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Utilization of Alternative Fuels in Diesel Engines

Samuel S. Lestz
The Pennsylvania State University

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Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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I. INTRODUCTION

This report covers work done under a grant (NAG 3-91) administered by the NASA Lewis Research Center for the United States Department of Energy (DOE). The grant duration was September 1980 through January 1984, essentially a forty one month continuation of an initial DOE grant that was begun three years before. Figure 1 illustrates the four elements of the initial grant. The continuing grant research program concentrated on the engine elements of Figure 1. After presenting a brief background, the accomplishments of this grant will be summarized.

II. BACKGROUND

In 1977 when the initial grant was started, it had as its purpose to investigate the use of alternative fuels for extending the present petroleum-based Diesel fuel oil supply. With the emergence at that time of the first domestic Diesel automobile, the major grant effort was targeted at the light-duty Diesel engine. Also at the time, for a variety of reasons, interest began to focus on the light alcohols as candidate near-term alternative motor fuels.

Unfortunately, the wide fuel tolerance of the Diesel engine does not include the alcohols. The autoignition properties of methanol and ethanol are such that they both are very poor Diesel fuels. However, since these light alcohols were so important, it was decided to investigate ways that they might be utilized as Diesel fuel extenders. Based on previous experience fumigation appeared to be a promising method and this was the approach selected. Also, because it is the

ALTERNATE FUELS PROGRAM

PHYSICAL PROPERTIES

1. Vapor Pressure
2. Decomposition Studies

COMBUSTION BOMB

1. Ignition Delay
2. Laminar Burning Velocity
3. Global Reaction Rate
4. Surface Ignition Studies

SINGLE CYLINDER ENGINE

1. Particulate Studies
2. Component Development

MULTI CYLINDER ENGINE FEASIBILITY STUDIES

1. Total Energy
2. Environmental Compatibility
3. Equipment Integrity

Fig. 1 - Alternate Fuels Program.

simplest alcohol and it can easily be synthesized from an abundance of raw materials, methanol was chosen as the alternate fuel for the initial study.

Fumigation is the term used to describe the introduction of a supplemental fuel into the intake air of a Diesel engine upstream of the intake manifold by spraying or carburization. This method of fuel induction is simple and has the advantage of improving the inherently poor air utilization of the Diesel engine because a portion of the total fuel supplied to the engine is premixed with the combustion air. Also, depending on the fuel being fumigated this premixing can result in a reduced ignition delay (1)*. The multicylinder engine used for the methanol studies carried out during the initial grant period was an Oldsmobile 5.7ℓ V-8 Diesel automobile engine. This fully instrumented engine was coupled directly to a cradled electric dynamometer (2). With the exception of the addition of a fumigation system to its intake manifold this engine was run in the "as-received" condition using a certified Diesel fuel oil (Phillips, DF-2 Control Fuel) and a commercial grade lubricating oil (Shell Rotella T, Multi-purpose HD).

Details concerning the equipment, procedures and results of this methanol fumigation study are found in Refs. (2-4). The results lead to the following conclusions (4):

(1) Methanol fumigation reduces nitric oxide emission at all conditions tested but had little effect on smoke opacity.

(2) Methanol fumigation in limited quantities (up to about 15 percent by energy) increases thermal efficiency at the 3/4 and full rack settings for all the speeds tested.

*Numbers in Parenthesis designate Reference List entries.

(3) Increased methanol fumigation eventually produces knock-limited operation at the higher rack settings for speeds of 1720 RPM and 2000 RPM.

(4) Since excess quantities of fumigated methanol reduce thermal efficiency at the lower rack settings and induce severe knock at the higher rack settings it would seem that the amount of methanol fumigation than can be used to an advantage is limited.

(5) The limited amount of particulate data obtained in this study indicates that methanol fumigation can increase the biological activity, as measured by the Ames and Comptests, of both the raw particulate matter and its soluble organic fraction.

The fact that methanol fumigation can reduce the operating range of a light-duty Diesel engine by inducing severe knock and also appears to enhance the bioactivity of the emitted particulate matter was deemed to be important enough to warrant further investigation in a single-cylinder engine. Also, because of the growing interest in ethanol, it was of interest to determine if similar results would be obtained upon the fumigation of the same engines with ethanol. Therefore, these tasks formed the basis for the initial work to be performed under the continuing grant. The following sections of this report will summarize all the various studies that were conducted during the continuing grant period.

III. RESULTS

During the grant period a variety of fuels were tested in both the multicylinder indirect injection (IDI) engine and in two identical single-cylinder direct injection (DI) engines. The fuels tested were methanol, ethanol, four vegetable oils, two coal derived oils, and two shale derived oils. In all cases the test procedures were similar. At selected load and speed conditions a series of steady state runs were made with the test fuel; the performance and emission characteristics obtained were then compared to those for the baseline DF-2 run at the same conditions.

Table 1 lists the specifications for the engines and Table 2 lists the baseline fuel and lubricating oil specifications. Selected test fuel properties are given in Table 3. This portion of the report is divided into three sections according to the types of fuels tested. The first section covers alcohols, the second vegetable oils, and the third coal and shale derived fuels.

3.1 Alcohol Fumigation Studies

Here the results of the multicylinder engine ethanol fumigation tests will be presented first, followed by the single-cylinder engine ethanol and methanol fumigation tests.

3.1.1 Multicylinder engine ethanol tests

The same Oldsmobile 5.7ℓ V-8 automobile Diesel engine and set-up that was used for the methanol work (2-4) was used for the ethanol study. Further specific details pertaining to the methods and procedures employed for the ethanol study may be found in Refs. (5,6). The objectives of the multicylinder engine ethanol tests were:

1. Establish a baseline test matrix for different engine speed and rack settings.

2. Obtain, for each condition in the test matrix, thermal efficiency, power output, smoke and gaseous emissions.

Table 1 Engine Specifications

	AVCO Lycoming Bernard Single-Cylinder Air Cooled DI Diesel	Oldsmobile V-8 (5.7ℓ) Prechamber Diesel
Bore	7.6 cm	10.279 cm
Stroke	7.78 cm	8.598 cm
Displacement	0.36 ℓ	5.7 ℓ
Compression Ratio	18:1	22.5:1
Connecting Rod (Center to Center)	---	14.949 cm
Intake Valve Specifications		
Diameter	3.25 cm	4.763 cm
Opens (Degrees Crank Angle)	19.0° BTDC	---
Closes (Degrees Crank Angle)	35.0° BTDC	---
Exhaust Valve Specifications		
Diameter	2.62 cm	4.128 cm
Opens (Degrees Crank Angle)	49.0° BBDC	---
Closes (Degrees Crank Angle)	5.0° ATDC	---
Injection Timing	27° BTDC	---
Rated Power (Continuous)	4.45 bkW at 3000 RPM	89.5 kW at 3600 RPM
Rated Torque	---	298 N-m at 1600 RPM

Table 2 Baseline Fuel and Lubricating Oil Specifications

PROPERTIES OF BASELINE TEST FUEL

Fuel Type: MILF 46162 A Grade 2 Diesel
Manufacturer: Phillips Petroleum Company

<u>Physical and Chemical Properties</u>	
Gravity (°API)	35.9
Flash Point (°C)	70.0
Pour Point (°C)	-23.0
Cloud Point (°C)	-18.0
Viscosity (SUS) 38°C	34.2
Cetane No. (calculated)	47.5
Total Sulfur (Wt.%)	0.549
Aromatics (%)	36.5
Constant Pressure LHV(MJ/kg)	44.64
(Btu/lb)	19197.0
<u>Distillation Properties</u>	
Initial Boiling Point (°C)	191.0
10%	221.0
50%	254.0
90%	301.0
End Point (°C)	331.0
Recovery (%)	99.0

PROPERTIES OF TEST ENGINE LUBRICATING OIL

Oil Type: Shell Rotella T Premium Multipurpose HD

<u>Physical and Chemical Properties</u>	
Saybolt Viscosity at 38°C (SSU)	560.0
Saybolt Viscosity at 100°C (SSU)	67.0
Viscosity Index	98.0
Pour Point (°C)	-15.0
Sulfate Residue (Wt.%)	1.0
Neut. No. (TBNE)	7.0
<u>Quality Specifications</u>	
Meets	MIL-L-2104C
Exceeds	MIL-L-46152
	MIL-L-2104B
API Classification	CD,SE

Table 3 Selected Test Fuel Properties

Property / Fuel	API Gravity	Const. Press. LHV (MJ/Kg)	Mid Boiling Pt.(°C)	Pour Point (°C)	Density (Kg/ℓ)	Viscosity (cSt)
DF-2	35.9	44.64	254	-23	.85	3.8 @ 20°C
Ethanol	--	27.00	78+	--	.79	1.5 @ 20°C
Methanol	--	20.16	65+	--	.80	0.75 @ 20°C
SSO	24.4	37.08	317	-11	.92	64.7 @ 20°C
CSO	24.0	37.08	316	-4	.91	70.4 @ 20°C
SBO	24.2	37.08	319	-9	.93	64.3 @ 20°C
PO	22.4	39.24	317	0	.91	82.3 @ 20°C
MSSO	29.3	38.52	~320	-7	.88	7.2 @ 20°C
MSCO	29.0	38.88	~320	-2	.87	6.8 @ 20°C
DFM	37.9	42.60	264	-1	.84	2.71 @ 37.8°C
LSO	38.4	41.66	217	-53	.83	1.60 @ 40°C
SRC-II	12.3	38.17	245	-48	.98	3.68 @ 40°C
EDS	16.5	41.05	260	-24	.96	3.89 @ 40°C

+Boiling temperature at 1 atm.

References
1. Fuel Suppliers.
2. CRC Handbook of Chemistry and Physics 61st Edition (CRC Press Inc., Boca Raton, FL, (1981)).
3. Obert, E. F., Internal Combustion Engines and Air Pollution (Harper and Row Publishers, New York, (1973)).

3. For each test point, by fumigation substitute ethanol for the fuel oil such that the total energy input remained constant. For each point, the percentage of ethanol substituted was calculated on an energy basis. Ethanol substitution was limited by the occurrence of severe knock or severe combustion degradation.

4. Determine the biological activity of the exhaust soot using the Ames Salmonella typhimurium assay.

Using the stock fuel injection timing program that was built into the pump by the manufacturer, the baseline test matrix of Table 4 was established. The information within each cell of the baseline test matrix was determined by first running the engine at its rated condition of 120 horsepower at 3600 RPM. With the injection pump locked in place at this rated condition the dynamometer load was increased until an engine speed of 2000 RPM was reached and the fuel rate noted. Further dynamometer load increases permitted the 1720 and 1500 RPM fuel rates to be noted. The fuel rates so determined defined the full rack condition for each speed. By multiplying the full rack fuel flow rate at each speed by the appropriate fraction the nominal fractional rack settings were obtained.

A test was run by starting at the baseline condition shown in each cell of the test matrix. Ethanol was then substituted in increasing amounts for the baseline DF-2 until the engine either started to misfire badly or to knock severely. During any test run data were collected which permitted the efficiency, gas phase emissions, smoke opacity, and knock intensity to be evaluated. In addition, exhaust particulate matter was collected and the bioactivity of it and its soluble organic fraction (SOF) was assayed using the Ames Salmonella typhimurim test with $TA98^{-}$ bacteria.

Table 4 - Baseline Data Matrix for 5.7ℓ Oldsmobile Diesel Engine

Rack \ RPM	1500	1720	2000
1/4	12.8* 19.3 0.687 13212. 2813.	14.5 19.1 0.691 13259. 3208.	12.5 14.1 0.818 15710. 3265.
1/2	39.20 59.1 0.427 8205. 5360.	39.65 52.1 0.453 8702. 5751.	40.4 45.7 0.488 9366. 6302.
3/4	51.9 78.34 0.447 8588. 7433.	62.1 81.6 0.458 8797. 9098.	65.7 74.3 0.454 8704. 9535.
Full	57.2 86.3 0.492 9439. 8996.	68.2 89.7 0.475 9113. 10360.	77.5 87.7 0.457 8783. 11348.

* Data in each block is tabulated as follows:

bhp
bmep in PSI
bsfc in lbm fuel/bhp-hr
bsec (brake specific energy consumption) in btu/bhp-hr
Total fuel energy input in btu/min
Corrected to standard Atmospheric Conditions;

T= 540°R, P = 29.38 in. Hg

Figures 2 and 3 illustrate some of the experimental engine data that was obtained when ethanol was fumigated at the 1/2 rack and full rack conditions. On these figures a $(K_S)_f > 1.5$ represents severe knock and a smoke opacity of between three and four percent represents the point at which the exhaust plume becomes visible when viewed against a light background.

As was the case with methanol fumigation it was found that ethanol fumigation tends to enhance the bioactivity of the emitted exhaust particulate matter and its SOF. Figure 4 is an example of the power specific revertant enhancement that occurs upon ethanol fumigation of the multicylinder Diesel automobile engine. Table 5 summarizes the multicylinder engine particulate data.

The following conclusions were drawn from the data collected during the multicylinder engine ethanol fumigation tests:

1. At higher loads (all 1/2, 3/4 and full rack settings) ethanol fumigation increases thermal efficiency. However, since at these conditions engine operation becomes limited due to severe knock or roughness for ethanol substitution amounts in the 15 to 30% range, these efficiency gains are of small consequence in terms of stretching petroleum supplies.

2. For all conditions tested ethanol fumigation ultimately reduces brake specific NO_x to below its baseline-value. It is felt that the production of the relatively large volumes of NO_2 as compared to NO when fumigating with ethanol at the lower rack conditions influences the shape of the brake specific NO_x plots.

3. Ethanol fumigation, while reducing the mass of exhaust particulate, seems to enhance the biological activity of the particulate.

3.1.2 Single-Cylinder engine alcohol tests

In order to obtain detailed information pertaining to the combustion of alcohol fumigants, a single-cylinder DI Diesel engine study was conducted. In particular, there were some questions

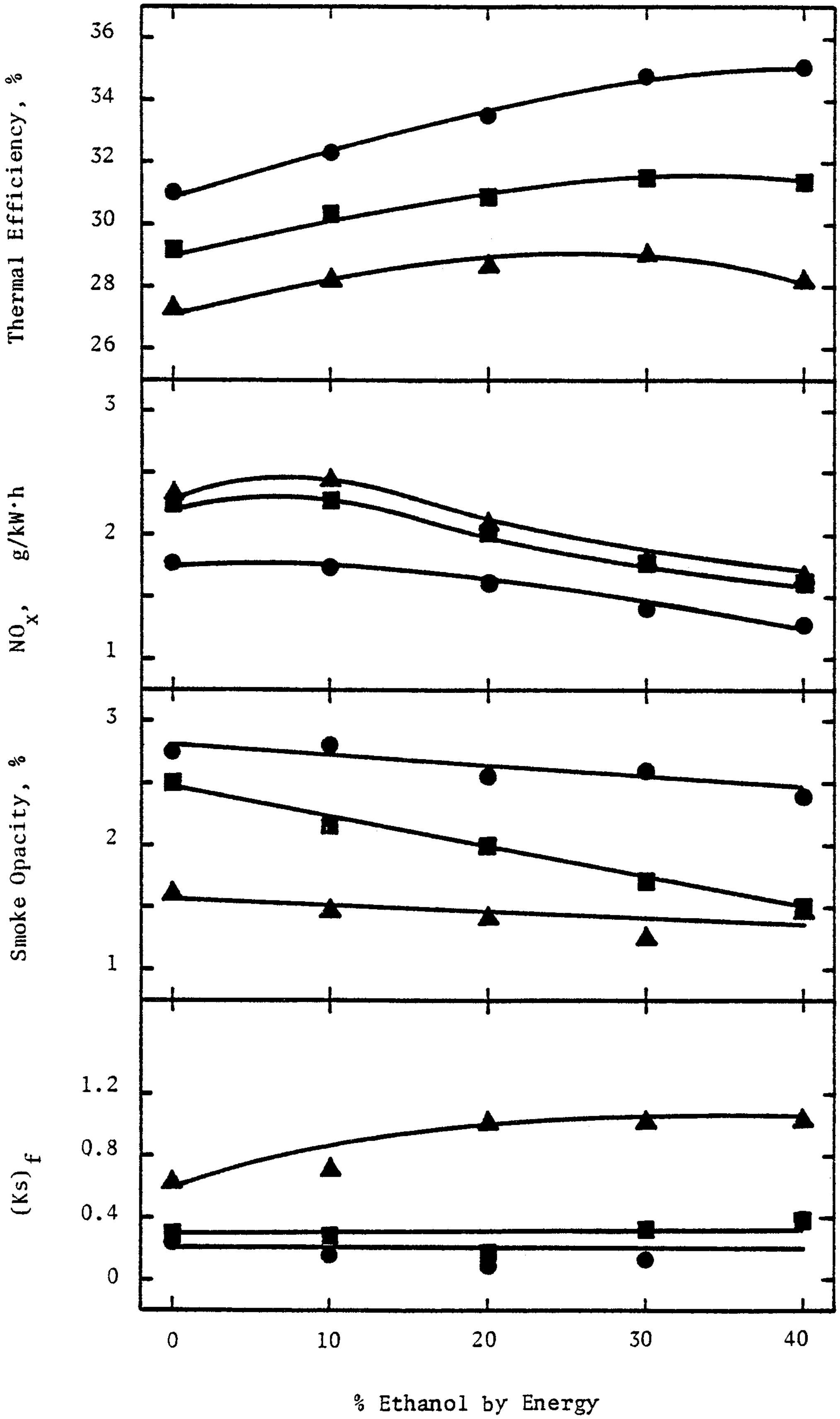


Fig. 2 - Fumigated Ethanol Results at 1/2 Rack for ●-1500 RPM, ■-1720 RPM, and ▲-2000 RPM. (5.7ℓ Oldsmobile Diesel Engine)

