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High-Alcohol Microemulsion Fuel Performance*
in a Diesel Engine

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ABSTRACT

Incidence of methanol use in diesel engines is increasing rapidly due to the potential to reduce both diesel particulate emissions and petroleum consumption. Because simple alcohols and conventional diesel fuel are normally immiscible, most tests to date have used neat to near-neat alcohol, or blends incorporating surfactants or other alcohols. Alcohol's poor ignition quality usually necessitates the use of often expensive cetane enhancers, full-time glow plugs, or spark assist. Reported herein are results of screening tests of clear microemulsion and micellar fuels which contain 10 to 65% C_1-C_4 alcohol. Ignition performance and NO emissions were measured for clear, stable fuel blends containing alcohols, diesel fuel and additives such as alkyl nitrates, acrylic acids, and several vegetable oil derivatives.

Using a diesel engine calibrated with reference fuels, cetane numbers for fifty four blends were estimated. The apparent cetane numbers ranged from around 20 to above 50 with the majority between 30 and 45. Emissions of nitric oxide were measured for a few select fuels and were found to be 10 to 20% lower than No. 2 diesel fuel.

INTRODUCTION

The move from petroleum-based fuels to alternative fuels is well underway in both the light and heavy duty transportation sectors. In the light duty sector, M85 (a blend of 85% methanol, 15% unleaded gasoline) has been a popular fuel (1-4). † The addition of gasoline to methanol improves flame visibility and cold starting, lowers flash point temperature, and discourages internal consumption. Methanol is an attractive alternative for the light duty sector as it has high octane, can be produced from non-petroleum feedstocks, and has the potential to reduce some tailpipe emissions.

It is possible that a fuel blend of alcohols and diesel fuel could provide a commercially acceptable solution to controlling the emissions of older heavy duty vehicles. The 1991 and 1994 emissions standards for new trucks and buses are demanding large reductions in NO_x and particulate emissions. Although this goal might be achieved by aftertreatment of diesel fuel exhaust or by changing to neat alcohol fuels, these methods can have inherent drawbacks. Particulate traps for diesel exhaust are complex to regenerate, have questionable reliability and durability, and can be very expensive (5-9). There are several demonstration fleets currently in operation using neat or near-neat methanol fuel in conventional diesel engines (1,10-15). Due to methanol's poor ignition quality (low cetane number) this usually requires spark plugs, glow plug operation at idle and low load, or expensive and explosive cetane enhancers (1,10-21). While new engines will have to meet the EPA standards, many older engines still on the road may not. For the older engines, it would be desirable to use a fuel which would inherently lower vehicle emissions with little or no engine modifications. A microemulsion or micellar fuel might provide a low emissions transition fuel which could function adequately in older engines. Reducing emissions of older heavy duty vehicles could actually have a more immediate effect on air quality than simply imposing more strict standards on new vehicles.

The major purpose of this exploratory study was to determine the possibility of blending a potential low emissions fuel which has sufficient ignition quality (cetane number near 40), to run in an unmodified diesel engine made up of only 40-70% diesel fuel, with remaining constituents being alcohol(s) and cost effective co-solvents and surfactants. An earlier study (22) indicated the potential feasibility of using long chain fatty acids and their derivatives to enhance both performance and stability of high alcohol diesel fuels. These materials combined stability with low cost and minimal toxicity. Similar surfactants and surfactant blends were also explored.

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† Numbers in parentheses designate references at the end of the paper.

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LITERATURE REVIEW

Hardenberg and Ehnert (23) studied the correlation between cetane rating and actual ignition delay for solubilized diesel fuel blended with wet ethanol (non-anhydrous). Cyclohexyl nitrate was used as a cetane enhancer in these tests. The authors found a substantial and significant improvement in rated performance of fuels evaluated in a conventional direct injected engine, as opposed to a cetane test engine. For example, a 4% triethylene glycol nitrate - 96% ethanol blend had performance equal to a cetane of 52 in the conventional engine and a cetane of less than 20 in the cetane test engine. The investigators obtained contrasting results with normal C_8 to C_{16} alkanes: ASTM D 613 values were higher than those extrapolated from the ignition delays of a conventional engine.

