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THE UTILIZATION OF ALTERNATE FUELS IN DIESEL ENGINES
Final Report

By
Samuel S. Lestz

September 1980

Work Performed Under Contract No. AS02-77CS54530

The Pennsylvania State University
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Division of Transportation Energy Conservation

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Final Report

The Utilization
of
Alternate Fuels in Diesel Engines

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September 1980

Prepared for

The United States Department of Energy

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ABSTRACT

This report summarizes the accomplishments during the three year period for the Department of Energy grant entitled "The Utilization of Alternate Fuels in Diesel Engines". Experiments were designed and test equipment set-up for the purpose of evaluating the use of methanol as a fumigant for light-duty Diesel engine service. The major experimental results were obtained from a multicylinder automotive Diesel engine. However, fundamental studies employing a GC/micro-reactor and a constant volume combustion bomb were also started. The purpose of this work was to measure some of the chemical and physical properties of methanol and methanol-air mixtures. The laminar flame velocity for various mixtures has been measured in the combustion bomb and thermal degradation studies have begun in the GC/micro-reactor.

An Oldsmobile 5.7L V/8 Diesel engine was fumigated with methanol in amounts up to 40% of the fuel energy. The primary objectives of the study were to determine the effect of methanol fumigation on fuel efficiency, smoke, nitric oxide emission, and the occurrence of severe knock. An assessment of the biological activity for samples of the raw exhaust particulate and its soluble organic extract was also made using both the Ames Salmonella typhimurium test and the B. subtilis Comptest. Generally, methanol fumigation was found to decrease NO emission for all conditions, to have a slight effect on smoke opacity, and to have a beneficial effect on fuel efficiency at higher loads. Also at higher loads, the methanol was found to induce what was defined as "knock limited" operation. The biological activity of the raw particulate matter was found to be less than that of its soluble organic extract. However for both, the fumigation of methanol did enhance the biological activity.

Finally, the report closes with a statement of the work that will be done under a continuation Department of Energy grant.

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I. INTRODUCTION

This grant was initiated in September 1977 to investigate two ways for extending the existing petroleum supply by supplementing Diesel fuel oil with an alternate fuel. These were: 1) fumigation with alcohol and 2) burning a blend of used lubricating oil and fuel oil. Further, in anticipation of the impact that the Diesel engine would make in the near future as an automobile powerplant, it was specified that this study be concerned with light duty Diesel engines. While the laboratory facilities were being readied, alcohol started to receive much attention as a candidate near-term alternate fuel. Therefore, the decision was made to concentrate the efforts of this study on the methanol aspects and to look at used lubricating oil blends at some time in the future.

Figure 1 illustrates the four elements of the Program which this grant became a part of. After presenting some background information the remainder of this report will summarize the accomplishments of this grant in each of these program elements.

II. BACKGROUND

The Diesel engine has two distinct advantages over the conventional spark ignition (S.I.) engine, viz., its superior part load fuel economy and its ability to burn a wide range of fuels. Therefore, as the world's petroleum supply dwindles it is inevitable that a segment of the automobile industry will turn to the Diesel engine as one means of meeting the pressure put upon their product due to a shortage of suitable S.I. engine fuels. As this begins to happen it is important that problems accompanying light duty Diesel engine operation be fully identified and viable solutions be sought.

ALTERNATE FUELS PROGRAM

FIGURE 1

Of immediate concern is the question of how to best take advantage of the Diesel engine's broad fuel tolerance. Might the most effective way to do this be with extenders to stretch the present petroleum-base fuel oil supply or might it be through the use of only fuels derived entirely from non-petroleum sources? The alcohols offer an opportunity to explore both since they can be obtained from non-petroleum sources and, in theory at least, they can be used either in conjunction with fuel oil or neat. Methanol, the simplest of the alcohols appears to occupy a prominent position among the alcohols because of the ease with which it can be synthesized from so many different raw materials. Therefore the main thrust of this grant was directed toward finding a viable way to burn methanol in a light-duty automotive Diesel engine.

Because methanol has a low cetane rating (high octane rating) it was recognized that in order to burn it alone in a conventional Diesel engine would not be possible without adding a relatively large amount of cetane number improver to it. Rather than do this the decision was made to treat the methanol as an extender and to use fumigation as the initial way to introduce it into the engine. Fumigation is the name applied to the addition of a supplemental fuel, in this case methanol, to the intake air of a Diesel engine. The supplemental fuel can be carbureted or air injected into the intake system. Here an air atomizing nozzle injected a fine methanol spray into the air as it flowed through the intake system.