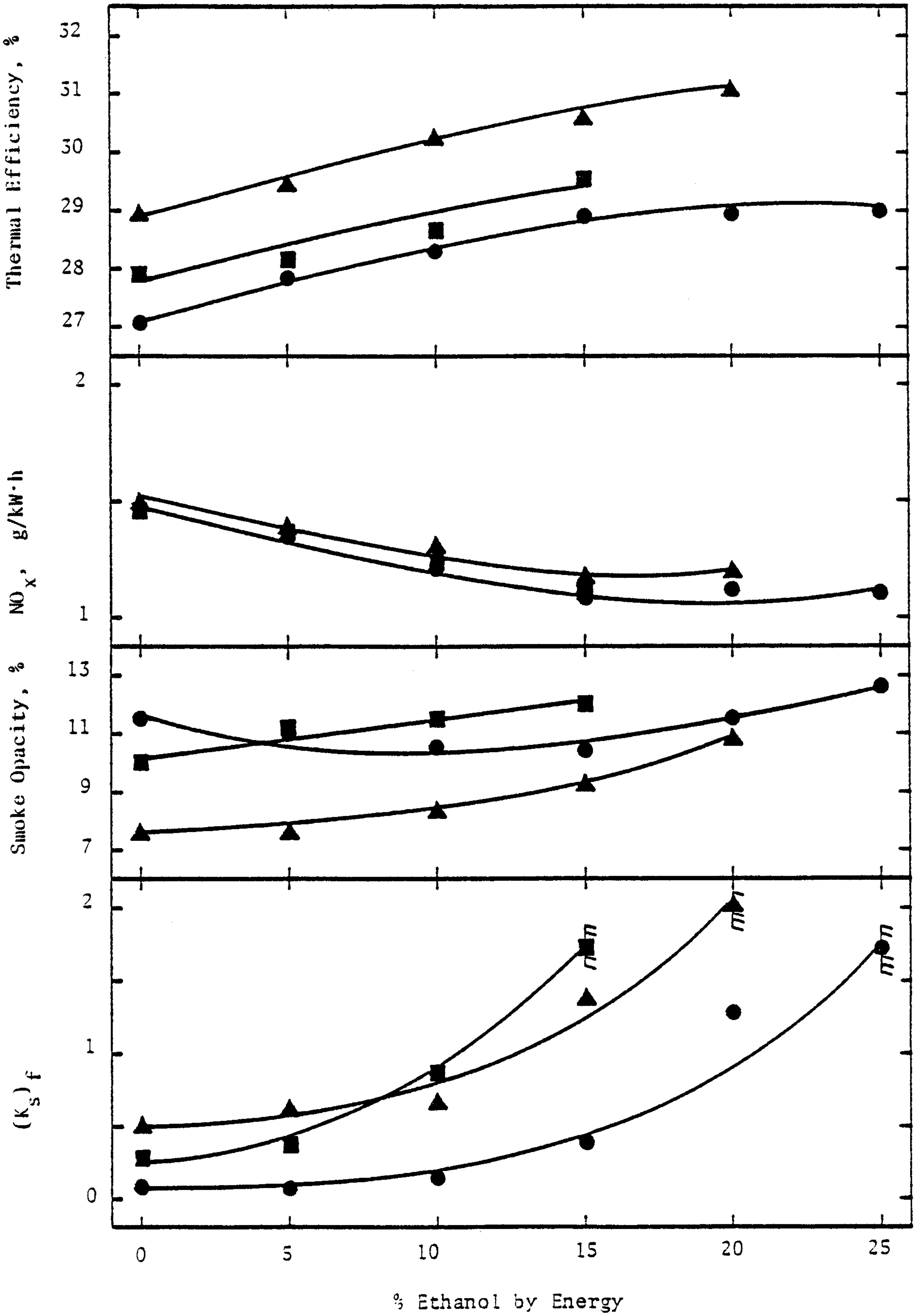


Fig. 3 - **Fumigated Ethanol Results at Full Rack for ●-1500 RPM, ■-1720 RPM and ▲-2000 RPM.** (5.7ℓ Oldsmobile Diesel Engine)

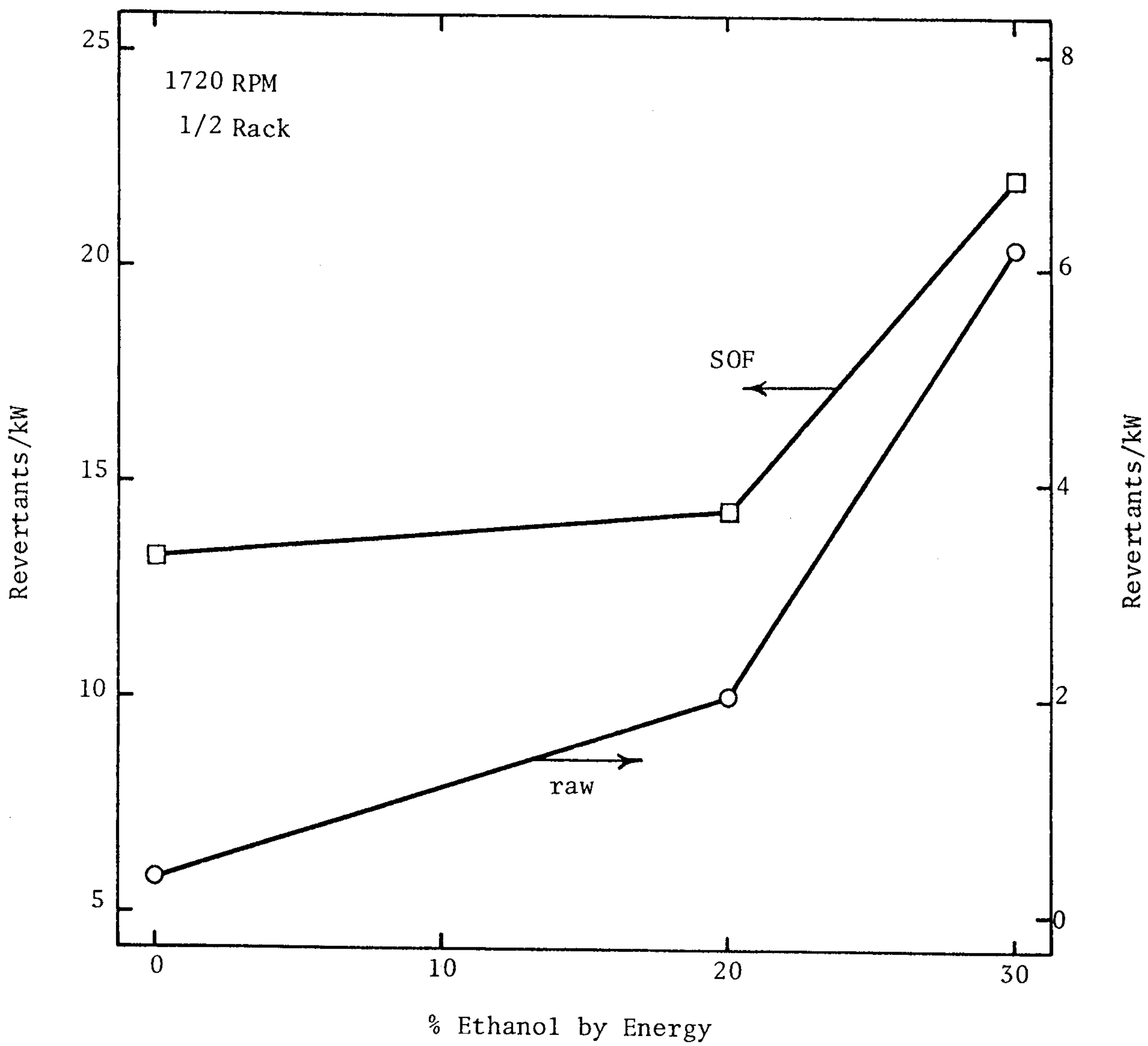


Fig. 4 - Power Specific Revertant Production for 250 μg/Plt Dose with TA98⁻. (5.7ℓ Oldsmobile Diesel Engine)

Table 5 - Summary of Particulate Data using Alcohol for the 5.7ℓ Oldsmobile Diesel Engine

RPM \ RACK	1/4	1/2			3/4	FULL
2000	3265.* 0 1.9392 56.81 0.29 ±0.02 2.9	6302. 0 1.7245 28.24 0.13 ±0.01 1.3 ±0.3	6302. 20 1.6452 43.07 0.4 2.7 ±0.2	6302. 30 1.7252 50.54 0.57 ±0.07 2.4 ±0.1	9535. 0 2.8300 6.63 NS+ 1.75 ±0.6	11348. 0 3.2250 6.18 NS 1.6 ±0.1
1720		5751. 0 2.5278 28.22 NS 1.35 ±0.05	5751. 20 1.9325 52.75 0.24 1.8	5751. 30 2.3450 59.90 0.7 3.1		
1500		5360. 0 2.7134 19.47 NS 2.2	5360. 20 2.2375 26.30 NS 2.8 ±0.2	5360. 30 2.4925 31.88 0.29 2.9		

* Data in each block is tabulated as follows:
- Total fuel energy input rate - btu/min
- Percent of total fuel energy input as ethanol
- Particulate deposition rate - mg/min
- SOF percent
- Ames Test Results, TA98, mean of slope ± stand. dev. (rev/μg)
- Raw
- SOF

+ NS - Not significant < 0.1 rev/mg

regarding the use of the lower quality ethanol that was beginning to be produced in farm stills around the country. While large commercial plants may easily produce ethanol with less than 5% water content (> 190 proof), the small farm-operated stills generally make a much lower quality ethanol whose water content is usually greater than 10% (< 180 proof). Since little knowledge existed concerning the performance of aqueous alcohol fumigants a comprehensive single-cylinder engine study was undertaken to provide such information. Complete details of this study appear in Refs. (7,8).

The specific objectives of the single-cylinder engine alcohol fumigation study were:

1. Establish a baseline matrix of engine operating conditions as defined by rack setting and engine speed. Document engine performance as well as exhaust emissions at these conditions for certified No. 2 Diesel fuel oil operation.

2. Develop and install instrumentation to provide information regarding injection timing, ignition delay, pressure, and rate of pressure rise for baseline and alcohol operation.

3. At each 2400 RPM test condition, fumigate various proofs of ethanol and methanol as limited by engine knock or misfire. Obtain for each operating condition, performance data including thermal efficiency and power output as well as regulated emissions data (CO, HC, NO_x).

4. For various test conditions, collect exhaust particulate to document the effects of alcohol fumigation on the biological activity of these solid phase emissions.

Table 6 is the baseline matrix established for the single-cylinder engine alcohol tests. The procedure followed to establish this baseline matrix was similar to that followed to establish the baseline matrix for the multicylinder engine. Here, each rack setting is the nominal appropriate fractional rate of the full rack energy input at the particular speed in question.

Table 6 - Baseline Data Matrix for AVCO-Bernard W51
Single-Cylinder DI Diesel Engine

Rack \ RPM	1800	2400	2800
Full	2.92 59.49 .559 31,304.	3.94 60.26 .572 43,317	4.50 58.94 .613 53,127.
2/3	2.08 42.35 .577 23,200.	2.84 43.50 .600 32,643.	3.30 43.24 .638 40,417.
1/3	.91 18.66 .847 14,885.	1.35 20.69 .847 22,027.	1.41 18.41 1.01 27,226.

Data in each matrix cell organized as follows:

BHP_c (horsepower)
BMEP (psi)
BSFC (lbm fuel/bhp-hr)
Energy input rate (Btu/hr)

Performance data corrected to
Standard Test Conditions
T=545°R (85°F)
P=29.38 in. Hg.

Full Rack Test Horsepower: 4.5 BHP_c @ 2800 rpm

Table 7 is an outline of the test program that was chosen for this aqueous alcohol study. At all fumigated alcohol test points, the total energy input rate to the engine was fixed at the value shown in the baseline matrix for the particular rack setting. Each test run started from the appropriate baseline condition and then subsequent test points were obtained by incrementally decreasing the DF-2 flow and substituting an energy equivalent amount of fumigated alcohol. Generally alcohol was substituted for the DF-2 in 10% energy increments until misfire was approached and then the increments were cut in half. A test run would be terminated by the occurrence of combustion quenching as manifested by severe misfire. It should be pointed out that this test procedure would invariably cause the engine to pass through a region of intense knock before the onset of misfire.

For comparison purposes, the methanol data and corresponding-proof ethanol data are presented together. This provides a basis for analysis of changes in engine efficiency, combustion intensity, and emissions during alcohol fumigation.

EFFICIENCY - Figure 5 is a comparison of the brake thermal efficiency results based on the lower heating value of the fuel. Note that these curves also represent the brake power trends because engine speed and energy input rate were held constant for each specific test condition. At all operating conditions, alcohol fumigation continued until severe engine misfire occurred; the last data point for each fuel and test condition represents the maximum amount of each proof alcohol fuel that can be substituted.

A general trend noted in the thermal efficiency data was the reduction in maximum possible alcohol substitution with lower rack

Table 7 Test Program Outline for the AVCO Lycoming Diesel Engine

Test Series	Rack	RPM	Alcohol Fuel	Alcohol Proof	% Alcohol Substitute
1	1/3				
	2/3	2400	-	-	0 (Baseline Only)
	Full				
2	1/3				
	2/3	2400	Ethanol	200	0 to Misfire Limit
	Full				
3	1/3				
	2/3	2400	Ethanol	180	0 to Misfire Limit
	Full				
4	1/3				
	2/3	2400	Ethanol	160	0 to Misfire Limit
	Full				
5	1/3				
	2/3	2400	Ethanol	140	0 to Misfire Limit
	Full				
6	1/3				
	2/3	2400	Methanol	200	0 to Misfire Limit
	Full				
7	1/3				
	2/3	2400	Methanol	160	0 to Misfire Limit
	Full				

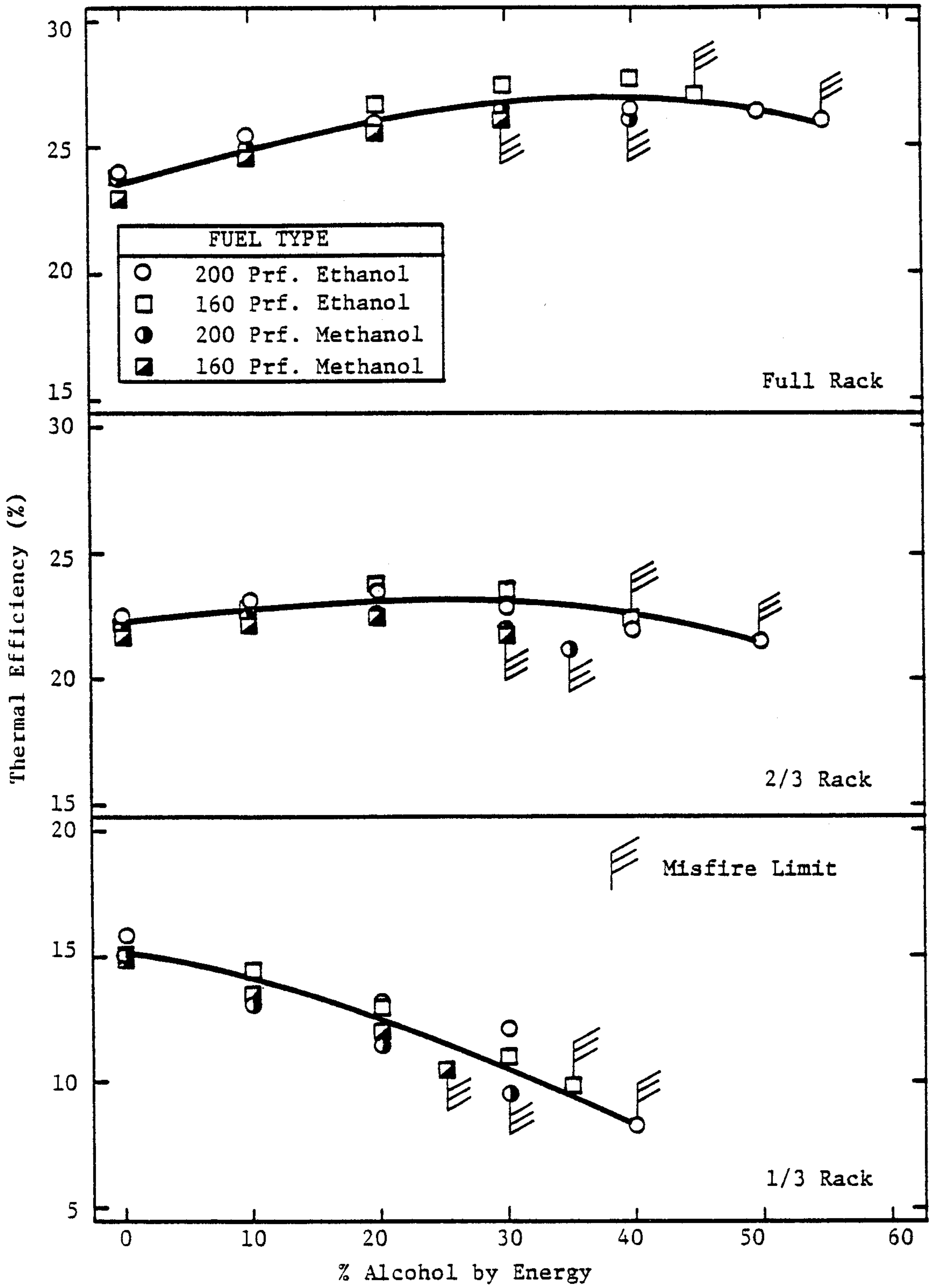


Fig. 5 – Comparison of Thermal Efficiencies for Ethanol and Methanol Fumigants at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

setting and higher water content; misfire due to combustion quenching was enhanced by the high heats of vaporization. The relatively higher latent heat of methanol compared to ethanol created combustion conditions that were significantly different - combustion quenching occurred at a much lower alcohol substitution quantity. This same effect was also observed as the amount of water in the fumigated alcohol was increased. These trends are illustrated in Figure 6. The similar behavior of 140 proof ethanol and neat methanol is also noted in this figure. The exact reasons for this similar behavior are not clear, however, calculations do verify the existence of a degree of correlation between the total latent heat of the fumigant and the maximum possible alcohol substitution level in each instance. The slight gains in thermal efficiency at the 2/3 and full rack settings with increased alcohol substitution are attributed to several factors. Increased ignition delays and large quantities of vaporized alcohol (inherent in fumigation) coupled to create rapid, nearly constant volume combustion near top dead center (TDC) - a more efficient process than typical Diesel combustion. Peak pressures were possibly increased by the rapid heat release and by the formation of more moles of products during alcohol combustion. Rapid rates of energy release and a less radiant flame may also have reduced heat loss from the engine. The pressure traces in Figure 7 illustrate these characteristics for the full rack condition.