Saeed and Henein (24) also experimented with ethanol, studying the cetane rating of fuel blends containing anhydrous ethanol and diesel fuel in a direct injection single cylinder prechamber CFR engine. With the exception of raising intake air temperature to permit measurements of low cetane fuel blends, experiments conformed to the ASTM D 613 cetane method. Two different intake air pressures were used, higher pressure being required for blends with greater than 30% ethanol. Cetane number decreased from 39 for neat diesel fuel to values less than 5 for blends containing more than 70% ethanol by volume. Substantial variation in the ignition delay times from cycle to cycle was noted, especially for higher alcohol content blends. There was no mention of use of any co-solvents or surfactants.

Needham and Doyle (25) studied the combustion and ignition quality of conventional, synthetic, and alternative fuels in both indirect and direct injection naturally aspirated light duty diesels. The fuels tested included normal and low quality middle distillate petroleum fuels; high-naphtha diesel fuels; a diesel fuel blended from a tar sands and hydrotreated cat-cracked cycle oil; a diesel fuel blended from diesel oil and coal liquids; a shale oil; degummed sunflower oil; sunflower oil fatty acid ethyl esters; and a blend of methanol, hexanol, and diesel fuel. The results were compared to values predicted by the ASTM D 613 procedure for estimating cetane number. Although the petroleum based fuel and ethyl sunflower oil fatty acid ester performance corresponded to that predicted by ASTM D 613, the performances of sunflower oil, naphtha blend, and methanol blend, were not well predicted by ASTM D 613. In addition, the sunflower oil based fuels had substantially lower NO_x values at load than did conventional diesel fuels.

In a companion paper, Siebers (26) presented the results of his combustion bomb evaluations of a similar cohort of fuels. In general, there was good agreement between the observed performance of the cohort of fuels in combustion bombs and in the full scale tests reported by Needham and Doyle (25). Combustion bomb tests indicated that ASTM D 613 cetane tests were adequate predictors of actual combustion performance of petroleum diesel fuels. However, these tests did not adequately model the performance of alternative fuels,

such as degummed sunflower oil or methanol. Siebers' results indicated that the cetane rating of a fuel is a useful predictor of its overall combustion properties only if reference fuels are similar in combustion characteristics to the fuels under evaluation.

Ryan (27) used a constant volume combustion bomb, operated at 427 °C and 4.1 MPa, to compare the physical and chemical ignition delays of a wide group of fuels to their ASTM D 613 cetane ratings. The combustion bomb tests were found to have excellent repeatability for a given number of fuels; ignition delay was usually repeatable to within a few tenths of a millisecond. However, when ignition delays of standard hexadecane - heptamethylnonane blends were used as a measure of cetane ratings, only straight-run petrochemical fuels were within the error band of the bench tests. The ignition behavior of coal liquids, degummed sunflower seed oil, or the methyl esters of sunflower seed oil fatty acids was not well predicted at the test combustion conditions.

Ryan, with Stapper (28), again investigated the correlation between cetane rating by ASTM D 613 and ignition delay in their constant volume combustion bomb. Ignition delays of forty-two different fuels ranging in viscosity from 0.4 to 34 cSt (40 °C) and in boiling point from 64 to 588 °C were measured, confirming the ability of the combustion bomb tests to cover diesel fuels ranging from coal-derived liquids to ASTM primary reference fuels. Fuel cetane values ranged between 8 and 100. The tests indicated limited correlation between CFR engine cetane rating and physical ignition delay. According to Ryan and Stapper, advantages of combustion bomb tests, as opposed to CFR engine tests, are the small amounts of material used, the excellent control over combustion conditions, the low cost of combustion bomb construction, and the ability to test materials outside of the ASTM D 613 range.