It was anticipated that many of the problems of heavy duty Diesel engines would also be common to the light duty Diesel engine as well. Some of these are noise, odor, smoke, NO_x and particulate emissions, and cold starting. However, in the case of the light duty automotive Diesel

these problems tend to be more acute because of the stringent requirements placed on it by the federal government and by the automotive industry itself. Since it was realized that this study could not give equal emphasis to each problem area, a concerted effort was made to investigate and report on smoke, NO_x and particulate emission, and energy efficiency as affected by methanol fumigation.

The following sections of this report will summarize the work carried out during the initial three years of the grant. Since the work concentrated on the multicylinder engine study this section will comprise the bulk of the report with the other sections being brief.

III. RESULTS

This portion of the report is subdivided into four sections, one for each of the elements shown on Fig. 1.

3.1 Physical Properties

A literature search as well as prior work done at this institution indicated that knock limited operation might be encountered when fumigating a Diesel engine with methanol. Therefore, in anticipation of this it would be helpful to understand certain physical behavior of methanol. The evaporation and decomposition of methanol at elevated temperatures and pressures was thought to be of importance when considering the onset of severe knock.

A simple experimental apparatus was constructed and used to determine the vapor pressure curve for methanol. Results obtained with this apparatus were compared with those calculated with the Antoine equation

(1)* and with those found in Ref. (2). The Antoine Equation is as follows;

$$\log_{10} P_v = A - \frac{B}{T_v + C}$$

where A, B, and C are constants for the various temperature ranges.

Figure 2 shows that the comparison is good and, therefore, if in the future similar data are required but not available, this apparatus should provide satisfactory information.

To study the thermal decomposition of methanol a micro-reactor was built and fitted to the inlet port of a gas chromatograph. In this micro-reactor methanol can be made to decompose surrounded by an inert atmosphere (helium) at simulated in-cylinder temperatures and pressures. At high temperatures and pressures near to atmospheric methanol dissociates to carbon monoxide and hydrogen. This process however has not been well studied at the elevated pressures found in a Diesel engine. The easy ignition and high flame speed of hydrogen if it is present in the proper concentration could be a contributing factor to the onset of severe knock.

Although the equipment for this study has been assembled for some time, to date no reliable information has been obtained. The problem centers about finding the proper technique for introducing the micro-reactor contents into the gas chromatograph without placing spurious signals on the chromatogram. Work is continuing to overcome this difficulty and it is hoped that this study will eventually produce some useful results.

* Numbers in parentheses designate Reference List entries.

FIGURE 2

3.2 Combustion Bomb

Since the operation of a Diesel engine depends on what happens during the combustion event fundamental knowledge of this event is very important. A spherical combustion bomb is an experimental device that can be used to obtain fundamental combustion information. In this instance it was used to determine the laminar flame velocity for the methanol fumigant as well as for one of its disassociation products, hydrogen. A brief description of the bomb and of the results obtained from it are presented here. For further details the reader is referred to Refs. (364).

The constant volume combustion bomb was fabricated of 303 stainless steel. The construction consisted of two flanged hemispheres which when bolted together gave a spherical chamber geometry with an inside diameter of 12.7 cm. Each hemisphere was provided with several access holes for the charging system, the ignition system, the various sample probes, and the pressure transducer. In addition, two quartz windows were installed which allowed for observations directly through the combustion chamber.

Two spark plugs with extended center electrodes were positioned so that the ignition process was initiated at the center of the bomb volume. The spark gap was set at 0.9 mm. In addition, one ionization pin was installed so that the junction was positioned 3.3 cm from the ignition point; this ion gap was used only to verify spherical flame development.

The wall of the bomb had controlled electric heaters on the outside surface which were used to maintain the wall temperatures at any desired constant value up to 500K. Wall temperatures were monitored using eight surface thermocouples located at different positions on both the inside and outside surfaces.

Charging of the bomb with the desired fuel-air-diluent mixture was accomplished in two different ways. For gaseous fuels the charging was done based on the partial pressures of the various components. Combustion air was supplied using bottled compressed air of certified purity (99.8%). The dilution gas was also supplied, premixed, as bottled compress gas (15% CO_2 in N_2 by volume). For liquid fuels, the bomb was first charged with the proper mass of air for each run. The appropriate amount of diluent was added next, again based on the partial pressure. This mixture was allowed to come to equilibrium with the wall temperature, which was maintained at 477 K for all runs, and then the desired mass of liquid fuel was injected directly into the chamber using a syringe and septum system. Figure 3 is a schematic of the bomb and the charging system.

After combustion the products were collected at atmospheric pressure in Tedlar bags. These products were then analyzed for CO , CO_2 and O_2 concentrations. These measurements were then used in a carbon balance calculation to check the air-fuel ratio. In all cases these calculated air-fuel ratios are in good agreement with the measured air-fuel ratios.