COMBUSTION INTENSITY - The maximum rate of pressure rise and ignition delay data presented in Figures 8 and 9 show that increases in both of these parameters occurred during initial alcohol substitution. The continual ignition delay rise along with aural and quantitative

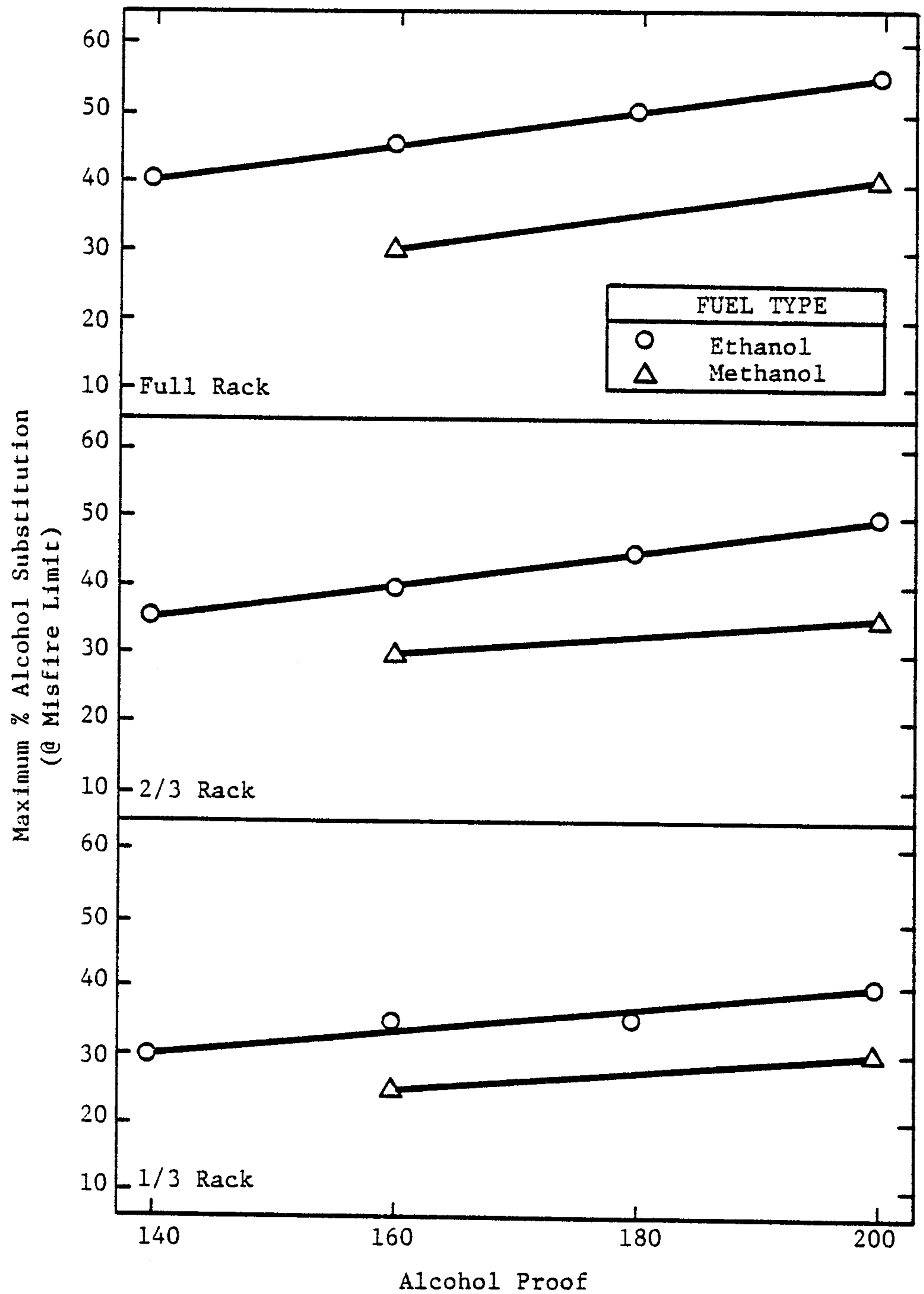


Fig. 6 – Maximum Percent Alcohol Substitution as a Function of Alcohol Proof at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

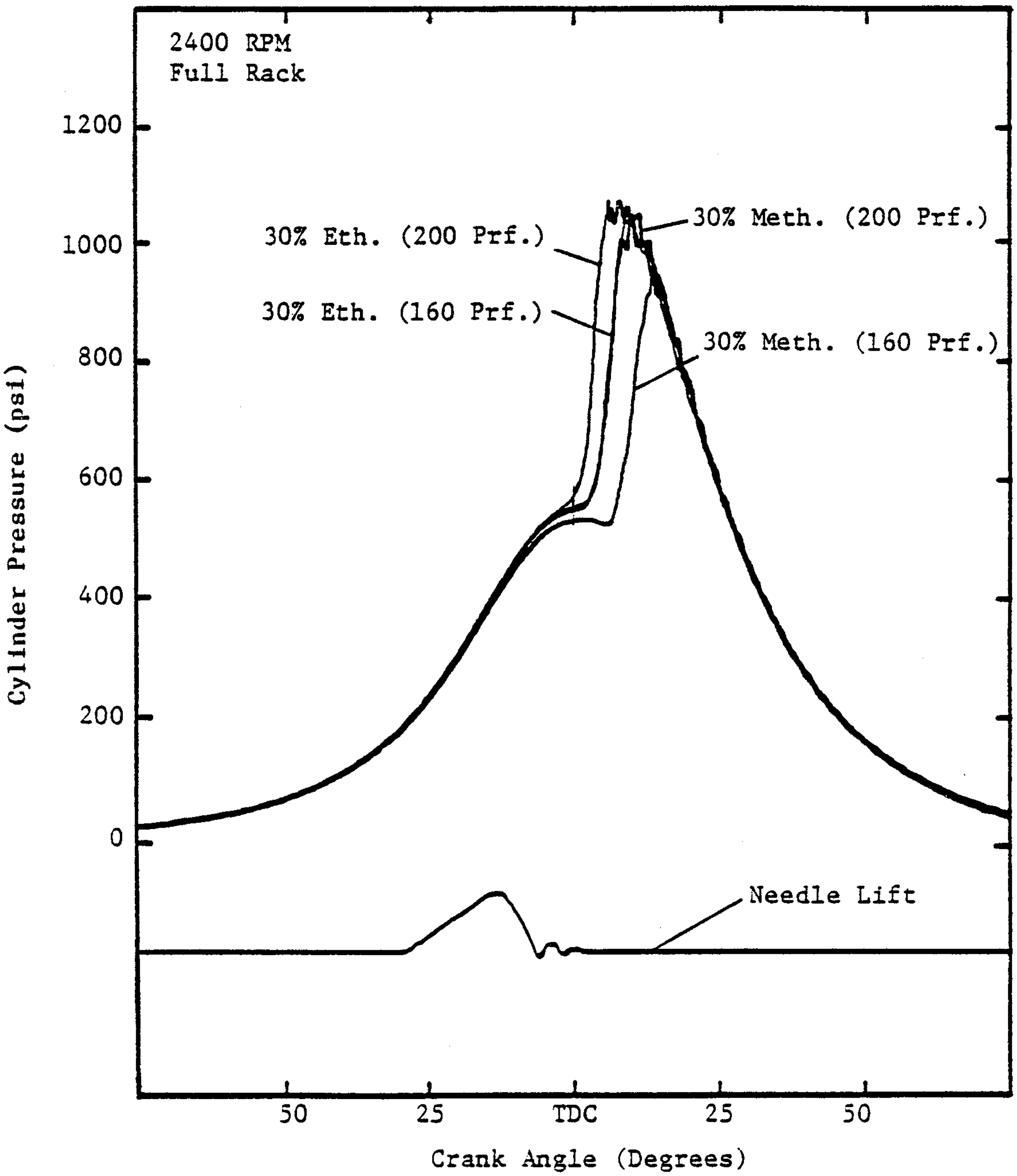


Fig. 7-Comparison of Pressure Histories for Various Proof Ethanol and Methanol Fumigants. (AVCO Lycoming Bernard Diesel Engine)

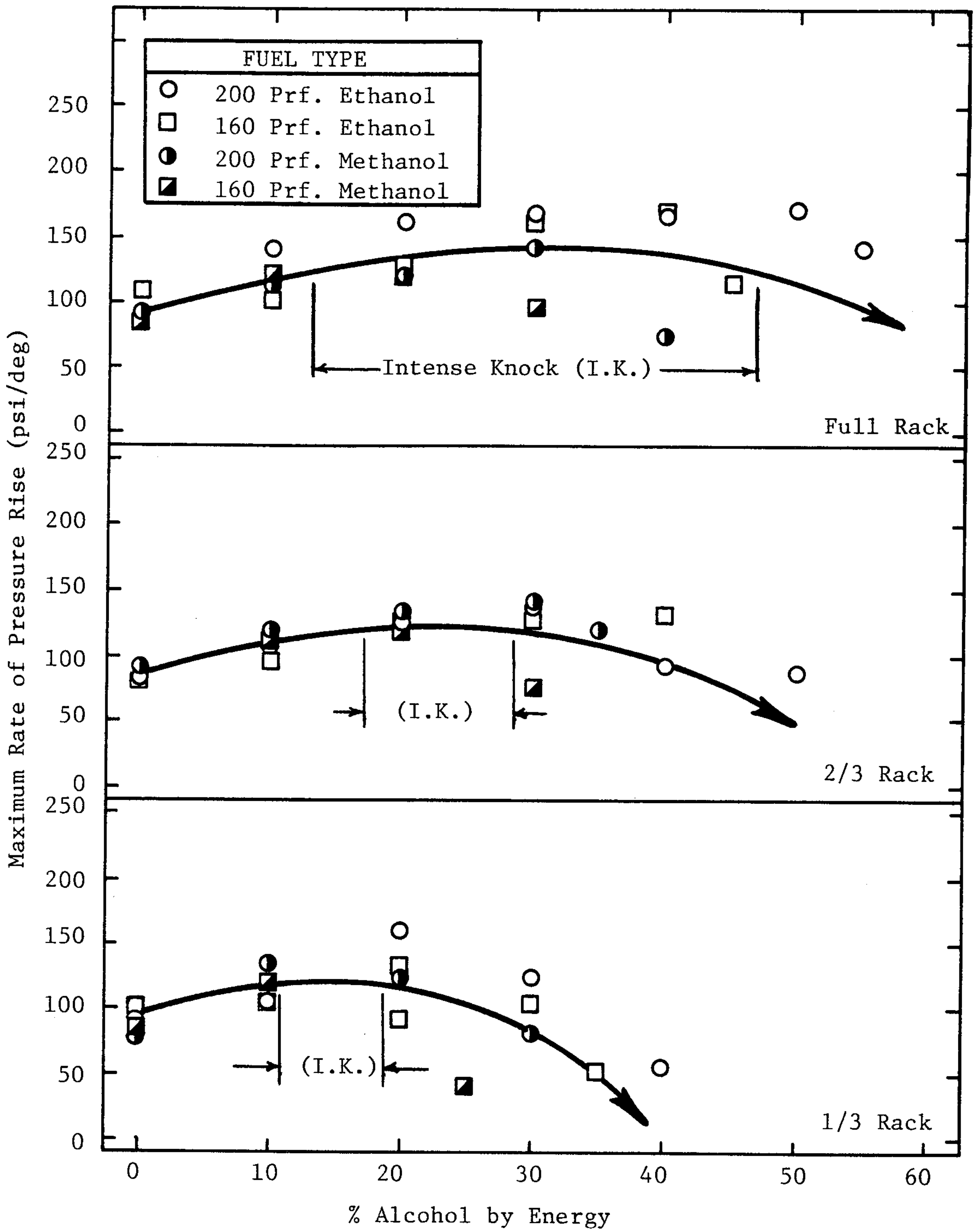


Fig. 8 - Comparison of Rate of Pressure Rise for Ethanol and Methanol Fumigants at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

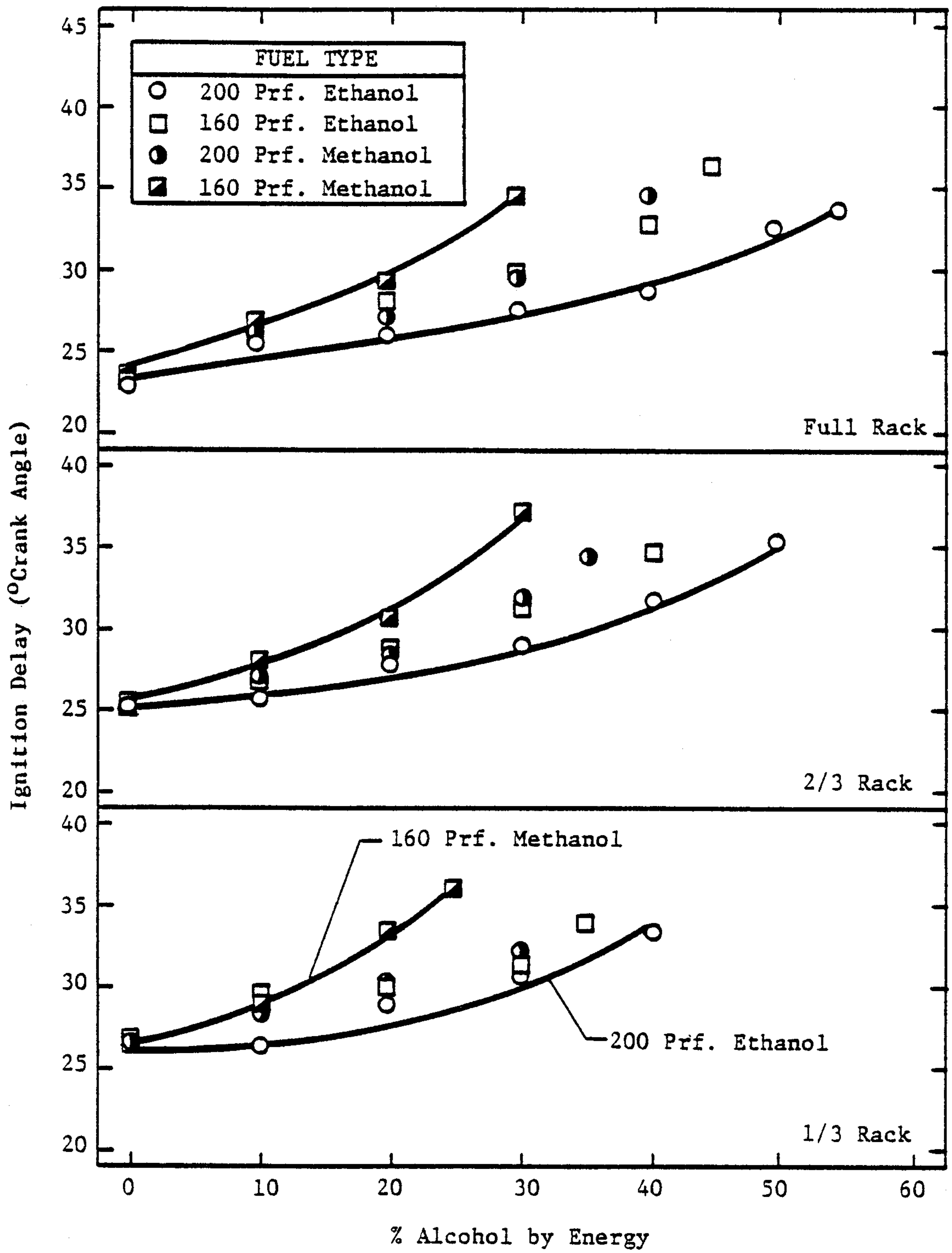


Fig. 9 – Comparison of Ignition Delays for Ethanol and Methanol Fumigants at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

measurement of knock (8) confirmed that combustion intensity increased at these alcohol fueled conditions.

Two characteristics of alcohol fumigation are responsible for the observed increase in combustion intensity:

(1) increased ignition delay resulting from the charge cooling of the vaporizing alcohol, and

(2) the presence of a vaporized, homogeneous alcohol fuel charge which ignites immediately as combustion starts.

The effect of both of these factors can be noted in Figure 7. Constant volume combustion near TDC occurred as high flame speeds enhanced combustion in the alcohol fuel charge. Correspondingly higher rates of pressure rise and peak pressure resulted.

However, peak pressure and rates of pressure rise declined below baseline values as the misfire limit was approached; a significant reduction in combustion noise accompanied these events. Autoignition delayed until well after TDC was responsible for the observed reduction of combustion severity.

EMISSIONS - As seen on Figure 10, exhaust levels of carbon monoxide increased with alcohol substitution at the 1/3 and 2/3 rack settings, but remained fairly constant at the full rack operating condition. An obvious rack (load) dependency is indicated by the data. As rack setting (and combustion temperature) increased, better air utilization due to the presence of a homogeneous alcohol charge may have lowered CO emissions. This effect, combined with higher combustion temperatures, would tend to minimize the increase in CO emission normally associated with increased alcohol fumigation. At the full rack setting, CO emissions remained constant or decreased

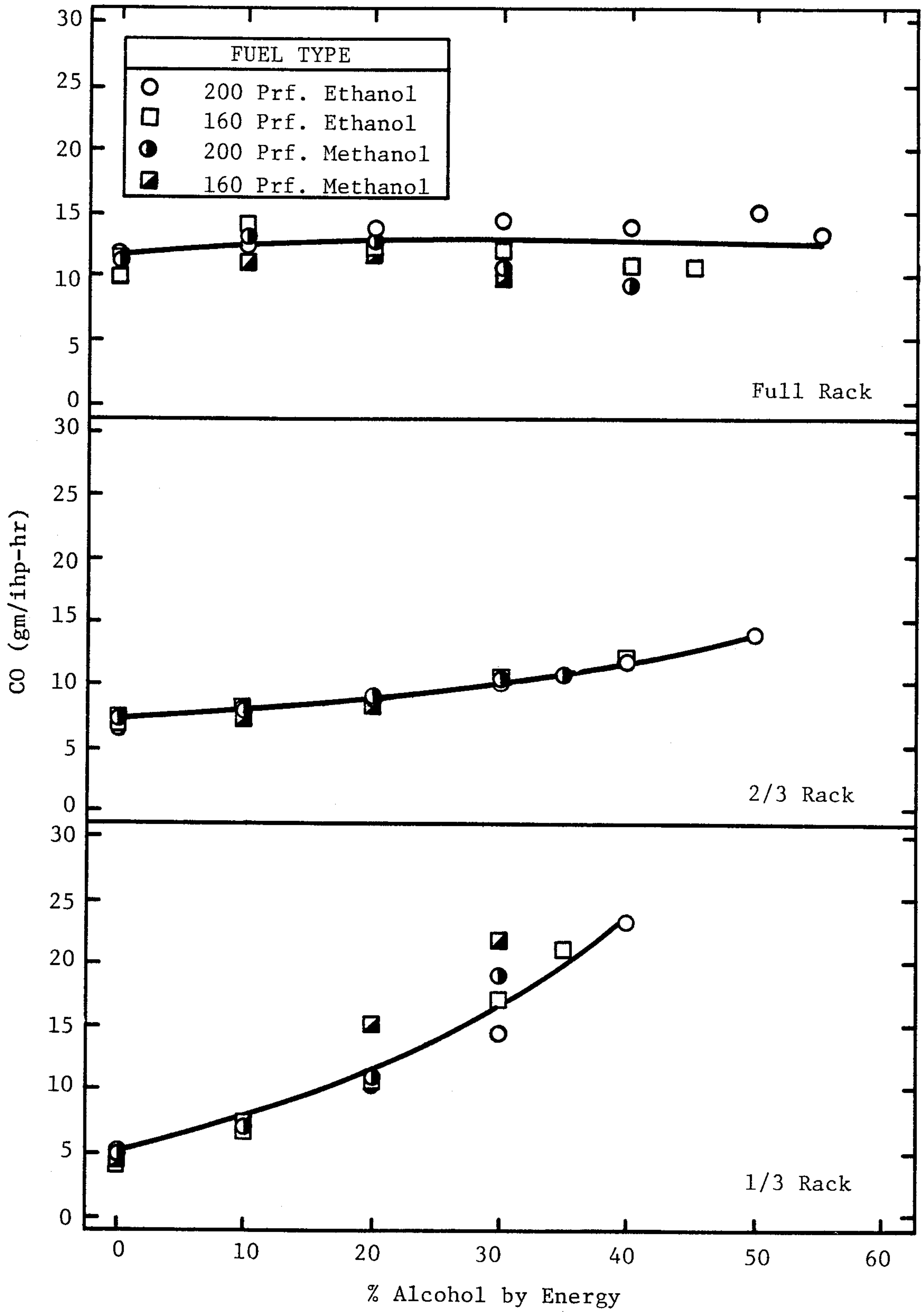


Fig. 10 - CO Emission as a Function of Fumigated Ethanol and Methanol at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

slightly; improved air utilization and a smaller quench effect apparently dominated at this condition.

Distinct differences in CO emission were not observed for ethanol and methanol; water content also did not appear to affect the emission levels of this pollutant. It was expected that combustion would be deteriorated due to the presence of water vapor in the combustion chamber and create higher CO emission levels.