Ryan, with Callahan (29), again compared and correlated the combustion performance of their constant volume combustion bomb and a variable compression ratio diesel engine. Using reference fuels with cetane ratings ranging between 15 and 100, they determined test conditions which permitted direct comparison of engine and bomb cetane ratings and ignition delays. They found that higher combustion bomb temperatures provided the best correlations with variable compression engine results. However, the tests were performed on predominantly petroleum-derived fuels. This is important because the influence of physical and chemical properties makes it necessary to use reference fuels similar in structure to the fuels whose cetane rating is being analyzed.

Freedman and coworkers (30) investigated the combustion of vegetable oil fatty acid derivatives and compounds as fuel. Their investigation was motivated by the paucity of information about the combustion of these materials in spite of their considerable potential as substitutes and extenders for diesel fuels. Diesel engine cetane tests were performed on materials available in sufficient quantity. Combustion bomb estimated cetanes were correlated with ASTM D 613 cetane tests to

provide a reliable base for estimating and predicting the properties of materials as a function of chain length and chemical structure. To a reasonable extent, this work confirmed and extended previous research by Klopfenstein (31). Freedman, et al., found a substantial decrease in ignition delay with increasing fatty acid chain length for monoesters and fatty alcohols. For triglycerides, there appears to be a minimum ignition delay which occurs around chain lengths of 14 to 18 carbons. Estimated cetane numbers for esters, fatty alcohols, and triglycerides decreased with increasing unsaturation. Cetane numbers of vegetable oil triglycerides were adequately predicted as the weighted sum of the delays of their constituents.

Johnson, Friberg, and Stoffer (32) evaluated various methanol or ethanol and water microemulsion diesel fuels for stability, performance, and emissions, in an effort to develop effective diesel fuel extenders. Over fifty candidate fuels were examined; the majority of these could not meet minimum requirements of single phase stability between 50 and 150° F. Other significant fuel properties evaluated were cetane number, lower heating value, and viscosity. Fuel performance was measured by both the CFR test engine and a modified direct injection engine. Fuels tested contained no more than 15 percent by weight alcohol (with 2-5% water), with the continuous phase being diesel fuel. Hexanol was the typical surfactant. Emissions testing showed that small amounts of water appear to reduce visible smoke and particulate emissions, and the ethanol blends appear to reduce oxides of nitrogen.

Donnelly and White (33) surveyed the work of several investigators using emulsions of alcohol, water, and diesel fuel. Like Johnson, et al., these investigators also used blends with large amounts of diesel fuel. They reported that stable emulsions with methanol can be difficult to achieve, but that unstable emulsions generated on board the vehicle might be effectively utilized, although maintaining emulsification during low-speed operation and idle could be a problem. In summary, they noted that use of up to 20% w/w methanol in diesel fuel can result in power losses up to 10 percent, up to 15 percent reduction of specific diesel fuel consumption and a small increase in thermal efficiency, 20 to 60 percent higher oxides of nitrogen emissions, and more than 60 percent reduction in particulate emissions.

Dubovisek and Savery (34) investigated the correlation between ignition delay and charge temperature, charge pressure, equivalence ratio, and cylinder air movement. The investigators developed two simplified kinetic models which adequately predicted total diesel ignition delay for high and low temperature combustion. The models were found to be adequate for prediction of combustion performance of diesel fuel, alcohols, gasoline, and mixtures of diesel fuel and alcohol in both conventional and spark assisted engines.

The literature review shows that many investigators have found the ASTM D 613 method to be less-than-perfect when rating non-petroleum fuels. Some of the methods predict engine performance well, and others do not. Some correlate well with ASTM D 613, usually

only when testing petroleum based fuels. The use of a conventional diesel engine (as opposed to the CFR engine) in this study is therefore well justified for rating non-petroleum fuels. As reported in the literature, alcohol-diesel fuel blends have been tested, as have vegetable oils, fatty acids, esters, etc., however none of the investigators have looked at using co-solvents and surfactants as cetane enhancers for microemulsion fuels.