The pressure-time data was collected using a Kistler Model 609A water cooled piezoelectric pressure transducer. The signal was amplified using a Kistler Model 503 charge amplifier. Both the amplified pressure signal and the ion pin signal were displayed simultaneously on a digital storage oscilloscope which also directly reduced the analog signals to digital form. The pressure measuring system had a frequency response of DC to 8 kHz and a resolution of 0.8 kPa.

CONSTANT VOLUME COMBUSTION BOMB SCHEMATIC

FIGURE 3

Charge introduction and preparation when dealing with gaseous fuels pose no serious problems in using the bomb. However this is not the case when dealing with a liquid fuel. A great deal of preliminary data using isooctane was collected in order to develop and verify the methodology for burning a liquid fuel in the bomb. In these preliminary runs the gas phase combustion products were measured and their concentrations used in a carbon balance to calculate the air-fuel ratio. This calculated air-fuel ratio was then compared to the actual air-fuel ratio which was measured during the charging process. The fact that the average percentage difference between the measured and calculated air-fuel ratios was only 3.5% indicated that the methodology developed for charging and burning liquid fuels was indeed valid.

A series of bomb experiments was run for the purpose of determining the laminar burning velocity for methanol-air mixtures at various initial conditions of pressure, temperature, equivalence ratio, and charge dilution. Charge dilution was included as a variable because when a Diesel engine is fumigated with methanol, the opportunity exists for the methanol to burn in the presence of an inert diluent, viz., the fuel oil combustion products.

Figure 4 shows some typical methanol data. This figure presents the laminar burning velocity (S_u) as function temperature for an equivalence ratio of one and various dilution ratios at a pressure of 0.6 MPa. This pressure was chosen because it represents a reliable midpoint pressure for comparing all the data. Here the following definitions are used for equivalence ratio and dilution ratio

$$\phi = \text{Equivalence Ratio} = \frac{\text{Air/Fuel Ratio (Stoichiometric)}}{\text{Air/Fuel Ratio (actual)}}$$

and

FIGURE 4 - Methanol Laminar Burning Velocity at Various Dilution Ratios for $\phi=1.0$ and $P=0.6$ MPa

$$\text{Dil} = \text{Dilution Ratio} = \frac{\text{Mass of Diluent}}{\text{Total Charge Mass}}$$

Also the laminar burning velocity was determined using a lumped model for the calculation in which the conservation of mass was applied across the flame, or

$$S_u = \dot{m}/A\rho$$

where,

$\dot{m}$ = the mass burn rate

ρ = density of unburned gas entering the flame

A = flame area.

It was found that all the methanol data which was taken over the range $P=0.4$ to 1.8 MPa and $T=470$ to 600 K conforms quite well to the following expression

$$S_u = b_1 P_u^{b_2} \exp(-b_3/T_u)$$

where,

P_u = Unburned pressure

T_u = Unburned temperature, and

the constants b_1 , b_2 and b_3 are given below.

ϕ	Dil	b_1	b_2	b_3
1.0	0.0	4680.9	-0.095	2086.6
1.0	0.2	1287.8	-0.124	1770.8
1.0	0.3	438.3	-0.030	1595.6

The presence of the inert diluent reduced the laminar burning velocity. For the diluent used in this study generally it was found that for each 10 percent increase in the diluent mass there was a 27 percent decrease in the laminar burning velocity. These results would

indicate then that normally the in-cylinder burning velocity of the fumigated methanol-air mixture would be reduced because of the presence of combustion products from burned fuel oil.

The spherical combustion bomb was also used to study the burning of hydrogen-oxygen and hydrogen-air mixtures. Since hydrogen is one of the two primary dissociation products of methanol and since it possesses wide flammability limits and a high burning velocity the possibility exists for hydrogen to contribute to onset of severe knock in a methanol fumigated Diesel engine. Therefore an initial investigation was undertaken to

1. Determine the detonation limit of H_2-O_2 and H_2 -air mixtures for various initial conditions,

and

2. Study to study the transition from deflagration to detonation in relation to flame acceleration as calculated from the pressure-time trace.

Figures 5 and 6 are typical plots of the laminar burning velocity for various H_2-O_2 and H_2 -air mixtures as a function pressure in the constant volume spherical bomb (CVSB). Here it is seen that the slopes of H_2-O_2 curves are generally steeper than those of the H_2 -air curves. This is indicative of the greater pressure dependence for the H_2-O_2 mixtures. On Figs. 7 and 8 the burning velocity is plotted as a function of the flame position in the CVSB. For the geometry of this bomb some H_2-O_2 mixtures did detonate while on the other hand no H_2 -air mixtures did. Figure 8 shows that the flame does accelerate as it approaches the wall but never does reach the transition burning velocity of 50 m/sec. This was true for all H_2 -air mixtures tested in this spherical bomb. Among the many initial conditions tested, only H_2-O_2 mixtures at $\phi=1.0$ and $\phi=0.5$ detonated.