Oxides of nitrogen results are presented in Figure 11. Here, NO_x emissions are observed to be dependent upon the water content and type of alcohol. As water content increased, the exhaust concentration of NO_x is observed to decline. Comparing ethanol and methanol in Figure 11, it is noted that 200 proof methanol has approximately the same effect on NO_x emission as 160 proof ethanol. Wet methanol (160 proof) produces a significant reduction in NO_x formation, especially when the amount of fumigated alcohol exceeds 15%. The relative difference in latent heats of vaporization of methanol and ethanol, and its effect on the degree of charge cooling probably help to cause this behavior. Similarly, increased water content of the alcohol should have depressed peak temperatures, explaining the relatively lower NO_x emission levels for the low proof alcohols.

Data indicating the dependence of rate of formation and biological activity of particulate emissions on baseline and ethanol fuels are presented in Table 8. Here, the mass loading rate of particulate emissions (gm/min) is observed to decrease as ethanol replaced the baseline fuel. Reductions of more than 70% of the baseline value occurred at some operating conditions.

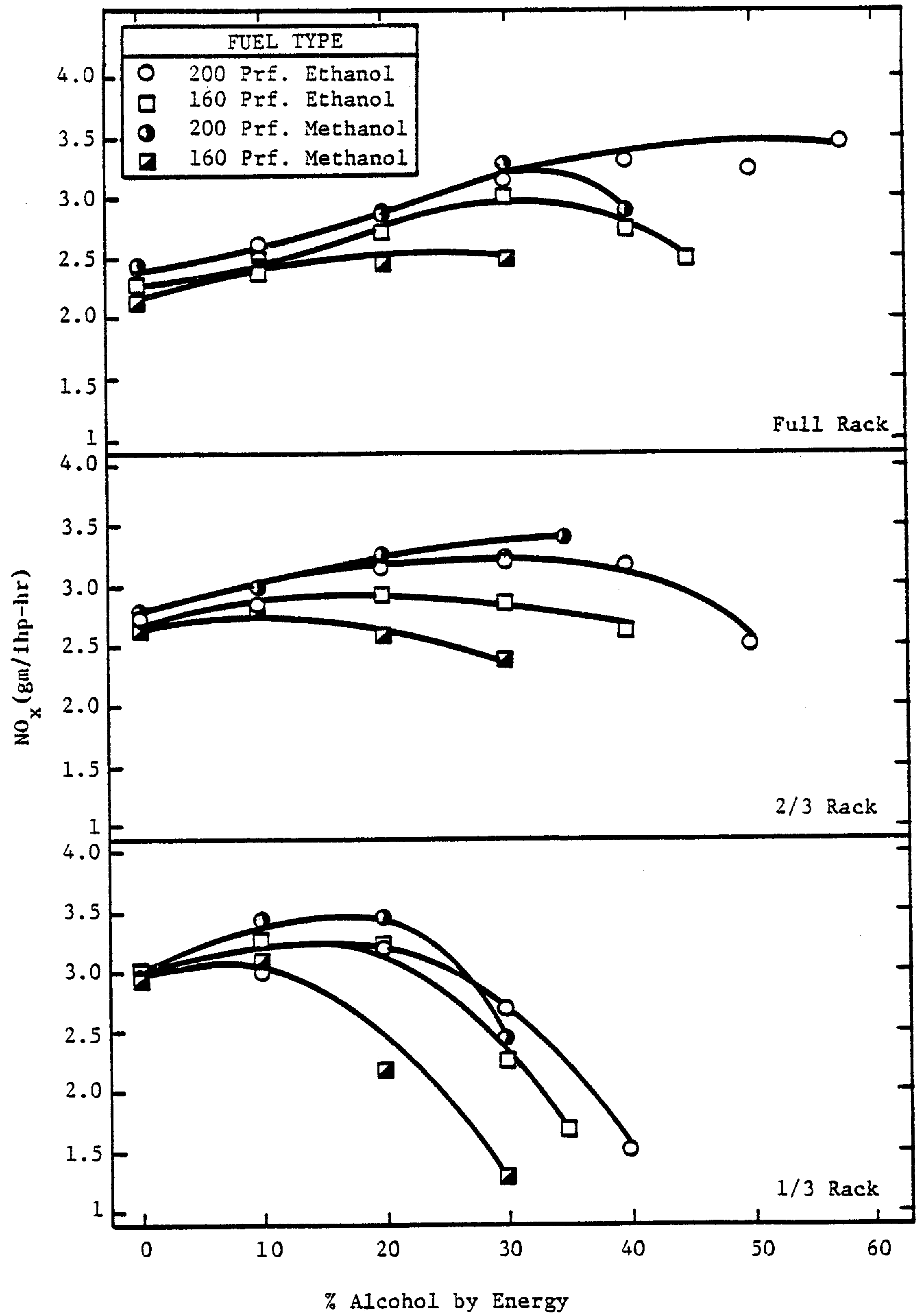


Fig. 11 – **Comparison of NO_x Emission for Ethanol and Methanol Fumigants at 2400 RPM.** (AVCO Lycoming Bernard Diesel Engine)

Table 8 - Summary of Particulate Data using Alcohol for the AVCO Lycoming Bernard Diesel Engine

Fuel \ Rack	1/3		2/3			Full		
200 Prf. Ethanol	22027. * 0. 3.06 41.7 1.12 8.9 ± .5	22027. 20. 2.68 61.9 - 4.6 ± .4	32643. 0. 7.21 20.0 .37 6.7 ± .7	32643. 20. 4.97 33.6 1.6 19.8 ± 3.5	32643. 40. 2.0 57.0 - 6.9 ± 1.1	43317. 0. 14.62 9.9 .11 5.5 ± 1.0	43317. 20. 10.18 7.3 .17 18.1	43317. 40. 5.14 23.1 .77 18.7 + 4.5
180 Prf. Ethanol	↓		↓	32643. 20. 5.07 28.1 - 21.7 ± 3.6		↓		
160 Prf. Ethanol	↓		↓	32643. 20. 5.69 53.9 - 10.1 ± 1.25		↓		
140 Prf. Ethanol	↓		↓	32643. 20. 5.38 43.1 - 6.9		↓		

*Data in each block is tabulated as follows:
- Total fuel energy input - Btu/hr
- Percent of total fuel energy input as ethanol
- Particulate deposition rate - mg/min
- SOF-percent
- Ames Test results, TA98, mean of slope ± stand. dev. (rev/μg)
  - Raw
  - SOF

The biological activity of the Diesel particulate as measured by the Ames *Salmonella typhimurium* test is also listed in Table 8. Both the raw particulate as well as the soluble organic fraction (SOF) for various racks, proofs, and percentages of alcohol were analyzed. It is of interest to see that ethanol appears to enhance the activity of both the raw particulate and its SOF so long as the engine is operating relatively far from its misfire point.

Very limited particulate analysis for methanol-fumigated conditions was performed in this phase of the work. As a result, a rigorous comparison of biological enhancement and mass loading rate for methanol and ethanol operation is precluded.

The experimental results obtained in this study permit the following conclusions to be made:

(1) Slight thermal efficiency improvements, resulting primarily from constant volume combustion of the homogeneous alcohol charge, are possible with limited alcohol fumigation (up to 30% by energy) at the 2/3 and full rack operating conditions. Alcohol type and quality (as low as 140 proof) have an insignificant effect on thermal efficiency up to the point of engine misfire.

(2) Fumigation of alcohol produces increased ignition delays; higher water content of the alcohol lengthens this delay period. Generally, the delay periods for methanol fuels are longer than those for corresponding proof ethanol fuels.

(3) Carbon monoxide formation increases during alcohol fumigation and shows a strong rack dependence. Water content and alcohol type have no significant effect on the emission of CO.

(4) Relative levels of NO_x emissions decrease with higher alcohol water content for all load conditions. Methanol fumigants generally produce lower NO_x emissions than do comparable proof ethanol fumigants.

(5) Particulate mass loading rates are reduced by ethanol fumigation. Limited biological analysis of this particulate indicates that ethanol fumigation increases the biological

activity, as measured by the Ames test, of the raw particulate and its soluble organic extract.

3.2 Vegetable Oil Tests

As the search for alternative motor fuels broadened in the late 1970's, interest developed in finding renewable fuel sources. Vegetable oils, which have received continuing attention among farmers as emergency fuels, are a renewable source of energy. Furthermore, the properties of vegetable oils made them best suited for Diesel engine use. Therefore, a single-cylinder Diesel engine study of four vegetable oils was conducted to evaluate their performance as Diesel fuels. Also, based upon this evaluation, the methyl esters of two of the oils, the one that was judged to have the best and the one that was judged to have the poorest overall performance were selected for further study. The full details and results of the single-cylinder vegetable oil tests are given in References 9-13. The procedure that was followed to make the methyl esters is found in Appendix A.

The specific objectives for the vegetable oil tests were set forth as follows:

1. Establish a baseline for the engine using a certified DF-2 at 2400 RPM and three load conditions.

2. At each load condition for sunflowerseed oil (SSO), methyl ester of sunflowerseed oil (MSSO), cottonseed oil (CSO), methyl ester of cottonseed oil (MCSO), Soybean oil (SBO), and peanut oil (PO), obtain performance data and gas-phase emission data for CO, HC, NO_x, and total aldehydes, as well as individual aldehyde concentrations from formaldehyde through heptaldehyde. Compare these data with that obtained for the baseline.

3. Collect exhaust particulate matter at each load condition to document the biological activity of the soluble organics extracted from these soid-phase emissions.

The same single-cylinder 0.36ℓ DI Diesel engine that was used for the aqueous alcohol work was used for the vegetable oil work. All tests were run at 2400 RPM at a fixed compression ratio and injection timing of 18:1 and 27° BTC respectively. The test matrix established for baseline and vegetable oil operation of the engine was:

Rack	bkw_c
1/3	1.12
2/3	2.24
Full	3.00

All performance data were corrected to standard test conditions of 302.4 K (29.4 C) and 1.0 bar.

The engine was fully instrumented so that strategic temperatures, injector needle lift, timing, and cylinder pressure could be measured. The outputs from the transducers were recorded on floppy discs using a Nicolet Explorer III digital memory oscilloscope. Further processing was carried out on an Apple II microcomputer to obtain peak pressure, the maximum rate of pressure rise, and ignition delay. In addition, the regulated gas phase emissions (CO, HC, and NO_x) were measured using the EPA specified analytical instruments by direct tailpipe sampling of the exhaust gases. Particulate samples were collected as shown on Figure 12 by passing the total exhaust gas stream over a 51 cm by 51 cm teflon-coated glass-fiber filter placed into a stainless steel filter holder.

Since vegetable oils contain oxygen, their combustion in an engine could lead to relatively high concentrations of aldehydes when compared to those from DF-2. It was for this reason that one objective of this study was to measure exhaust aldehydes. The aldehyde collection system

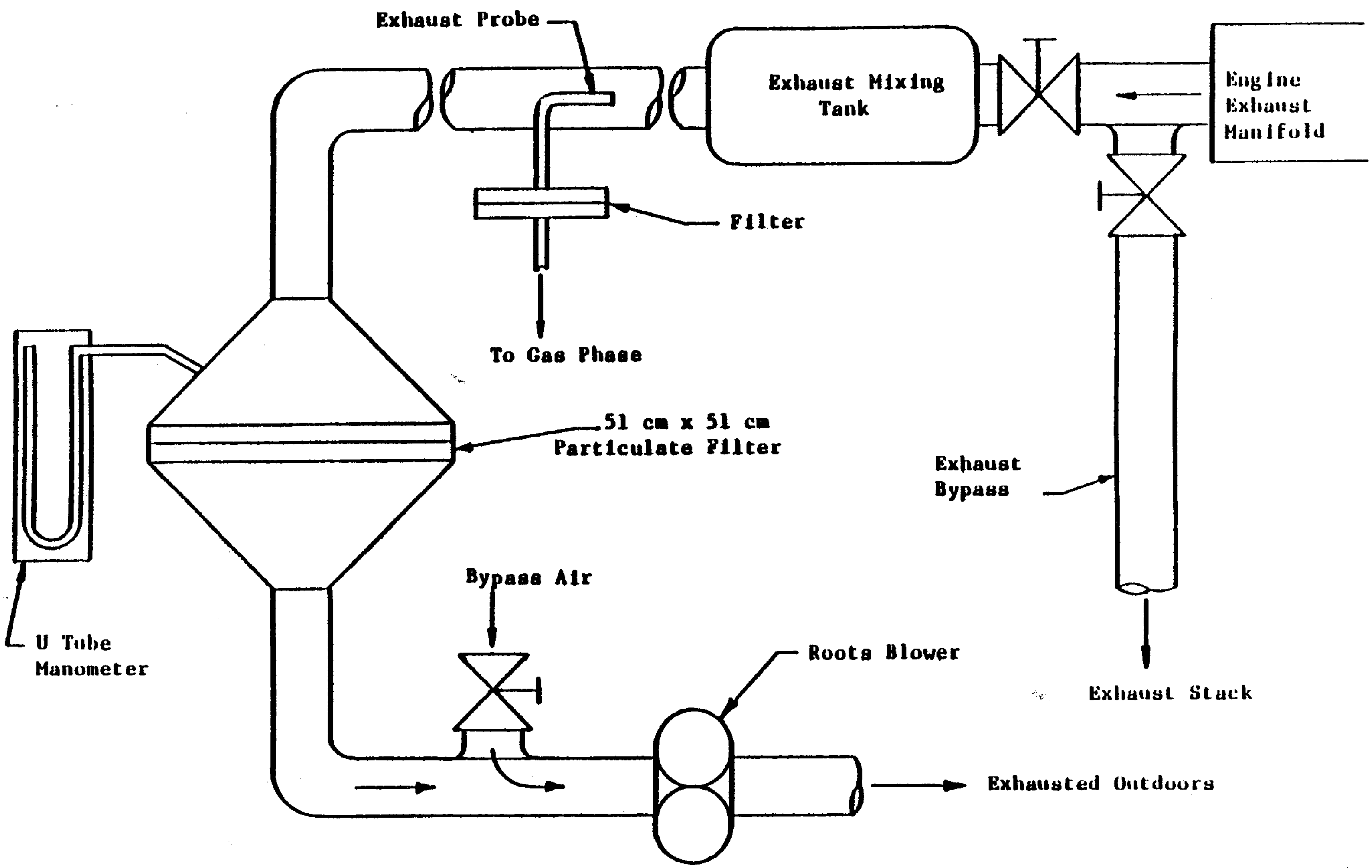


Fig. 12- Exhaust Sampling and Particulate Matter Collection System.
(AVCO Lycoming Bernard Diesel Engine)

is shown in Figure 13 and some of the details of the procedure are given in Appendix B.

Here, for comparison purposes, selected data for two neat vegetable oils and their methyl esters are presented, along with the baseline DF-2 data. It should be pointed out that based on overall performance SSO was judged to be the best neat vegetable oil and CSO the poorest neat vegetable oil. It was for this reason that the methyl esters of these two oils were selected for this comparative study.

Typical comparative pressure and needle lift traces are shown in Figure 14. In general, the combustion was more severe with the methyl esters than with the neat vegetable oils. Figure 15 shows the brake thermal efficiency (BTHEFF) and ignition delay)IGNDLY) data. For clarity, the vegetable oil values are presented as averages and ranges. The BTHEFF for the neat vegetable oils were slightly improved when compared to the DF-2 baseline. The BTHEFF for the methyl ester vegetable oils were approximately equal to the DF-2 baseline. The IGNDLY for the neat vegetable oils and their methyl esters were generally shorter when compared to the DF-2 baseline. The reduced viscosity and improved spray characteristics resulting from the esterification process are the probable cause for the shorter IGNDLY for the esterified vegetable oils at 1/3 rack and 2/3 rack when compared to the neat vegetable oils. However, at full rack, the shorter IGNDLY observed for the neat oils are probably caused by increased combustion temperatures resulting in better atomization of the neat oils; the esterified oils are probably limited in their combustion characteristics by the radicals which are added during the

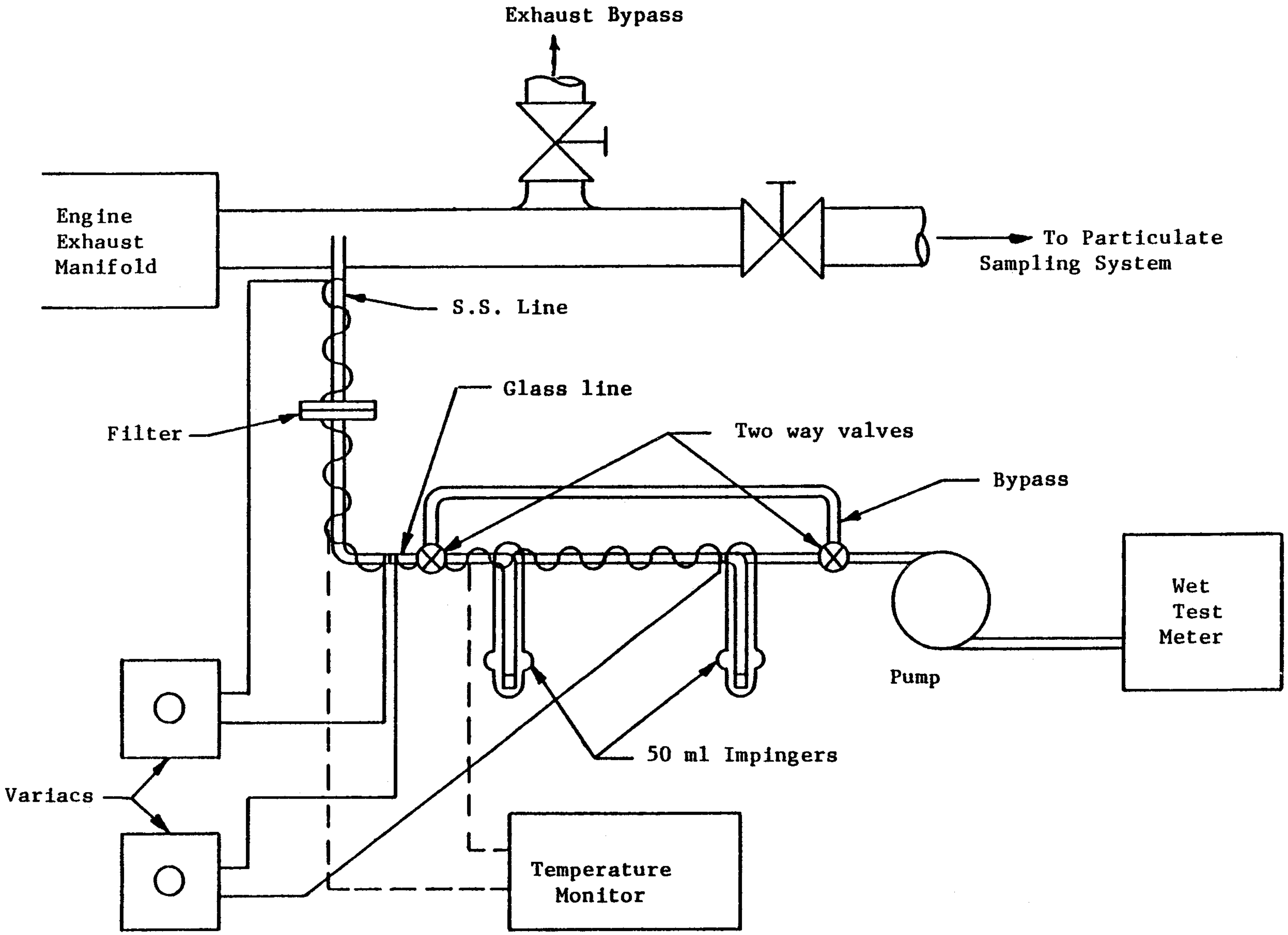


Fig. 13 - Aldehydes Sampling System. (AVCO Lycoming Bernard Diesel Engine)