MATERIALS AND METHODS

FUEL FORMULATION. The amounts of materials used in each fuel were weighed into a single bottle in the following order: water, fatty acid(s), base, alcohols, other additives, and diesel fuel (D2). Weights of components other than D2 were to the nearest 0.1 g; weights of D2 were to approximately 0.2g. Sample bottles were capped after addition of the last component. If a clear, single phase was not formed during weighing, the bottle was swirled or inverted a few times to form a clear microemulsion. Fuels were used within a week of mixing.

REAGENTS. Chemical reagent, abbreviation, grade and supplier, respectively, are given in Table 1. Unless otherwise indicated, materials were standard industrial grade products.

ESTIMATING FUEL PHYSICAL PROPERTIES. Where possible, density, enthalpy of formation, chemical structure, and molecular weight for the materials used in fuels were obtained from the open literature or from manufacturers. Where this information was not available, average chemical composition, molecular weight, and structure were determined. From these, enthalpy of formation was calculated by summing the contributions of individual structural groups as described by Danner and Daubert (35). Density was generally estimated by interpolation of values from related compounds.

EQUIPMENT, INSTRUMENTATION, AND PROCEDURES. The engine used for fuel screening was a Deutz F1L-511W single cylinder, indirect injection diesel engine with 0.825 liter displacement and 19:1 compression ratio, coupled to a water-cooled eddy current dynamometer. Ignition delay (ID) was measured for reference fuels and test fuels, and equivalence ratio was used as an independent parameter for comparison. The ignition delay period is defined as the time from the start of injection to the start of ignition, and is shown for a typical engine cycle trace in Figure 1. The start of fuel injection was measured with a Wolff Controls injector needle-lift sensor, and cylinder pressure was measured with a Kistler water cooled pressure transducer mounted in an auxiliary port in the head, from which the start of ignition was determined. An incremental shaft encoder was used to track crank position and engine speed. All electronic signals were captured by a high-speed data acquisition system.

The engine was calibrated by measuring the ID of four known cetane number (CN) reference fuels, at three different loads and 1950 RPM. The reference fuels and their cetane numbers are given in Table 2. The cetane

Table 1. Materials used in blended fuels

Compound[a]	Abbreviation	Grade or purity[a]	Manufacturer
Acrylic acid	AA	T	Sargent
n-Butanol	NBA	AR	Mallinckrodt
t-Butanol	TBA	98%	MCB
Butoxyethoxyethyl acetate	BEEA	T	Sargent
Butoxyethyl stearate	BES	T	Stepan
Butyl carbitol	BCA	RD	
Butyl cellosolve	BCU	RD	Sargent
Cellosolve	ECU	RD	Sargent
Coconut fatty acids	CFA	T	Procter and Gamble
Dibutyl carbitol	DBC	T	Union Carbide
Diethylene glycol dioctanoate	792	T	Stepan
Diesel fuel	D2	REF	Phillips
Ethanolamine	EA	T	Eastman
Heavy aromatic naptha	HAN	T	Exxon
Hexadecane	HD	R	Aldrich
Light cycle oil	LCO	T	Phillips
L PEG - PPG BCP, 70% PEG, mw 6760	F77	T	BASF
L PEG - PPG BCP, 50% PEG, mw 1940	L35	T	BASF
L PEG - PPG BCP, 20% PEG, mw 1660	L42	T	BASF
L PEG - PPG BCP, 30% PEG, mw 1760	L43	T	BASF
L PEG - PPG BCP, 40% PEG, mw 2100	L44	T	BASF
Linolenic acid	E315	T	Emery Group
Methanol	MEOH	99+%, ANH	Aldrich
Methyl cellosolve	MCU	R	Sargent
Methyl dodecanate	MDD	95%	Procter and Gamble
Methyl oleate	MOA	70%	Ald
NS, Tergitol 15-S-5	T15-S-5	T	Unio
Nonylphenylethoxylate, Igepal CO-660	CO-660	T	G.
Oleic acid	OA	T	Eastman
Oleamide diethylaminoethyl ODA	ODA	T	Scher
PEG 200 dilaurate	P200DL	T	Stepan
PEG 400 dioleate	P400DO	T	Stepan
PEG 400 monooleate	P400MO	T	Stepan and Glyco
PEG (5) oleylamine	P2000A	T	Stepan
PEG (5) stearate	P200MS	T	Stepan
PPG (7) average mw 425	P425	T	Union Carbide
QA L PEG - PPG BCP, 70% PEG, mw 3460	T701	T	BASF
n-Propyl nitrate	PNO3	T	Eastman 6951
Soy oil ethyl monoester	SEE	T	
Soy oil fatty acids	SFA	T	Procter and Gamble
Triacetin	TA	99%	Aldrich