Fig. 5 Burning Velocity vs. Pressure in the CVSB for Various Equivalence Ratio of $\text{H}_2\text{-O}_2$ Mixtures.

Fig. 6 Burning Velocity vs. Pressure in the CVSB for Various Equivalence Ratio of H₂-Air Mixtures.

Fig. 7 Burning Velocity vs. Flame Radius for various Equivalence Ratio of $H_2 - O_2$ mixtures at $T_1 = 477.4^\circ K$ and $P_1 = 0.3448 MPa$.

Fig. 8 Burning Velocity vs. Flame Radius for various Equivalence Ratio of H_2 - Air mixtures at $T_i = 477.4^\circ K$ and $P_i = 0.3448 MPa$.

Ignition delay was also measured for each test. In general it was found that both the H_2-O_2 and the H_2 -air ignition delays, as expected, minimized at equivalence ratios that were slightly fuel rich. Those for the H_2 -air flames being richer than those for H_2-O_2 flames.

3.3 Single-Cylinder Engine Work

A small (6 Hp at 3000 RPM) single-cylinder air-cooled Diesel engine mounted to a cradled electric dynamometer was used extensively in the development of methodologies and techniques. Specifically the engine served as the test-bed for the development of the exhaust particulate collection system. It was decided that both gas phase and particulate emission information would be obtained from exhaust samples drawn isokinetically from the engine tail pipe without dilution.

All samples of exhaust particulate matter were collected on teflon-coated glass fiber filters. This type of filter has a low background level of organics and is compatible with the soxhlet extraction process used to remove the soluble organics from the particulate matter.

Figure 9 illustrates in total the various steps followed for the analysis of the particulate matter in the engine exhaust. Support for much of this analysis developmental work was provided by an Environmental Protection Agency grant (EPA Grant #806558010), the purpose of which was to chemically characterize the soluble organic extract. The detailed chemical methodologies for the three boxes appearing below the dotted line on Fig. 9 were developed for use in the EPA grant work. The methodologies for all the boxes appearing above the dotted line, while developed primarily for use in the EPA grant, were used extensively in the work here.

DIESEL PARTICULATE MATTER ANALYSIS

FIGURE 9

The primary interest here was to study the effect of fumigating the engine with various amounts of methanol on the biological activity of the raw particulate matter and its soluble organic fraction. The biological activity was assessed using two test systems, 1) the Ames Salmonella typhimurium test (5) and, 2) the Bacillus subtilis Comptest (6). These tests can never replace animal and human epidemiology studies on the potential health hazard of Diesel exhaust particulate matter but they do provide rapid and economical means for obtaining information about their mutagenic and/or carcinogenic activity.

The methodologies for exhaust particulate collection and analysis developed using the single-cylinder engine were then adapted for use with the multicylinder engine tests described in the next section.

3.4 Multicylinder Engine Work

In light of all the attention presently being given to methanol as an alternative fuel and the rapid increase in the use of the Diesel engine for personal transportation, the question of the possibility and consequences of utilizing methanol in the Diesel engine has become quite relevant. To obtain some initial answers to these questions a study involving the fumigation of methanol into a light-duty Diesel engine was carried out. The objective of this study was to assess the effects of methanol fumigation on the operation of a light-duty automotive Diesel engine. This was done by making measurements on fuel efficiency, smoke, nitric oxide emission, biological activity of emitted particulate matter, and the occurrence of severe knock. This was done with a production engine in the "as received" condition except for the addition of a methanol system.

The engine used in this study was an Oldsmobile 5.7ℓ V-8 automotive Diesel engine. It was of the indirect injection type utilizing a swirl precombustion chamber cast from stainless steel, ground to size and pressed into the cylinder head. The engine was coupled directly to a Westinghouse type SK cradled dynamometer with a balance beam resolution of 0.3 pounds-force and a dynamometer constant of 1000. The use of methanol was accomplished by means of a dual-fuel system. Diesel fuel was introduced in the conventional manner through the stock fuel injection system and methanol was introduced through an air atomizing spray nozzle into the intake air with the charge entering the main combustion chamber through the intake valve.