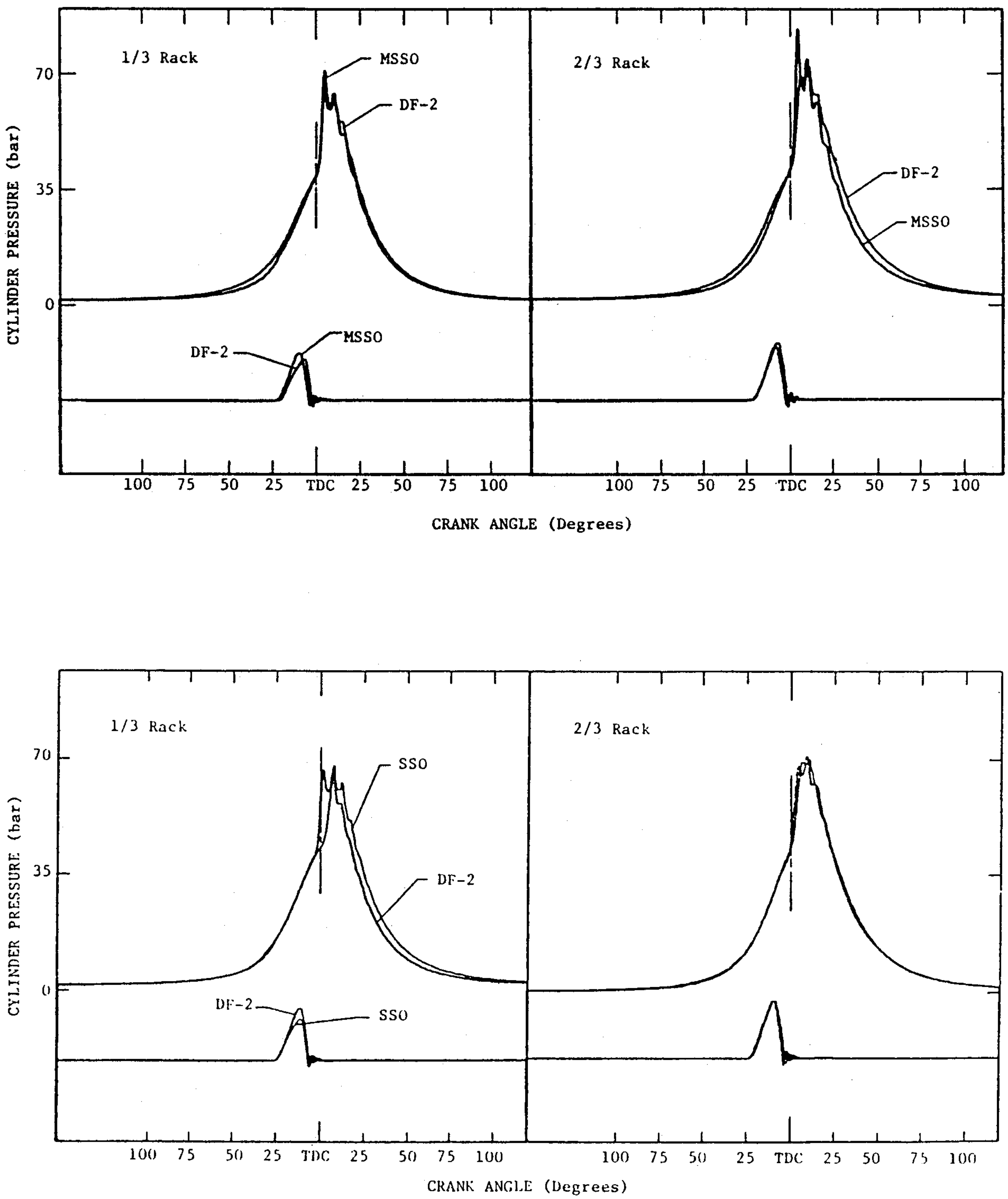


Fig. 14- Comparative Pressure and Needle Lift Histories for Number 2 Diesel Fuel (DF-2), Sunflowerseed Oil (SSO), and Methyl Esters of Sunflowerseed Oil (MSSO). (AVCO Lycoming Bernard Diesel Engine)

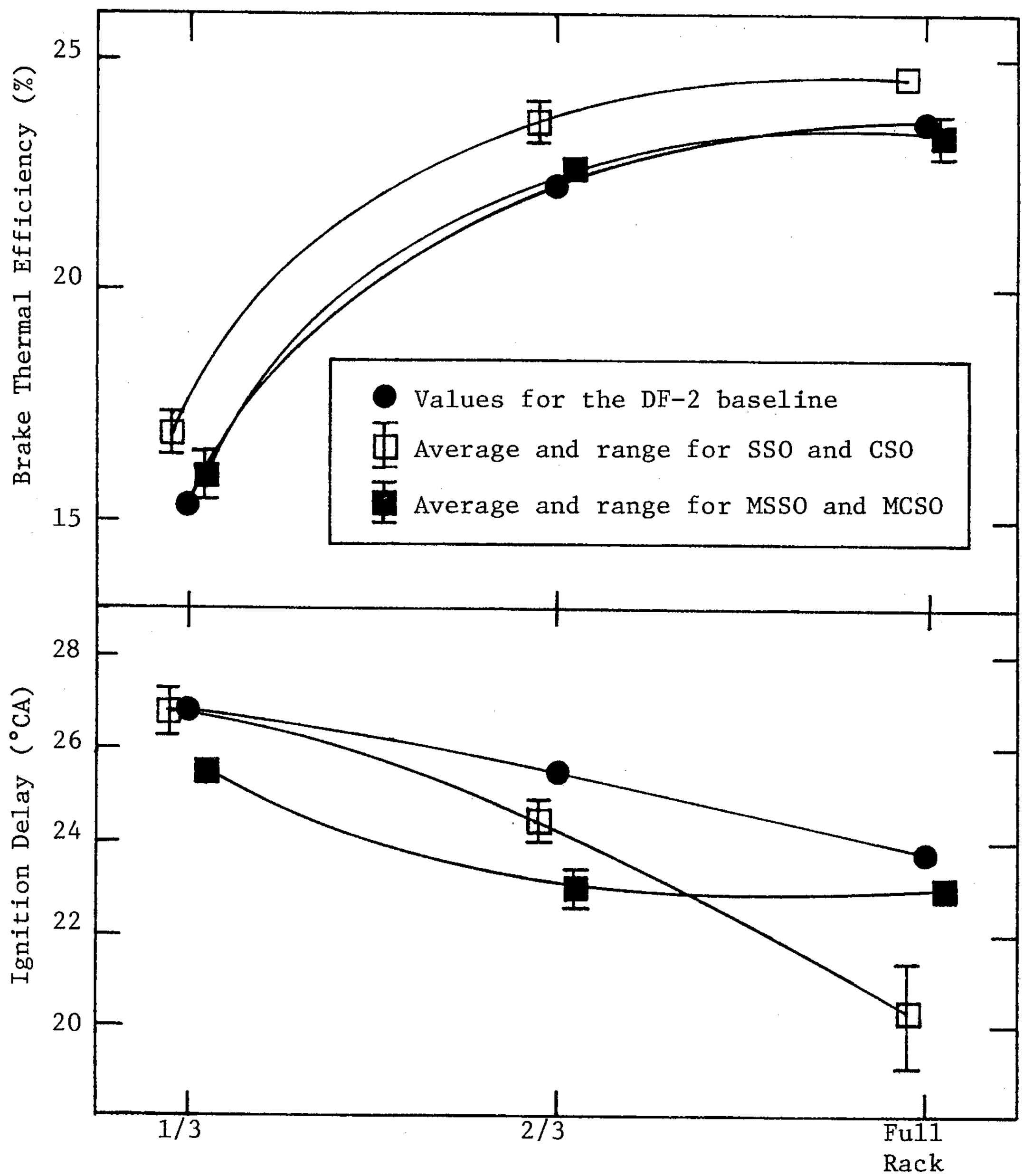


Fig. 15- Brake Thermal Efficiency and Ignition Delay as a Function of Rack at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

esterification process, causing very little change in the IGNDLY of the esterified oils from 2/3 to full rack.

Shown in Figure 16 is a comparison of normalized exhaust emission data. The subscript V indicates the vegetable oil or methyl ester data and the subscript D indicates the DF-2 data. The reduced data for the baseline condition is presented in Appendix C. The unburned hydrocarbons and carbon monoxide emissions generally decreased with rack and converged to the DF-2 value at full rack. However, the MSSO had significantly higher carbon monoxide emissions at the full rack setting. The response of the unheated flame ionization detector to oxygenated compounds present in vegetable oils is not known; therefore, unburned hydrocarbon data presented should only be used as a trend indicator. Generally, oxides of nitrogen emissions of the vegtable oils and their methyl esters increased with rack and were significantly higher at full rack when compared to DF-2. The oxides of nitrogen for MSSO were also significantly higher at 1/3 rack. The composition and structure of vegetable oils was the probable cause for the overall increase in gas-phase emissions as compared to DF-2.

Shown in Table 9 is a summary of particulate and total aldehyde data. The particulate deposition rates for the neat vegetable oils were higher than the DF-2 values at all conditions except SSO at full rack; the particulate deposition rates of the methyl esters were lower than the DF-2 values for all conditions tested. The soluble organic fractions (SOF) from the particulate matter for all the vegetable oils were comparable to the DF-2 values, except for the neat vegetable oils at full rack where the SOF were much lower than the DF-2 values. The Ames Test values for particulate matter from the neat vegetable oils

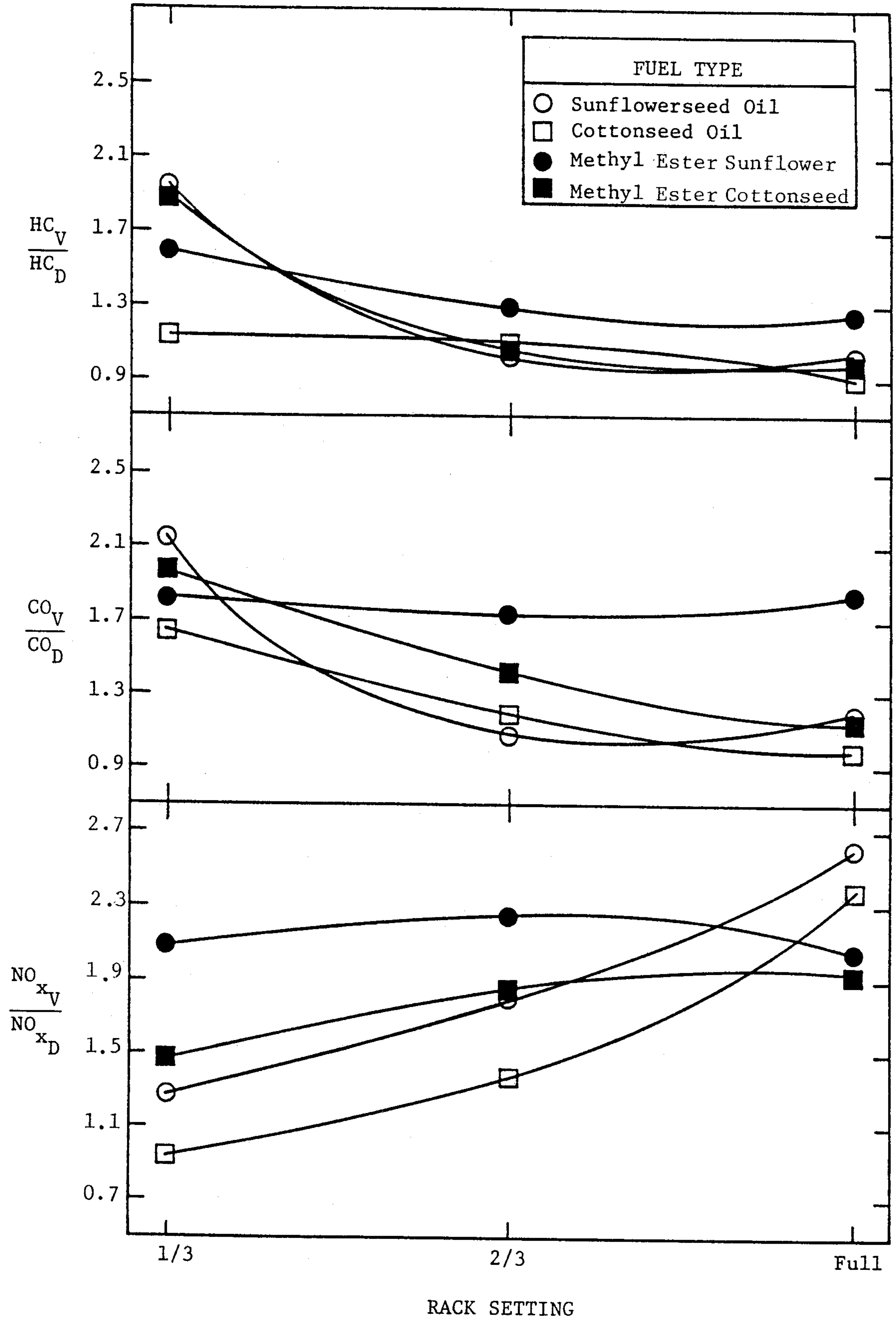


Fig. 16 - Comparison of Normalized Gaseous Exhaust Emission Data at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

Table 9 - Summary of Particulate and Total Aldehyde Data using Vegetable Oils for the AVCO Lycoming Bernard Diesel Engine

Rack \ Fuel	DF-2	SSO	MSSO	CSO	MCSO
1/3	23924 109 79 1.54 2280 53.7	22967 129 80 0.29 580 677.5	24233 98 87 0.19 310 404.2	25064 144 81 0.57 1270 284.1	22717 77 73 0.79 840 658.8
2/3	35432 173 62 1.88 2850 61.8	33759 197 68 0.61 1150 504.6	35838 129 68 0.48 600 475.0	34395 182 53 0.42 560 323.2	32467 105 54 0.93 750 417.4
Full	44128 271 44 1.55 2160 73.6	41914 226 19 0.63 330 336.5	43774 218 47 0.63 780 578.2	41575 333 20 1.00 820 325.6	43227 147 35 1.47 880 521.9

*Data in each block is tabulated as follows:
Total energy input (kJ/hr)
Particulate deposition rate (mg/min)
SOF - percent
Ames Test TA98 mean slope at 100 (rev/μg)
Indicated specific revertants (kRev/ikW-hr)
Total Aldehydes (mg/ikW-hr)

and their methyl esters were consistently lower than the Ames Test values for the DF-2. For the purposes of comparison, the indicated specific revertants for each condition are shown graphically in Figure 17. For clarity, the averages and ranges of the vegetable oil data are shown together with the baseline DF-2 curve. The indicated specific revertants were similar for the neat vegetable oils and their methyl esters, with the methyl esters slightly lower at 1/3 and 2/3 rack and the neat oils slightly lower at lower rack. In all cases, the vegetable oils had indicated specific revertants which were significantly lower than the DF-2 values.

The total aldehydes are also shown graphically in Figure 17. As for indicated specific revertants, the averages and ranges of the vegetable oil data are shown together with the baseline DF-2 curve. Total aldehydes show a dramatic increase with the vegetable oils when compared to DF-2. The primary reason for this result is most likely enhanced aldehyde formation because of oxygen which is contained in the vegetable oils. The DF-2 aldehydes increased with rack setting, consistent with the observed increase in unburned hydrocarbons; the vegetable oils did not follow this trend. Bar graphs of individual aldehydes from formaldehyde through heptaldehyde are presented in Figure 18 as a function of fuel and rack.

A good indicator of formaldehyde trends seems to be the percent of the total aldehydes which is formaldehyde. A graph of the percent formaldehyde by weight for DF-2, together with the averages and ranges of vegetable oil data, is presented in Figure 19. With few exceptions, the weight percentage of formaldehyde from all fuels increased with rack setting. This observation likely resulted from the increased