[a]Abbreviations used: ANH, anhydrous; AR, analytical reagent grade; BCP, block copolymer; L, linear; NS, nonionic surfactant; PEG, polyoxyethylene or polyethylene glycol; PPG, polyoxypropylene or polypropylene glycol; QA, quarternary amine; R, reagent; RD, redistilled; REF, reference fuel; T, technical
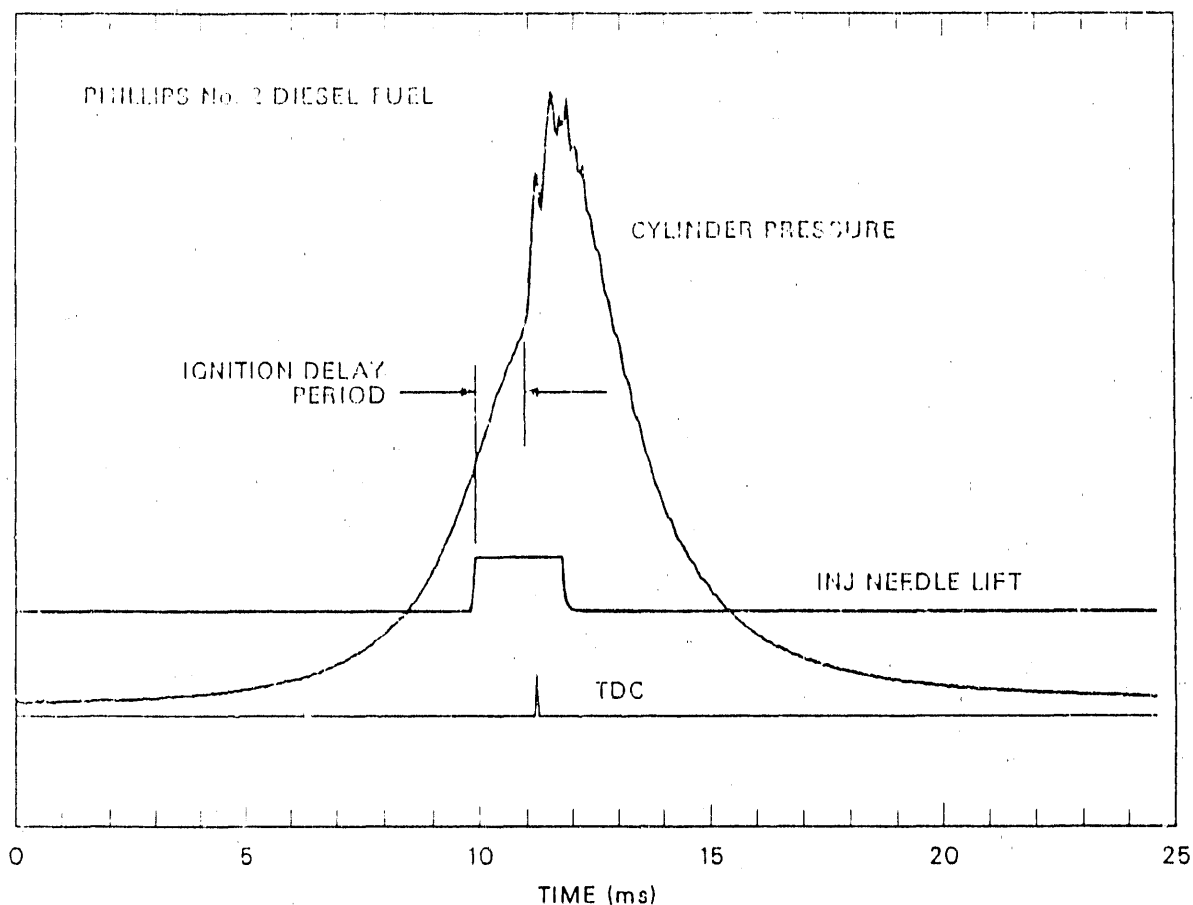
Figure 1. Engine cycle trace for Phillips No. 2 diesel fuel at 1950 RPM.