The number one cylinder fuel injector was equipped with needle-lift instrumentation. A Kristal Type 6031, acceleration-compensated, quartz crystal piezoelectric pressure transducer also communicated with the precombustion chamber of the number one cylinder. This transducer was housed in an adapter which was the identical shape of the glow plug it replaced and had the same volume. The output of a quartz transducer, a current which equals the rate of change of charge with time, is proportional to the rate of pressure change with time. Depending on the diagnostics to be performed this signal, the current, could be directed through a charge amplifier or a current amplifier to provide a voltage proportional to pressure or time rate of pressure change. The rate of pressure signal was used as the input to a knock quantification system. The pressure signal was used to generate P-t traces to provide some insight into the combustion event.

The particulate sample train through which the gas phase sample was also drawn was constructed solely of stainless steel. The sample was drawn out of the exhaust stream with a 0.372 in. ID stainless-steel

tube bent at a 90° angle and positioned at the center of the 3.500 in. ID exhaust stack approximately 40 inches above the mixing tank. The velocity of the exhaust gases in the stack at all engine operating conditions considered gave a calculated Reynold's number which indicated the flow at the point of sampling was turbulent, and thus the positioning of the sample probe was not as critical as it would have been had the velocity profile been laminar. Isokinetic sampling prevented any mass discrimination of the exhaust particles by the probe thus insuring a representative sample. All particulate matter samples were collected on 47 millimeter Pallflex type T60A20 filters, (Pallflex Products Corp., Putnam, Conn.). These were teflon-coated, glass-fiber filters which did not add any artifacts to the soluble organic fraction (SOF) that was Soxhlet extracted with dichloromethane.

Smoke opacity measurements were carried out using an end-of-the-line United State Public Health Service Full-Flow Light Extinction Smoke-meter. Although all regulated gas phase exhaust emissions were monitored, particular attention was paid to nitric oxide. The NO was measured using a REM Incorporated, Source NO_x monitor.

The experimental procedure followed was to organize the engine operating conditions into a test matrix consisting of nine cells each of which had a specified energy input rate and engine speed (Table 1). This test matrix represents in addition to the full load condition the normal steady-state driving conditions as determined from 0.0, 4.0 and 7.2 percent-grade road-load horsepower curves. These load conditions were then called 1/4, 1/2, 3/4, and full "rack" which derived from the nominal position of the fuel-flow control valve on the rotary injection pump for the test engine. The data for the test matrix was

Table 1 - Baseline Data for Multicylinder Engine

RPM RACK	1500	1720	2000
1/4	14.7* 22.1 0.593 11522. 2817.	13.5 17.8 0.739 14185. 3196.	11.0 12.4 0.918 17834. 3273.
1/2	40.8 61.50 0.409 7940. 5393.	35.2 46.3 0.510 9789. 5743.	41.1 46.5 0.468 9098. 6283.
3/4	52.0 78.50 0.446 8661. 7511.	59.2 77.9 0.482 9256. 9129.	66.2 74.9 0.444 8628. 9516.
Full	56.3 84.9 0.494 9596. 8999.	65.6 86.3 0.497 9531. 10416.	81.4 92.1 0.432 8404. 11411.

* Data in each block is tabulated as follows:

bhp

pmep 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°F, P = 29.38 in. Hg

generated using the baseline fuel and a commercial lubricating oil in the crankcase (see Table 2).

The main purpose of this work was to determine the effect of substituting methanol for Diesel fuel on engine performance and emissions. The substitution being performed on an energy basis was determined to be the most experimentally sound in that it would not be a function of any engine specific parameters. This method is dependent on the definition of full "rack" which is derived from the rated maximum power operating condition. Each operating condition was defined by a rate of energy input. Addition of methanol was accompanied by a reduction in the flow rate of Diesel fuel such that the energy input based on the lower heating values of the methanol and Diesel fuel did not change from the established baseline value.

The engine was allowed to run until steady-state operation as indicated by oil and coolant temperatures ($230 \pm 5^\circ\text{F}$ and $180 \pm 5^\circ\text{F}$ respectively) was reached before recording any data. Performance and exhaust emission data were collected for various percentages of total energy supplied by methanol over the range of 1/4, 1/2, 3/4, and full rack for engine speeds of 1500, 1720 and 2000 RPM. All testing with methanol was performed with unheated inlet air, all of which entered the engine through the methanol system. The biological activity of the raw particulate and the SOF was assessed using the Ames Salmonella typhimurium test and the Bacillus subtilis Comptest. For further details concerning the experimental equipment and procedures used in this study see Refs. (7&8).