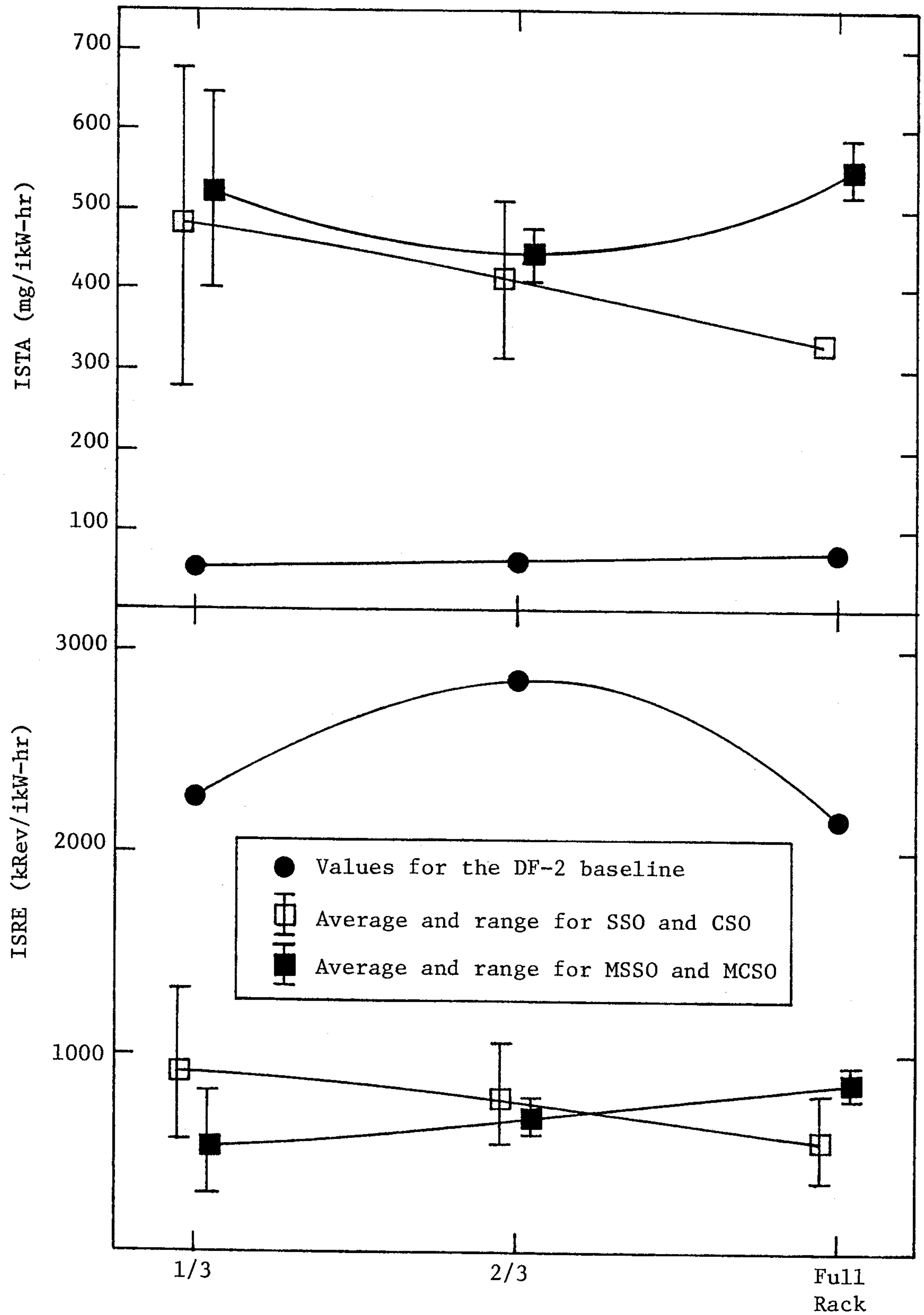
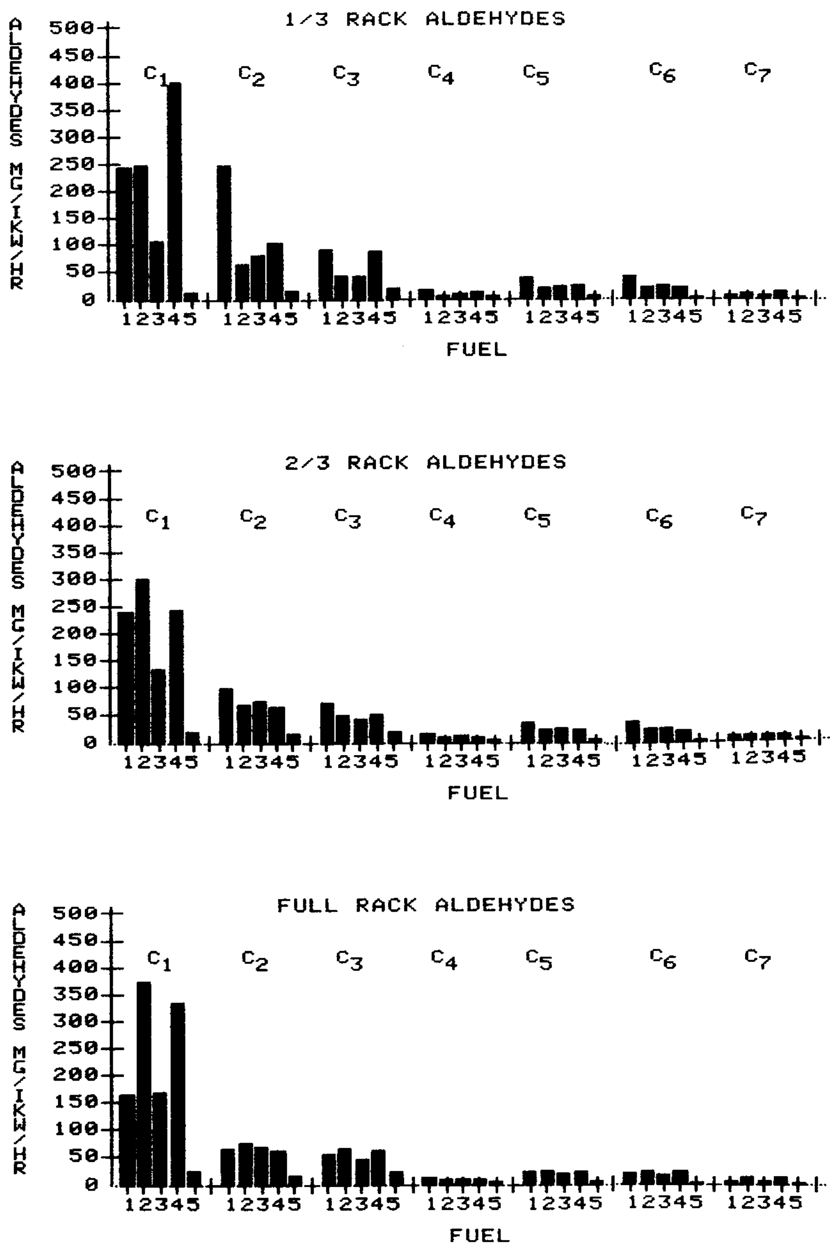


Figure 17- Indicated Specific Total Aldehydes and Indicated Specific Revertant Emissions as a Function of Rack at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)



LEGEND

C_1 - Formaldehyde C_2 - Acetaldehyde C_3 - Acetone

C_4 - Butyraldehyde C_5 - Valeraldehyde C_6 - Hexaldehyde

C_7 - Heptaldehyde

1 - SSO 2 - MSSO 3 - CSO 4 - MCSO 5 - DF-2

Fig. 18 - Bar Graphs of Individual Aldehydes as a Function of Fuel and Rack at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

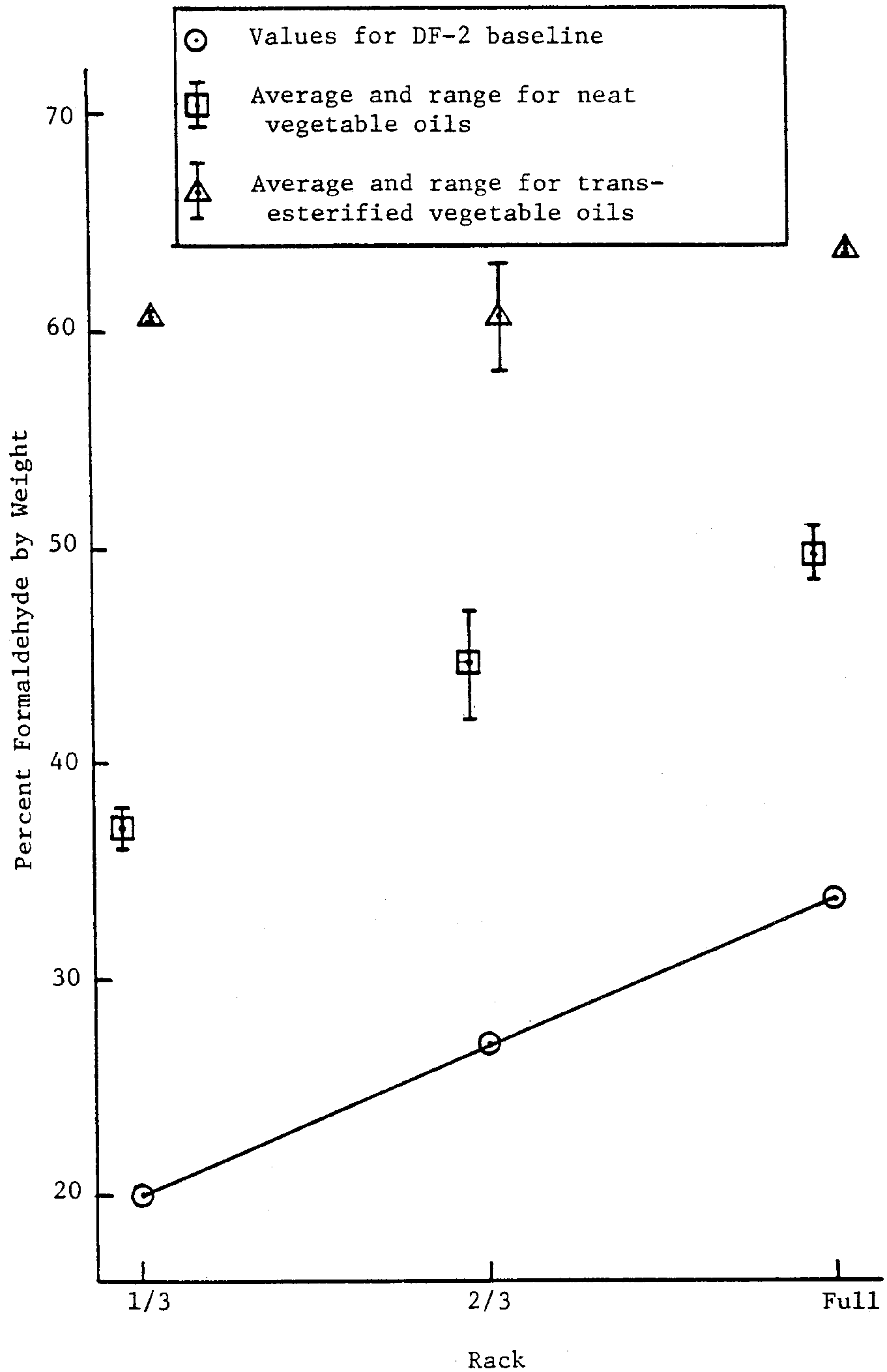


Fig. 19 - Percent Formaldehyde by Weight as a Function of Rack at 2400 RPM. (AVCO Lycoming Bernard Diesel Engine)

combustion temperatures with rack setting. The curve also shows that the percentage of formaldehyde was clearly higher for the vegetable oils when compared to DF-2, and still higher for the transesterified vegetable oils. This must be a result of different fuel structures, since all other variables were essentially constant.

Almost without exception, the weight percentage of individual aldehydes from the vegetable oils decreased with increasing molecular weight of the aldehydes. The major exception to this observation for the vegetable oils was butyraldehyde, which consistently had the second lowest or the lowest value of all the aldehydes. The DF-2, on the other hand, had a consistent decrease in the weight percentage of each aldehdye from acetone through heptaldehyde. The neat vegetable oils had a significantly lower percent butyraldehyde than did the DF-2, while the transesterified oils had an even lower percent than the neat vegetable oils.

From the data collected in the performance of the single-cylinder Diesel engine vegetable oil tests the following conclusions were drawn:

1. The neat vegetable oils appear to yield a slightly higher brake thermal efficiency than either their methyl esters or DF-2 which are about equal (see Figure 15).

2. Generally, the gas-phase emissions for the vegetable oils tested are slightly higher than the values for DF-2 (see Fig. 16). The NO_x is significantly higher for the methyl esters at all rack settings and for the neat vegetable oils at 2/3 and full racks.

3. With the exception of SSO at full rack, the neat vegetable oils had higher particulate mass loading rates than DF-2 and the methyl esters had lower particulate mass loading rates than DF-2 (see Table 9). The SOF for all the vegetable oils were comparable to the DF-2 values except for the neat oils at full rack.

4. According to Figure 17, the indicated specific revertants are much lower at all load conditions for the neat vegetable oils and their methyl esters than for DF-2.

5. As evidenced by Figure 17, total aldehydes increased dramatically with the vegetable oils when compared to DF-2; the averages of the methyl esters were slightly higher than the neat oils, with the difference most pronounced at full rack.

6. Figure 19 shows that the percent formaldehyde for the vegetable oils was consistently higher than the DF-2 values, and the values for the methyl esters were consistently higher than the neat oils. In general, the percent formaldehyde increased with rack setting.

3.3 Tests of Shale and Coal Derived Fuels

Several synthetic fuels derived from shale and coal were evaluated with respect to a reference petroleum-based Diesel fuel. Tests conducted using the V-8 Oldsmobile IDI Diesel engine and the single-cylinder DI Diesel engine were designed to quantitatively compare the fuels on the basis of performance, combustion characteristics, gaseous emissions, particulate emissions, and biological activity of the solid phase soluble organic fraction. The biological activity was assessed using the Ames *Salmonella typhimurium* test.

The shale fuels studied were a Paraho marine Diesel fuel (DF-M) and a light shale oil (LSO) condensate received from Occidental Petroleum Corporation's Logan Wash Colorado *in situ* retorting operation. The coal liquids, Solvent Refined Coal-II (SRC-II) and Exxon Donor Solvent (EDS), were products of two separate coal liquefaction techniques which utilize an in-process derived hydrogen donor solvent. These fuels could not be run neat; therefore, they were blended 20% and 40% by volume with the baseline DF-2.

In this section the results of the multicylinder screening tests will be given first followed by the results of the more comprehensive single-cylinder engine tests. Details of the shale and coal derived fuel tests appear in References 14 and 15.

3.3.1 Multicylinder engine tests

Of the synthetic fuels tested, only the DF-M could be considered a finished alternative Diesel fuel. Therefore, it was decided to run a brief series of multicylinder engine tests with this fuel. The objectives of these tests were:

1. To screen a shale-derived Diesel fuel (DF-M) prior to starting a detailed single-cylinder engine study.

2. At selected points, collect performance and emissions data. Compare these data with baseline data for the same points and note any significant differences.

For purposes of comparison with operation on the baseline DF-2 oil, the 1978 Oldsmobile V-8 engine was run on DF-M shale oil at 1720 and 2000 RPM to obtain performance data and a limited amount of particulate data. Particulate samples drawn directly from the tailpipe were obtained at the 2000 RPM, 1/2 and 3/4 Rack and 1720 RPM, 1/2 Rack conditions. All samples had the soluble organic fractions (SOF) extracted and were assayed using the Ames test.

The 2000 RPM data for thermal efficiency, corrected brake horsepower, oxides of nitrogen emissions, and carbon monoxide emissions are presented graphically in Figures 20 and 21. Pressure and needle lift histories were virtually identical; consequently, they have not been presented.

As seen on Figures 20 and 21 there really are no significant differences in either the performance or the emission data obtained

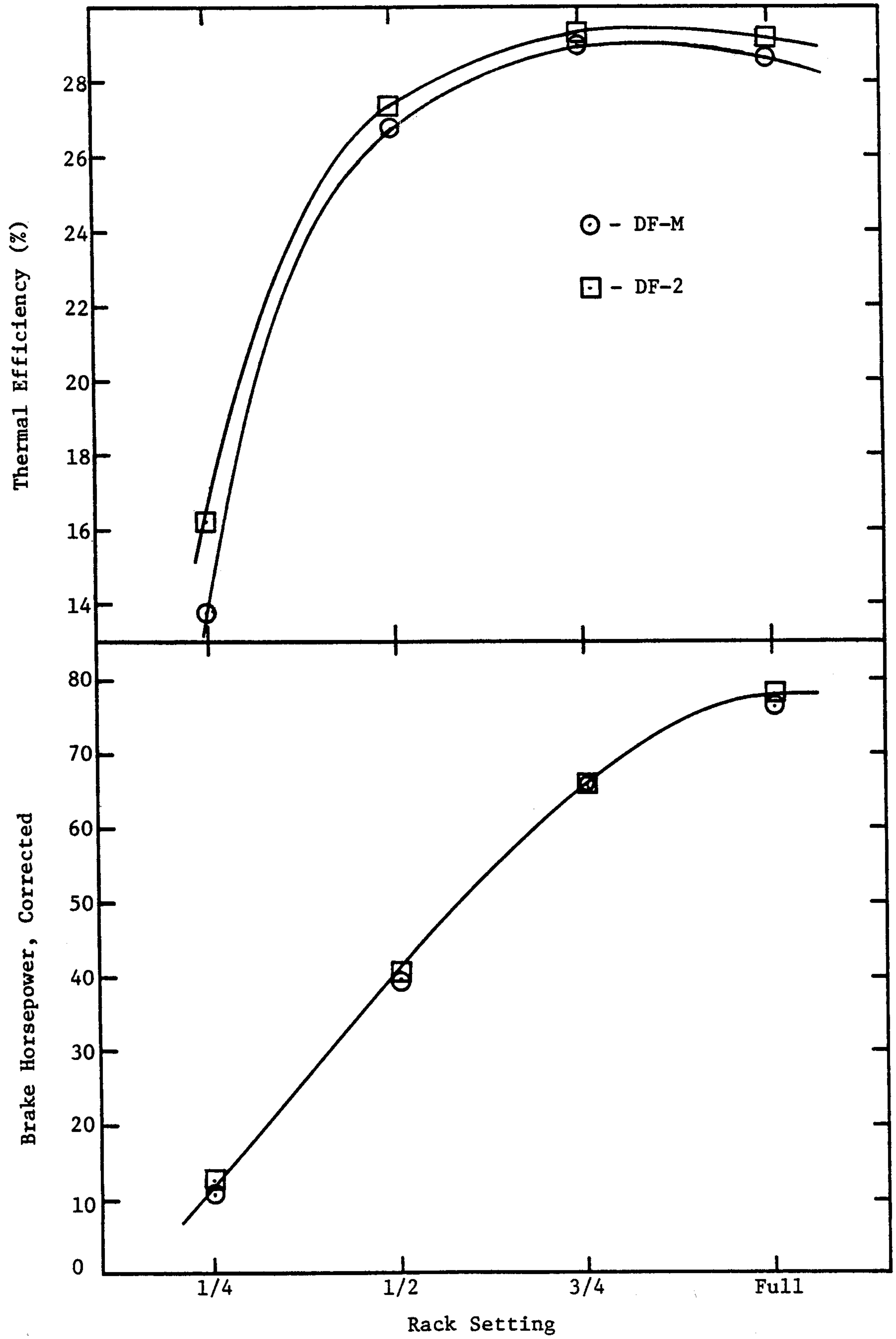


Fig. 20- 2000 RPM Performance Data Comparison.
(5.7ℓ Oldsmobile Diesel Engine)

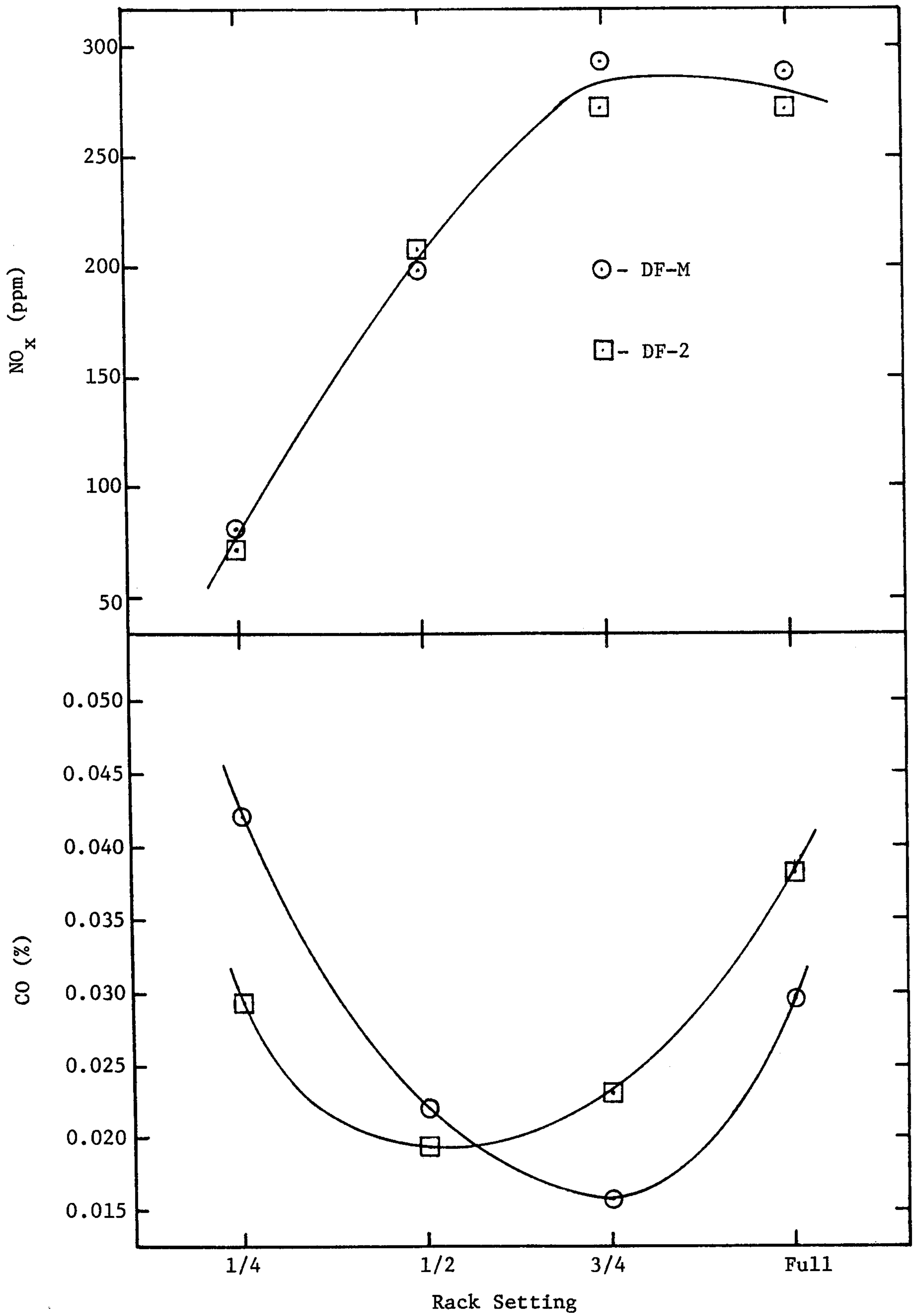


Fig. 21- 2000 RPM Emission Data Comparison.
(5.7ℓ Oldsmobile Diesel Engine)

with DF-2 and DF-M at 2000 RPM. Similar results were obtained at 1720 RPM. For all conditions except the 1/4 rack, 2000 RPM condition the differences in the performance data for the two fuels are less than 6%. It is interesting to note, however, that while the DF-2 efficiency was consistently slightly higher than the DF-M efficiency at 2000 RPM, just the opposite trend was observed at 1720 RPM.

