reasons for using this fuel and presents a survey about the subject. It also includes brief comments about the place of the automobile in the present transportation system, future automotive engines, other uses of methanol, several sources to produce this alcohol and a review of the most important aspects concerning the use of methanol to fuel the present internal combustion engine (spark ignition).

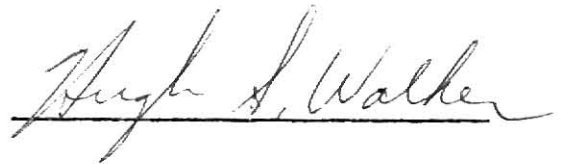
The startability study was carried out by ob-

serving the number of revolutions to start an engine, under a given air-fuel ratio and temperature, using several fuels and a special starting test apparatus.

Findings and Conclusions: The startability tests confirmed the expected hard-starting of straight methanol, when using normal carburetion below 40°F (even at richest conditions), but showed no substantial difference between blends of 0-25% (by volume methanol in gasoline) for 10-85°F temperature range.

The review of most important references in this study indicated that methanol as a fuel for transportation will have its place in the near future. The reasons for that are its availability, physical properties and its advantages of being a liquid fuel. Another aspect which encourages further studies is the fact that its properties would be enhanced if fuel injection systems or new types of carburetors (like the "Dresserator" — which provides better fuel vaporization) could be employed.

MAJOR PROFESSOR'S APPROVAL

A handwritten signature in dark ink, reading "Hugh S. Walker", written over a horizontal line.