Figures 10 through 13 present the results obtained upon methanol fumigation for the baseline condition in each cell of the test matrix. Generally, the addition of methanol proceeded in steps of five percent

Table 2

Baseline Fuel and Lubricating Oil Specifications

PROPERTIES OF BASELINE TEST FUEL

Fuel Type No. 2 Diesel MIL F-46162

Properties

Gravity, °API	35.6
Cetane, Calculated	42.0
Viscosity, Kinematic @ 100°F	2.31
Flash Point, °F	140.0
Pour Point, °F	-5.0
Cloud Point, °F	7.0
Net Heat (ASTM D240) Btu/lbm	19429.0
Aromatics, %	32.6
Olefins, %	1.0
Distillation	
IBP, °F	394.0
50% point, °F	470.0
EP, °F	626.0
Recovery, %	99.0
Residue, %	1.0
Loss, %	0.0

PROPERTIES OF TEST ENGINE LUBRICATING OIL

Oil Type Shell Rotella T Premium Multi-Purpose HD

Saybolt Viscosity @ 100°F	560.0
" @ 210°F	67.0
Viscosity Index	98.0
Pour point, °F	5.0
Sulfate Residue, % wt.	1.0
Neut. No., (TBNE)	7.0

Quality Level

Meets	MIL-L-2104C
Exceeds	MIL-L-46152
	MIL-L-2104B

API Classification CD, SE

Figure 10

1/4 Rack 5.7l Oldsmobile Diesel Engine Results

● - 1500 RPM, ■ - 1720 RPM, ▲ - 2000 RPM

Figure 11

1/2 Rack 5.7L Gldsmobile Diesel Engine Results

● - 1500 RPM, ■ - 1720 RPM, ▲ - 2000 RPM

Figure 12

3/4 Rack 5.7L O'dsmobile Diesel Engine Results

● - 1500 RPM, ■ - 1720 RPM, ▲ - 2000 RPM

Figure 13

Full Rack 5.7L Oldsmobile Diesel Engine Results

● - 1500 RPM, ■ - 1720 RPM, ▲ - 2000 RPM

by total energy to a point where either knock-limited operation was reached or the combustion process deteriorated such that the engine no longer ran smoothly.

A brief discussion of the important results obtained from the methanol fumigation study follows.

THERMAL EFFICIENCY - Since the engine energy input rate and speed were held constant for each fumigation condition, the thermal efficiency curves also represent power curve trends as well. Here the thermal efficiency is defined as the corrected brake horsepower divided by the rate of fuel energy supplied. For the 1/4 and 1/2 rack settings, thermal efficiency generally dropped off with increased methanol fumigation. However, for the 3/4 and full rack settings, an increasing trend was observed for all engine speeds.

NITRIC OXIDE - Emission of NO was observed to decrease for all rack settings and speeds as the amount of methanol fumigated was increased. For the lower rack settings (1/4 and 1/2) it appears as though there is a threshold value in the vicinity of five to ten percent methanol addition above which the reduction of NO becomes insignificant. For the higher rack settings, this trend does not seem to exist. Also, there does not seem to be any consistent speed effect displayed throughout the data.

SMOKE OPACITY - In order to put these data in proper perspective, it must be pointed out that between three and four percent on this opacity scale represents the point at which the engine exhaust plume becomes visible when viewed against a light background. The 3/4 and full rack curves indicate that the addition of methanol does permit an increase in power with little or no increase in smoke. This trend also prevails for the 1/2 rack 2000 RPM curve until the addition of methanol

reaches 15 percent. A general observation that can be seen by looking at all the smoke data is that the addition of methanol generally does not change the smoke opacity appreciably from the value observed at the baseline condition.

OCCURRENCE OF KNOCK - In this study severe knock (K_g) has been defined as a rate of pressure change whose magnitude exceeds the rate of pressure change present at all times during a hypothetical "knockless" combustion event by 50 psi per degree of crank angle. Each data point on the K_g curves is the number of severe knock events per combustion stroke averaged over 100 combustion strokes. Each plotted value thus represents the frequency of severe knock occurrence, $(K_g)_f$, for a particular engine operating condition. The trend shown by the plotted data for each rack setting considered indicates the sensitivity of the occurrence of knock to methanol fumigation at a particular energy input rate. As expected for the baseline conditions, knock was least likely at high loads and increased in frequency of occurrence as the load was decreased. This relationship was reversed however as methanol was substituted for Diesel fuel due to the greater knock sensitivity of the higher rack settings. Operation with methanol was limited by excessive occurrence of severe knock at the 1/2, 3/4 and full rack settings. It was arbitrarily chosen to set this limit as the condition for which the frequency of occurrence of severe knock exceeded 1.5. For the 1/2 rack 2000 RPM condition, an additional step of 5 percent by energy methanol introduction was taken to verify the large increase in knock observed from the two previous points. It is interesting to note that at 1500 RPM knock-limited operation as defined here is never reached. The knock data for the 1/4 rack setting are of no consequence and are plotted for comparison purposes only.