Ames test results as well as the SOF for all particulate samples are presented in Table 10. Standard deviations are presented where possible, but some of these results are based on a small number of samples - as low as only two; consequently, care should be exercised when interpreting these data. In all cases, the Ames results for DF-M and DF-2 overlap within one standard deviation, indicating no significant measurable difference; however, in all cases, the DF-M did result in a lower mean value. The soluble organic fraction was consistently higher for DF-M than for DF-2, but again differences are not statistically significant.

These limited DF-M multicylinder engine screening tests provided the following information:

1. With respect to performance and gas-phase emissions, the results obtained with DF-M were in every way comparable to those obtained with the baseline DF-2.

2. The soluble organics extracted from the particulate matter from the combustion of DF-M did not differ significantly in biological activity from that of the baseline DF-2 as assayed by the Ames Test.

3.3.2 Single-cylinder engine tests

The engine used for these tests was identical to the one use for the single-cylinder engine aqueous alcohol tests and vegetable oil tests.

Table 10 - Comparative Multicylinder Engine Particulate Data using DF-M

	1/2 RACK, 1720 RPM		1/2 RACK, 2000 RPM		3/4 RACK, 2000 RPM	
FUEL	DF-M	DF-2	DF-M	DF-2	DF-M	DF-2
Soluble Organic Fraction (%)	43.0	30.3 ± 6.9	57.1 ± 7.6	40.2 ± 11.6	10.9 ± 0.9	7.5 ± 1.5
Ames Test Results of SOF*	0.94 ± 0.29	0.99	0.61 ± 0.25	0.77 ± 0.18	1.32 ± 0.05	1.75 ± 0.6

*Ames test results using TA98^{-}, slope at 100 micrograms per plate ± std. dev.

The objectives of the single-cylinder engine tests were:

1. With the baseline DF-2, characterize performance, combustion, emissions, and bioactivity for three operating conditions established at 2400 RPM on the basis of energy input.

2. Obtain similar information for the neat shale oils and the coal liquid blend and compare this information to that obtained with the baseline DF-2.

Figure 22 is a schematic of engine setup used to generate the data for this study. The instrumentation included the dynamometer scale, strategically located thermocouples, and electronic transducers for sensing top dead center timing, needle lift, and cylinder pressure. The electronic signals were fed to a digital oscilloscope and stored on floppy discs for computer processing to obtain information regarding ignition delay and combustion characteristics.

The exhaust system was insulated prior to the gas-phase sampling port to prevent condensation of unburned hydrocarbons. Gas-phase analysis provided the volumetric content of carbon monoxide, carbon dioxide, unburned hydrocarbons (heated and unheated FID), oxides of nitrogen, and oxygen.

Full volume undiluted exhaust was cooled to 52 C for particulate matter collection on 51 cm x 51 cm teflon-coated glass-fiber filters. The particulate matter was soxhlet extracted with methylene chloride to isolate the soluble organic fraction (SOF). Ames tests were conducted to observe the direct mutagenic activity of the SOF.

A repeatable data baseline was obtained for the engine using the certified petroleum-based DF-2. Test conditions were established at 2400 RPM over a range of three energy input rates corresponding to full (15.87 kW), 2/3 (9.94 kW), and 1/3 (7.19 kW) rack (brake power). The

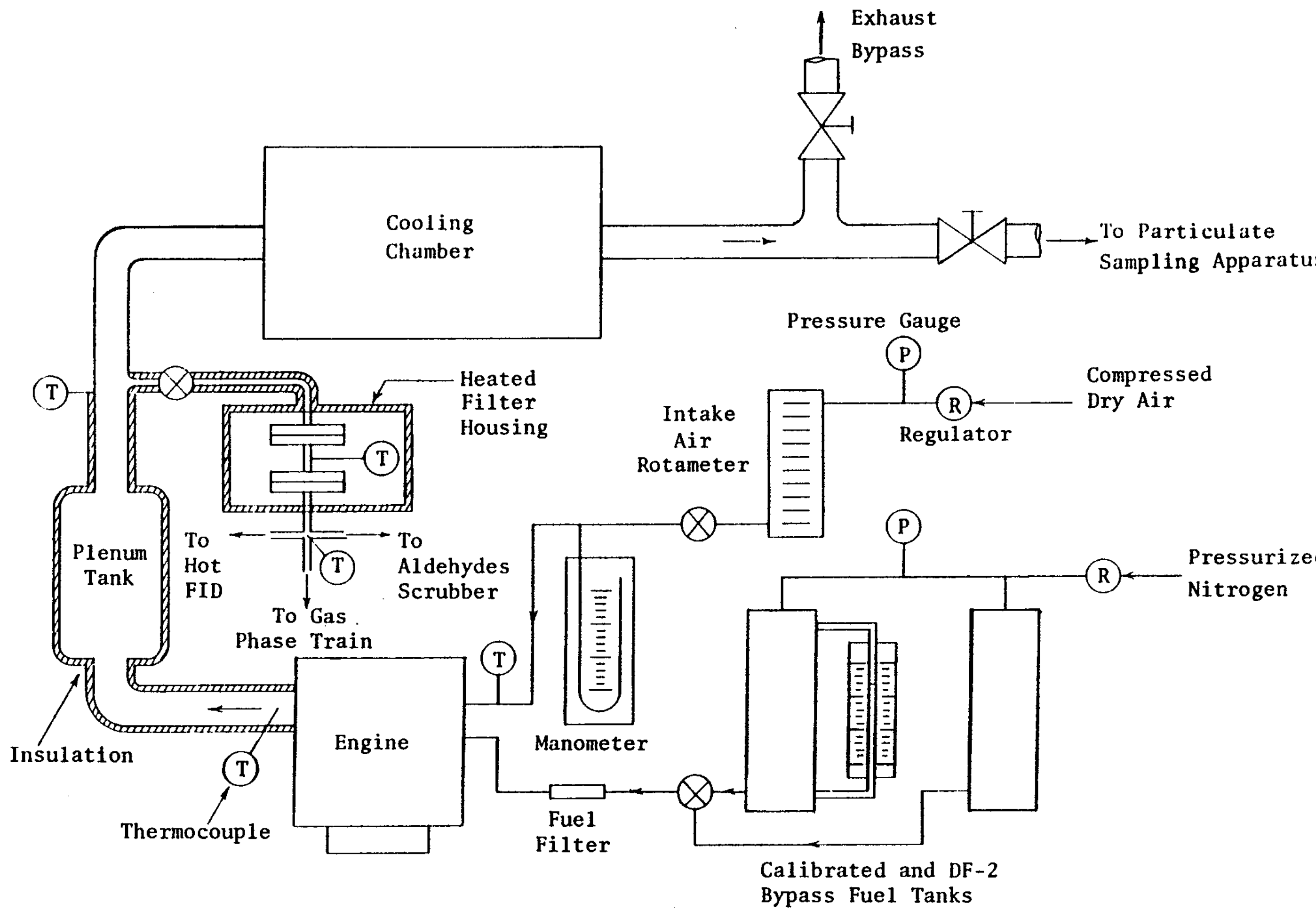


Fig. 22 - Schematic of the AVCO Lycoming Bernard Diesel Engine Test Set-up used for Coal and Shale Derived Fuels.

neat shale oils and the blended coal liquids were then tested at these same conditions and comparisons made.

Figure 23 displays typical pressure traces observed for each fuel at 2/3 rack. It illustrates the relative peak pressures, combustion harshness, and ignition delays. The DF-M burned smoothly with a short ignition delay. In contrast, the LSO ignited abruptly after a long ignition delay. The blending of coal liquids with the DF-2 deteriorated the combustion characteristics. The blends had longer ignition delays and harsher combustion compared to those for the baseline DF-2. These characteristics were very sensitive to the percentage of coal liquid in the blend as well as to the energy input rate. Furthermore, the lengthened ignition delays were more pronounced for the SRC-II than for the EDS. The ignition delays appear on Figure 24.

The indicated thermal efficiencies presented in Figure 25 reveal that the shale oils burned very efficiently. The 20% SRC-II blend had similar efficiencies to those of the DF-2 at higher rack settings, but its efficiency dropped at 1/3 rack where combustion faltered. The 20% blend efficiencies were consistently lower than those for the baseline DF-2. However, at its 40% condition, the EDS had a surprisingly high efficiency. This can be attributed to a spontaneous ignition located near top dead center which favors efficiency but produces severe knock.

With few exceptions, the regulated gas phase emissions were similar to those for the baseline DF-2. At the 1/3 rack condition incipient lean misfire was encountered with the SRC-II blends. Relatively high hydrocarbon and relatively low oxides of nitrogen emissions signaled this condition.

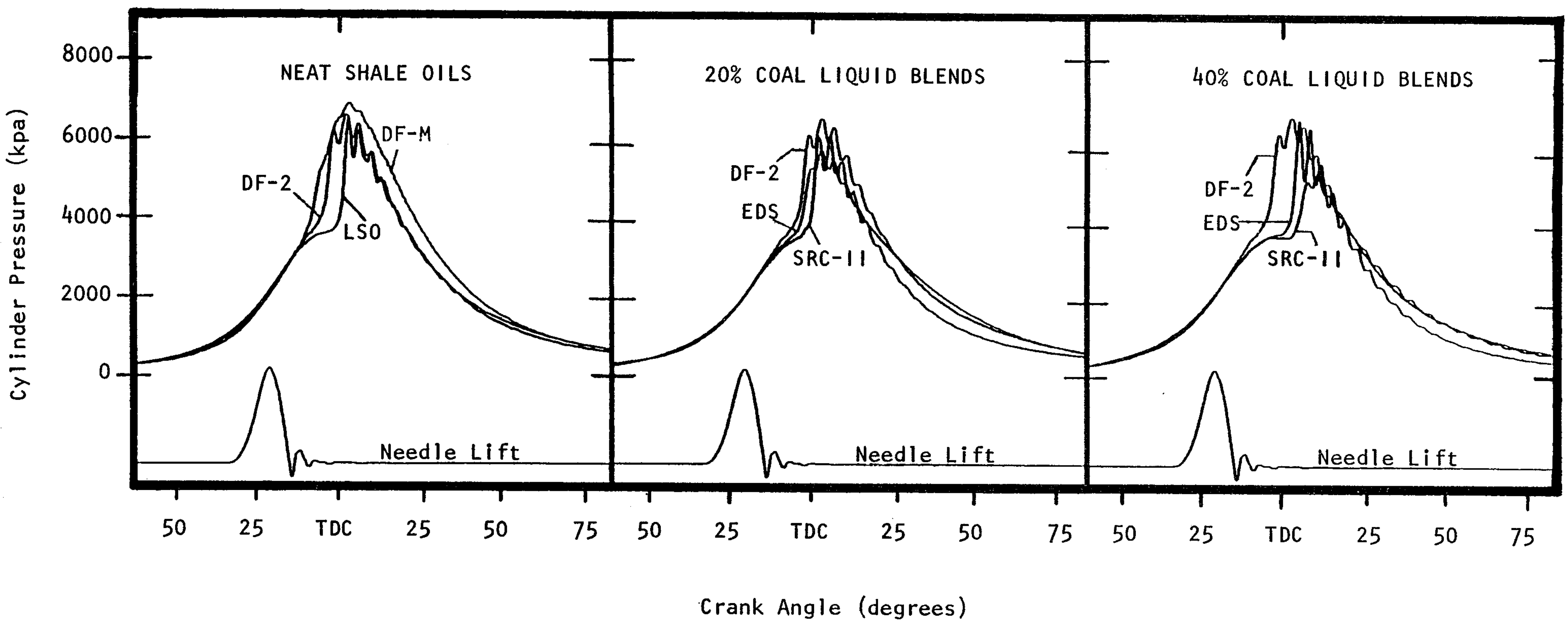


Fig. 23 - Comparative DF-2, DF-M, LSO, EDS, and SRC-II Pressure and Needle Lift Traces at 2/3 Rack, 2400 RPM for the AVCO Lycoming Bernard Diesel Engine.

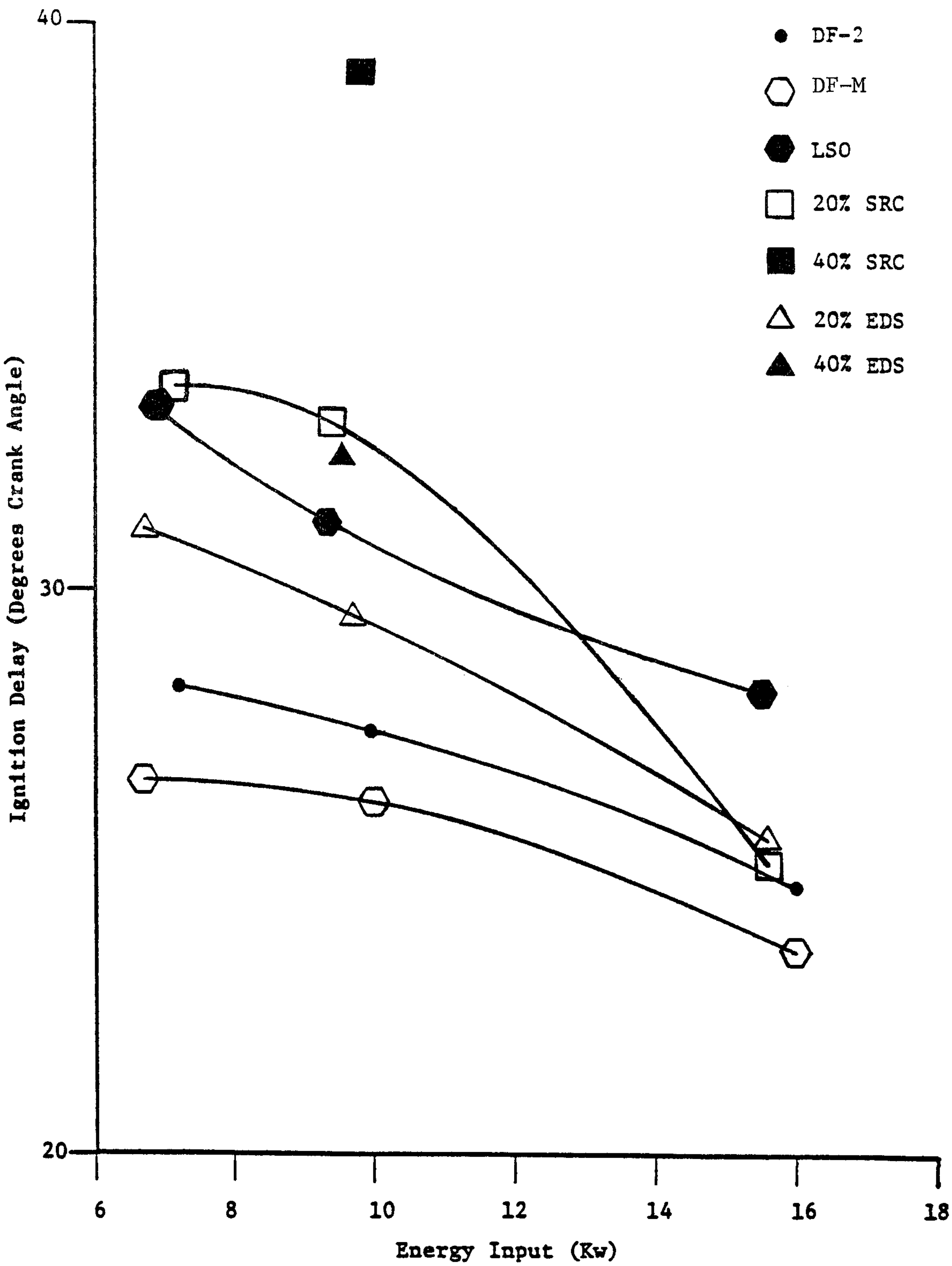


Fig. 24 - Comparison of Ignition Delays Using DF-2, DF-M, LSO, SRC-II and EDS at 2400 RPM for the AVCO Lycoming Bernard Diesel Engine.

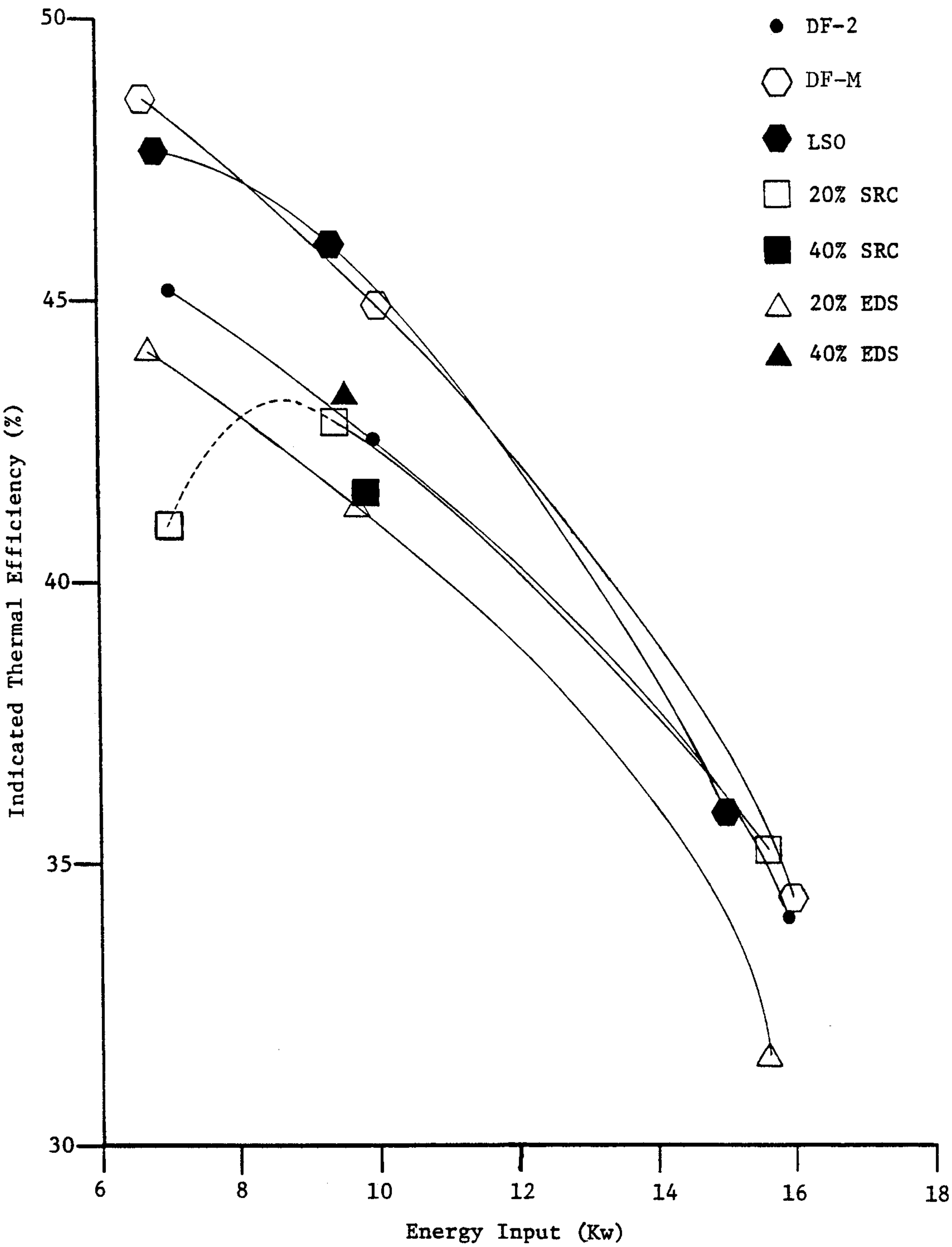


Fig. 25 - Comparison of Indicated Thermal Efficiencies Using DF-2, DF-M, LSO, SRC-II and EDS at 2400 RPM for the AVCO Lycoming Bernard Diesel Engine.

The SOF of each soot sample was examined for direct mutagenic activity using TA-98⁻ in the Ames Salmonella typhimurium test. The initial linear slope of the dose-response curve was multiplied by the particle generation rate and the SOF to provide a comparative index termed power specific biological activity (PSBA).

The PSBA trends are shown in Figure 26. The DF-M exhibited roughly half the PSBA of the baseline DF-2. The 20% SRC-II also had a lower PSBA trend. On the other hand, the 20% EDS blend had a higher PSBA than the baseline DF-2, especially at 1/3 rack. Significant increases in PSBA were encountered with both 40% coal liquid blends. The most notable PSBA trend occurs with the Light Shale Oil (LSO) for which the PSBA was very low at 1/3 and 2/3 rack, but extremely high at full rack. The high full rack value probably resulted from the injection difficulties that were most troublesome at this condition. Secondary injection or nozzle dribble can significantly enhance the formation of direct mutagens (16).

The following conclusions were drawn from the data collected for this single-cylinder engine study of two neat shale oils and two coal-derived blends:

1. The shale derived fuels burned more efficiently than the baseline DF-2 and generated fewer HC and CO emissions. The DF-M displayed good finished Diesel fuel qualities. It had a short ignition delay and a relatively low power specific biological activity (PSBA). The LSO had a long ignition delay, harsh knock, and a tendency to foul the injection nozzle. Its PSBA was very low at the lower rack settings, but it was extremely high at full rack.

2. Increasing the percentage of coal liquid in the blends narrowed the usable power band of the engine, lengthened the ignition delay, and intensified knock severity. These characteristics were more drastic for the SRC-II than for the EDS; but, in both cases, the ignition delay increases became more pronounced at low inputs.

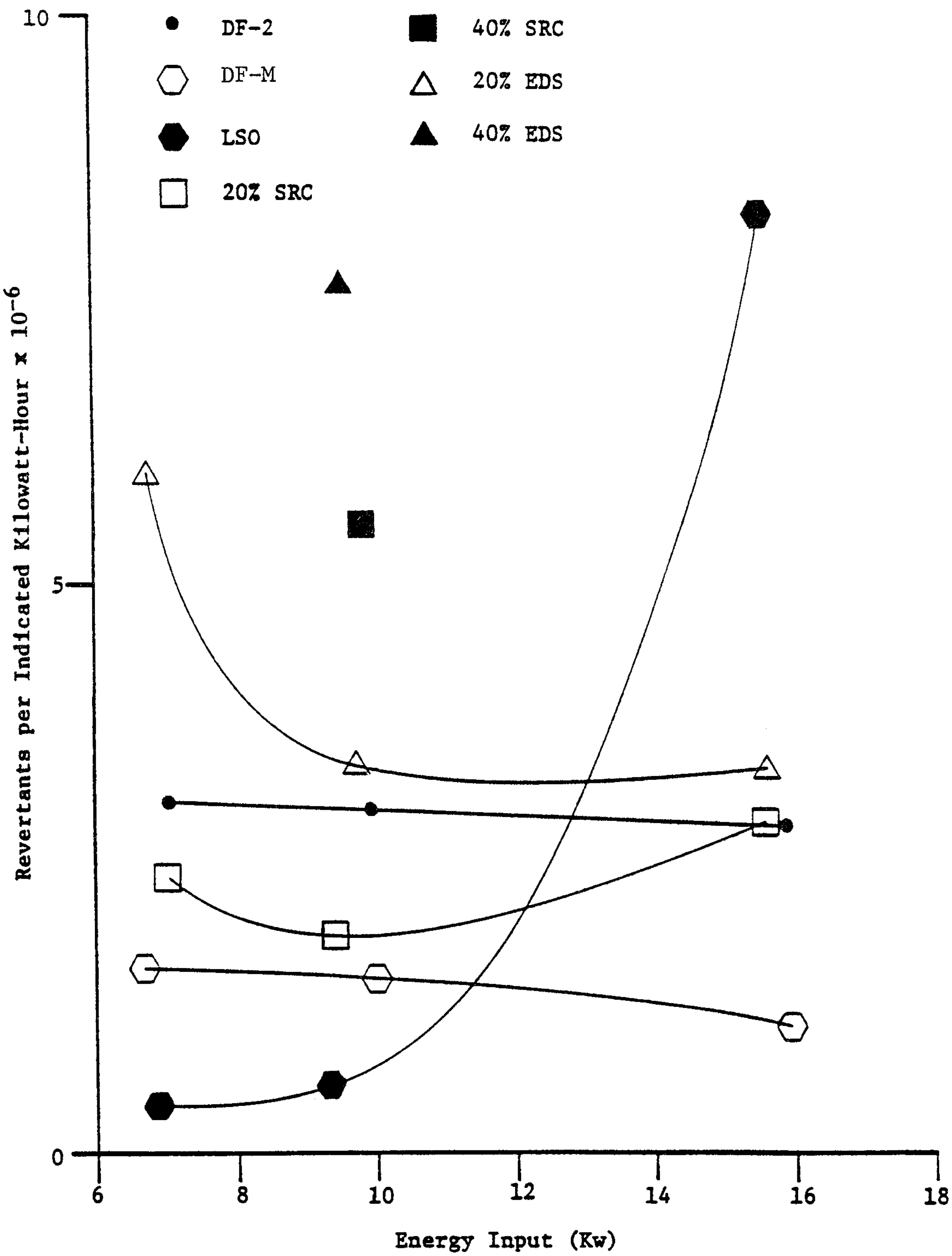


Fig. 26 - Comparison of Power Specific Biological Activity using DF-2, DF-M, LSO, SRC-II and EDS at 2400 RPM for the AVCO Lycoming Bernard Diesel Engine.

3. The 20% SRC-II blend had comparable thermal efficiencies and gas-phase emissions to those of the baseline DF-2 at higher rack conditions. At 1/3 rack its thermal efficiency dropped which resulted in high HC and CO emissions but low levels of NO_x. Particulate emissions and PSBA of this blend were relatively low at the lower rack conditions. At full rack it produced high particulate emissions though its PSBA remained comparable to the DF-2 value.

4. The 20% EDS blend had nearly the same gaseous and solid phase emissions as those of the baseline DF-2. It did burn less efficiently than the baseline fuel as well as produce a higher level of PSBA.

IV. CLOSURE

During the grant period covered by this report, engine tests of various candidate alternate Diesel fuels were conducted. A single-cylinder DI engine and a multicylinder IDI engine were used to burn the lower alcohols, four vegetable oils, two coal derived liquids, and two shale derived fuels. Comparisons of performance and emissions characteristics with baseline values for a certified DF-2 burned under the same conditions in the same engines provided the basis for the conclusions that were drawn in each phase of the study.

The test fuels were either injected into the engines using the stock injection systems or were introduced via fumigation. While fumigation, on the surface, appears to be simple, there are operational difficulties that would make any practical system quite complex. Also, the findings of this study seem to speak against the use fumigation as a means for utilizing the lower alcohols in a Diesel engine. Therefore, at this point in time fumigation does not appear to be a contending method for easing the use of low cetane number alternative fuels in Diesel engines. However, fumigation does remain a valuable research tool for studying such fuels and, therefore, investigators should not hesitate to use it.

This study did show that from the fuel management point of view it was advantageous to be able to inject any alternate fuel using the stock injection system. Indeed, if the specifications of the alternative test fuel render it close to being a finished fuel then performance comparable to a petroleum-based fuel should be achievable.

For the test fuels of this study that were injected using the stock injection systems, it did become apparent that the standard methods for specifying the fuel combustion quality were not adequate. For example, the cetane index is a correlation developed for full-boiling range petroleum-based fuels and, as such, should not be expected to yield useful synthetic fuel cetane numbers. Also, since the ASTM method determines the cetane number of a fuel at room temperature it yields erroneous results for high viscosity fuels such as the vegetable oils. In the case of vegetable oils the cetane index is also useless because these oils are neither petroleum based or full-boiling range oils. All this goes to point up the need for a better method of specifying combustion quality of any Diesel fuel.

It is hoped that studies such as the one reported here will continue in order to provide the data base so that in the future useful information can be deduced concerning the overall performance of possible alternate Diesel fuels. This is one way to prepare for the day when petroleum will no longer be available to supply the large quantities of motor fuel required by the United States.

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APPENDIX A

Procedure for Transesterification of Vegetable Oils

The following ingredients were used to transesterify a 2ℓ batch of vegetable oil:

1. 2ℓ methanol
2. 2 gm NaOH (sodium hydroxide)
3. pH paper (range of 4-5)
4. pH paper (range of 6-7)
5. sulfuric acid
6. distilled water (deionized water)
7. NaCl (sodium chloride) if needed

The following was the equipment used for the small batch transesterification process:

1. 2-4ℓ beakers
2. 2 hot plates and stirrers
3. 2 thermometers or other temperature sensors
4. clean storage tank for mixing and storing small batches of finished fuel

To transesterify vegetable oil, a solution of methanol (2ℓ) and NaOH (2 gm) was prepared, to which 2ℓ of once refined, degummed vegetable oil was added. The mixture of vegetable oil, methanol, and catalyst was heated to 65°C and was continuously stirred for 2-4 hours. When the vegetable oil and methanol were first put together, the vegetable oil became the bottom layer because of its higher density. After the vegetable oil, methanol mixture was heated and stirred, these layers switched positions because the vegetable oil lost its triglycerides which made it more dense than methanol. With the same reasoning, the methanol should become more dense because of the addition of the triglycerides. However, depending on the vegetable oil's composition, this layer switch may not occur. After sufficient time for the completion of the esterification reaction elapsed, H_2SO_4 was added to the mixture while it was stirring until a pH value of 4.5 was obtained. This freezes the esterification reaction and prevents the triglycerides from reforming in the vegetable oil. The methanol solution was located and removed. The methanol solution can be distilled and the pure methanol reused. The properties (i.e., pour points, density, etc.) of the esters were checked to ensure esterification reaction went to completion.

The esterified vegetable oil was then washed with distilled water at 50°C. If soap formed, NaCl was used to remove it. The water layer, which should be the bottom layer, was removed. Additional water washes without NaCl were performed until a pH value of 6.5 was obtained in the water. The esterified fuel was allowed to stand in the beaker until all trace amounts of water had settled to the bottom. The final fuel was stored under nitrogen until used.

Note: Safety precautions must be taken when working with methanol.

APPENDIX B

Aldehyde Measurements

Exhaust aldehyde samples were collected for Diesel fuel and for the vegetable oils. The aldehydes were collected by bubbling the exhaust gas through a solution of 2-4, dinitrophenylhydrazine (DNPH). This caused the highly reactive aldehydes to form their DNPH derivatives which have a much higher molecular weight and increased stability. After collection, solid DNPH derivatives were filtered out and remaining derivatives, which were in solution, were extracted using pentane. Following extraction, the solid precipitate and extracted derivatives were combined and analyzed with a gas chromatograph to obtain an indication of the aldehyde breakdown, as well as total aldehyde emissions. Separation of the aldehydes into components from formaldehyde through heptaldehyde was performed with a Hewlett Packard Model 5710A gas liquid chromatograph using a six-foot glass column packed with 3% SP-2100 coating on 100/120 mesh Supelcoport. The acrolein, propionaldehyde, and acetone were all measured as acetone since the column used could not resolve these similar, three-carbon compounds. The injection port and detector were maintained at 300°C with the oven temperature programmed from 200° to 290°C at 16°C/min, followed by a two minute hold at 290°C. The nominal flowrates were 50 ml/min hydrogen, 60 ml/min nitrogen, and 420 ml/min air. The output from the gas chromatograph was fed to a Hewlett Packard Model 7127A strip chart recorder. Complete details of the aldehyde procedures used in this study are available in Ref. (10). A schematic of the GC setup is shown in Fig. B.1.

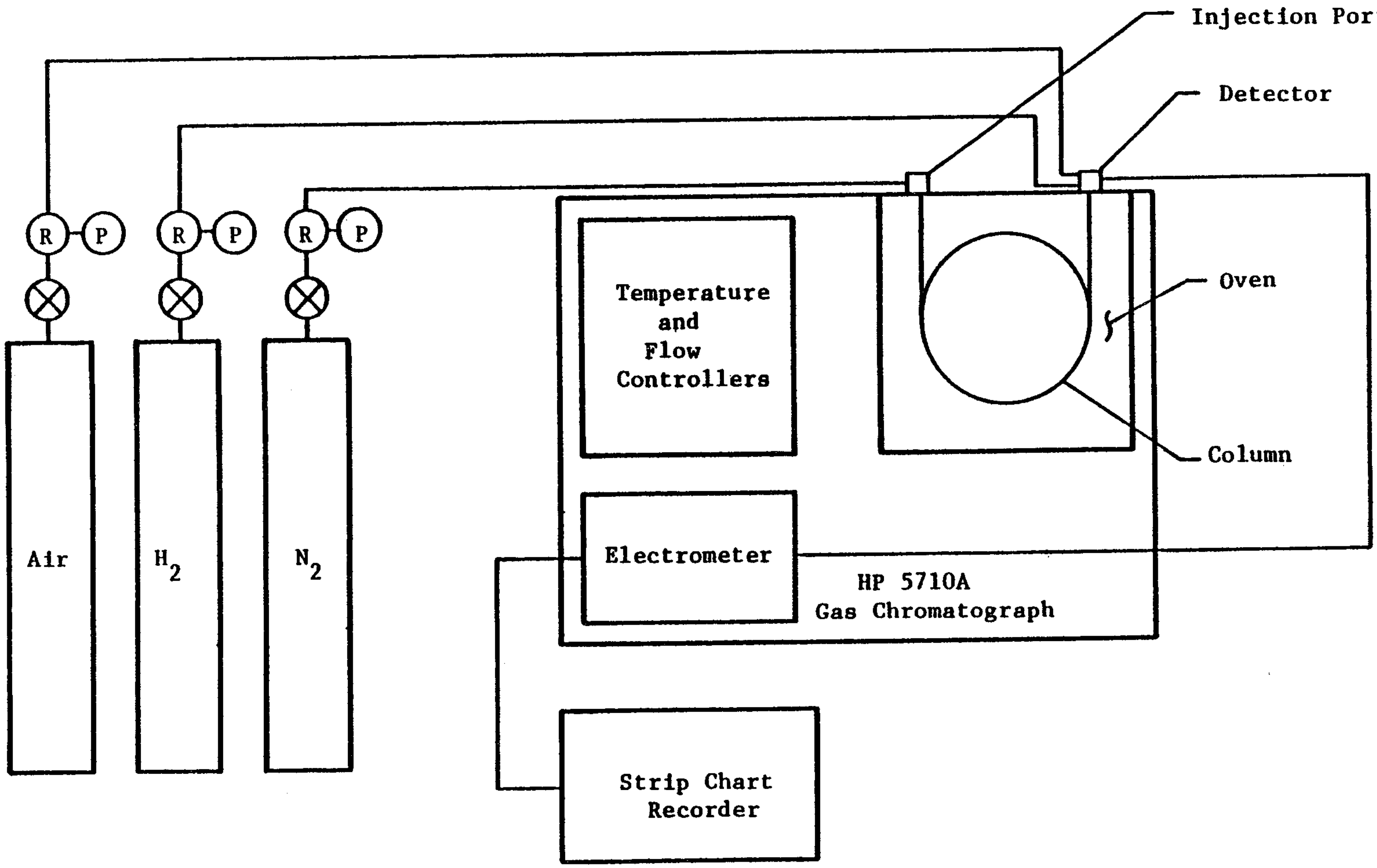

Fig. B.1 - Schematic of GC Setup.

APPENDIX C

Reduced Baseline DF-2 Data at 2400 RPM

Rack	1/3	2/3	Full
BTHEFF(%)	15.4	22.3	23.8
ISFC (g fuel/IkW-hr)	0.162	0.176	0.194
ISEC (kJ/IkW-hr)	7231	7920	8721
AF (air-fuel ratio)	49.8	32.9	24.5
PHI (equivalence ratio)	0.30	0.44	0.61
TEX (^{o}C)	476	559	654
VOLEFF (%)	88.5	87.0	85.8
CO (g/IkW-hr)	6.5	9.6	14.5
HC (g/IkW-hr)	1.05	2.07	2.92
NO_x (g/IkW-hr)	4.0	3.67	3.12
PMAX (bar)	60.7	63.6	66.8
PRATMAX (bar/degree crank angle)	6.25	5.94	7.22
IGNDLY (degrees crank angle)	26.9	25.4	23.8

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16. Abstract

This report summarizes the important findings for a 41-month research grant entitled "The Utilization of Alternate Fuels in Diesel Engines." The procedure followed was to collect performance and emission data for various candidate alternate fuels and compare these data to that for a certified petroleum-based number two Diesel fuel oil. The method of test-fuel introduction was either via fumigation or to use the engine stock injection system. Results for methanol, ethanol, four vegetable oils, two shale-derived oils, and two coal-derived oils are reported. Based upon this study, alcohol fumigation does not appear to be a practical method for utilizing low combustion quality fuels in a Diesel engine. The reasons being, the need for a complex fuel management system and a narrow operating range bounded by "wet" misfire on the low load end and by severe knock at medium to high loads. Also, it was misfire on the low load end and by severe knock at medium to high loads. Also, it was found that alcohol fumigation enhances the bioactivity of the emitted exhaust particles. Finally, this study showed that while it is possible to inject many synthetic fuels using the engine stock injection system, wholly acceptable performance is only obtained from a fuel whose specifications closely approach those of a finished petroleum-based Diesel oil. This is illustrated by the contrast between the poor performance of the un-upgraded coal-derived fuel blends and the very good performance of the fully refined shale-derived fuel.

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