The percentage by energy of methanol which could be fumigated into the engine was knock limited, according to the established definition, for five of the conditions shown on Figs. 11-13. The knock quantification system could not, however, provide any information concerning the particular mechanisms acting to produce the knock for each given condition, or for that matter, whether the same or different mechanisms were acting at each condition. Some insight, however, can be gained by examining pressure history recordings at various conditions. For example, Fig. 14 presents the baseline and 20 percent methanol conditions at 1/2 and full rack. For the 1/2 rack condition shown, the engine was running smoothly and the pressure traces indicate about the same peak pressures. In fact, the only discernable difference between the two 1/2 rack pressure traces is the slightly lower compression curve that results from cooling when methanol is fumigated. For the full rack condition, which was knock-limited, it is seen that combustion starts early, in fact before the injection of any Diesel fuel, and it is the result of the homogeneous methanol-air mixture autoigniting. This produces a peak pressure which is considerably higher than that for the zero methanol condition and this causes the severe knock. The knock-limited condition for which methanol supplied 40 percent of the total energy at 1/2 rack and 2000 RPM is presented in Fig. 15 along with the 1/2 rack baseline condition and the hot compression trace. In this figure all peak pressures are about the same, but the fumigated methanol trace shows that ignition did occur quite late and began with a large, rapid pressure rise. The cycle-by-cycle pressure histories for the 40 percent methanol case were quite similar, all appearing as shown here. The initial rate of pressure change was great enough to exceed K_g , and thus this condition

Figure 14 - Comparison of Pressure Histories

Figure 15 - Comparison of Pressure Histories

was knock limited. Here knock-limited operation is caused by the autoignition of all the Diesel fuel and methanol-air mixture; a mechanism that is quite different from the mechanism which caused knock-limited operation for the full rack condition of Fig. 14.

The needle lift traces of Figs. 14 and 15 give some indication of the injection timing schedule which is programmed into the stock injection pump. In all cases the injection pump was operated in the "as received" condition and no attempt was made to temper the results by optimizing the injection timing.

PARTICULATE ANALYSIS - All the particulate data resulted from direct (undiluted) sampling of the combustion products in the exhaust stack. Particulate was collected on 47 mm filters and care was then taken to light-guard the collected material at all times, i.e. while in storage, during the Soxhlet extraction, and while doing the biological assays. Table 3 summarizes the particulate data that was generated as part of this study. The information in each cell of Table 3 resulted from material collected on several filters and then combined and/or averaged. At constant speed the particulate deposition rate increases with rack setting, while at a constant rack setting it generally decreases with an increase in speed. It is curious that whenever the percent of the particulate represented by the SOF is greater than 45 the raw particulate exhibits significant biological activity as measured by the Ames test. Figures 16 and 17 present some of the typical biological data in graphical form. On Fig. 16 the dose response curves are characteristic of the Ames test and it is seen that the activity of the raw particulate is much lower than that of the SOF except for the case where 30 percent methanol was fumigated. The same trend for the Comptest is also seen in Fig. 17. On both figures it appears as though the fumigation of methanol increase biological activity.

SUMMARY OF PARTICULATE DATA

RACK RPM	1/4	1/2			3/4	FULL
2000	3273. [*] 0 1.1496 56.2 0.21 4.0 1000 116	6238. 0 1.0729 26.6 NS ⁺ 1.6 1250 172	6238. 20 0.7938 46.4 0.80 3.5 NR [‡] 136	6238. 30 0.6725 56.2 0.3 4.4 NR 110	9516. 0 1.3410 23.8 NS 2.0 NR 166	11,411. 0 1.6245 11.5 NS 1.68 NR 240
1720		5743. 0 1.2225 35.0 NS 2.0 NR 230	5743. 20 1.1927 34.2 NS 6.20 NR 50	5743. 30 0.8099 55.3 1.4 5.70 1125 90		
1500		5393. 0 1.1254 28.4 NS 2.65 NR 71	5393. 20 1.6760 34.4 NS 1.6 NR 390	5393. 30 1.0442 34.29 3 2.1 1360 160		

* DATA IN EACH BLOCK IS TABULATED AS FOLLOWS:

TOTAL FUEL ENERGY INPUT - BTU/MIN

PERCENT OF TOTAL FUEL ENERGY INPUT AS METHANOL

PARTICULATE DEPOSITION RATE - MG/MIN

SO₂ PERCENT

AMES TEST RESULTS, TAGS, REV/UG @ 100UG/PLATE RAW, SO₂

COMPTON DOSE UG/MR AT RELATIVE TRANSFORMATION OF 0.05. RAW, SO₂

+ NS - NOT SIGNIFICANT < 0.1 REV/MG

‡ NR - NO REDUCTION TO RELATIVE TRANSFORMATION OF 0.05

TABLE 3

Figure 16

Results of Ames Test on Various Samples
Using TA98 Strain of Salmonella typhimurium

Figure 17
Results of Compeat on Various Samples

Here the two short-term prokaryotic (bacterial) test systems used were the Ames Salmonella test and Bacillus Comptest. It is important to note that these test systems can give an indication of an agents ability to cause DNA damage. However, data provided by these test systems cannot provide information on "permissible levels". Again, such levels can be established only when it is completely known how a chemical interacts with biological systems (man and his environment). However, it is possible to arrive at certain conclusions from the data presented in Table 3 and in Figs. 16 and 17. Specifically, the SOF is capable of causing a significant number of mutations in the Ames test even at a dose of 50 µg/plate while the raw particulate has considerably less activity. Also, the data of this study demonstrate that at least part of the damage done to the DNA, by Diesel particulate, is capable of causing the induction of the B subtilis "SOS" system. This is of importance since a high correlation exists between an agents ability to cause cancer and its ability to induce "SOS" functions in bacteria (9,10,11). Thus, the data suggest that Diesel particulate may represent an important environmental pollutant. Finally because fumigation with methanol appears to increase biological activity and the reasons for this are not understood this phenomena certainly deserves further study.

It is important to remember that all the work done here on methanol fumigation was done with a stock engine in the "as received" condition except for the alcohol induction system. No attempt was made to override the injection timing program that was built into the injection pump in order to optimize the Diesel fuel oil injection timing as the amount of fumigated methanol was changed.

The conclusions that can be drawn from this phase of the study are as follows:

- (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. See Figs. 12 and 13.
- (3) Increased methanol fumigation eventually produces knock-limited operation at the higher rack settings for speeds of 1720 RPM and 2000 RPM. See Figs. 12 and 13.
- (4) Since excess quantities of fumigated methanol reduce thermal efficiency at the lower rack settings (see Figs. 10 and 11) and induce severe knock at the higher rack settings (see Figs. 12 and 13) it would seem as though 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 (see Table 3 and Figs. 16 and 17).

IV. CLOSURE

This report has summarized the work done during the first three years of a grant which has now been continued. A large portion of the effort during the first three years of this project was expended in developing facilities and methodologies for obtaining fundamental information. During the continuation period it is anticipated that these facilities will prove to be useful for the study of the various alternate fuels as they become available. Based partially on what has been learned thus

far in this grant and on what is now perceived to be of immediate importance in the light-duty Diesel engine field, the following work statement has been developed for the continuation period.

1. All work done thus far was directed at collecting data with the fuel system components of the engine in the as-received condition. Thus, the fuel injection pump was operating on a timing program built into it by the manufacturer. Also, even though the intake manifold was altered to accommodate the fumigation system, no intake charge heating was done. Therefore, the effect of changing injection timing and of heating the intake charge will be investigated in an attempt to optimize fuel energy utilization. In this effort, means for recovering engine waste energy for the intake charge heating will be studied.

2. Fundamental combustion bomb and GC/micro-reactor studies will be continued in an effort to help explain the occurrence of severe knock and increased carbon monoxide formation when methanol is fumigated.

3. A rather flexible single cylinder Diesel engine test set-up has been built during the initial grant period. This facility shall be used for the following tasks:

A. To delineate the trade-offs between anhydrous and aqueous ethanol; solutions from 190 proof all the way down to 100 proof will be considered. This study is considered to be of some urgency with the advent of increasing ethanol distillation by farmers for the purpose of fueling their tractors.

B. To obtain a direct comparison between methanol introduction via fumigation and via an emulsion. The latter being either a stabilized ethanol-fuel oil emulsion or a mechanical mixture of the two. Therefore, this study will entail a comparison among three approaches.

C. To investigate ignition assists for the purpose of using both neat methanol and ethanol as a fuel in a Diesel type engine. These assists will not be of the chemical additive types known as ignition improvers, but rather in the nature of a spark or glow plug.

4. The adaptability of petroleum fuel oil extenders other than the alcohols will be investigated using the constant volume combustion bomb and the single cylinder Diesel engine. In particular, blends of used lubricating oil, various vegetable oils, and coal or starch slurries are possibilities.

5. With the use of all extenders it is important that the health effects of the generated particulate matter be assessed. In this connection then, biological assays will continue to be done for all pertinent engine tests.

It is understood that the Department of Energy has some large projects underway now in several of the areas mentioned in the specific tasks of this work statement. These large programs tend to be screening efforts using many different engines and fuels. The work proposed here is in no way intended to compete with these projects but rather is intended to provide supplemental basic back-up knowledge to help understand some of their findings.

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