Table 2. Reference fuel composition and properties

Fuel	Component	Concentration, % w/w	Density, 60 °F, g/cc	Stoichiometric air/fuel ratio[a]	Heat of combustion, kcal/g	ASTM D-613 cetane number
Ref. 1	HD	100	0.773	14.95	10.49	100
Ref. 2	D2	100	0.850	14.47	10.07	45.6
Ref. 3	D2	50	0.882	14.18	9.99	33.7
	Ref. 4	50				
Ref. 4	HAN	46.5	0.909	14.02	9.87	25.3
	LCO	53.5				

[a] Calculated.

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numbers of reference fuels REF 2, 3 and 4 were determined by ASTM D 613 at Southwest Research Institute (SwRI), San Antonio, TX. Fuels REF 3 and 4 were purposely blended by SwRI to have distillation curves similar to diesel fuel, which the authors believe enhances their relevance as reference fuels. Cetane, or n-hexadecane (REF 1) is a primary reference fuel and has a cetane number of 100 by definition. The ID of the reference fuels was found to be a quasi-linear function of the equivalence ratio (ϕ) as shown in Figure 2. Note that there are two sets of curves, for pre-rebuild and post rebuild. This will be discussed in more detail later. The equivalence ratio is defined as:

$$\phi = \frac{\text{stoichiometric A/F (airfuel) ratio}}{\text{actual A/F ratio}}$$

The stoichiometric A/F ratios of the test fuels are calculated by summing the products of the mass fraction and stoichiometric A/F ratio of each of the fuel's constituents. The apparent CN of a test fuel is then calculated by double linear interpolation. Linear interpolation is first used to approximate the ID of the two reference fuels which "bracket" the test fuel, at the

same equivalence ratio as the test fuel. The test fuel's apparent CN is then found by a second interpolation.

Determining Ignition Delay Times. The stock Deutz fuel system consists of a small diaphragm pump (primary pump) which provides fuel at relatively low pressure (< 2 psig) to the cam operated injector pump, which provides high pressure (2-3000 psi) fuel to the fuel injector at the proper time in the engine cycle (approximately 15° before top dead center (BTDC)). A stock fuel injector modified to measure injector needle lift was used to determine the time of the start of injection; a needle lift trace is shown in Figure 1 along with cylinder pressure and TDC marker traces. The data acquisition system digitizes data and is capable of 100 kHz operation, i.e., the time step is 10 microseconds. From the cylinder pressure trace it is possible to estimate the start of ignition to within 20 or 30 microseconds. In most cases, a distinct pressure drop and subsequent recovery was not apparent, however a significant change in the slope was evident, and was used as the indication of the start of ignition. The time delay between the start of injection and the start of ignition is the ID. For all reference fuels and test fuels, ID was measured for at least four consecutive engine cycles and the numerical average used in interpolation of CN.
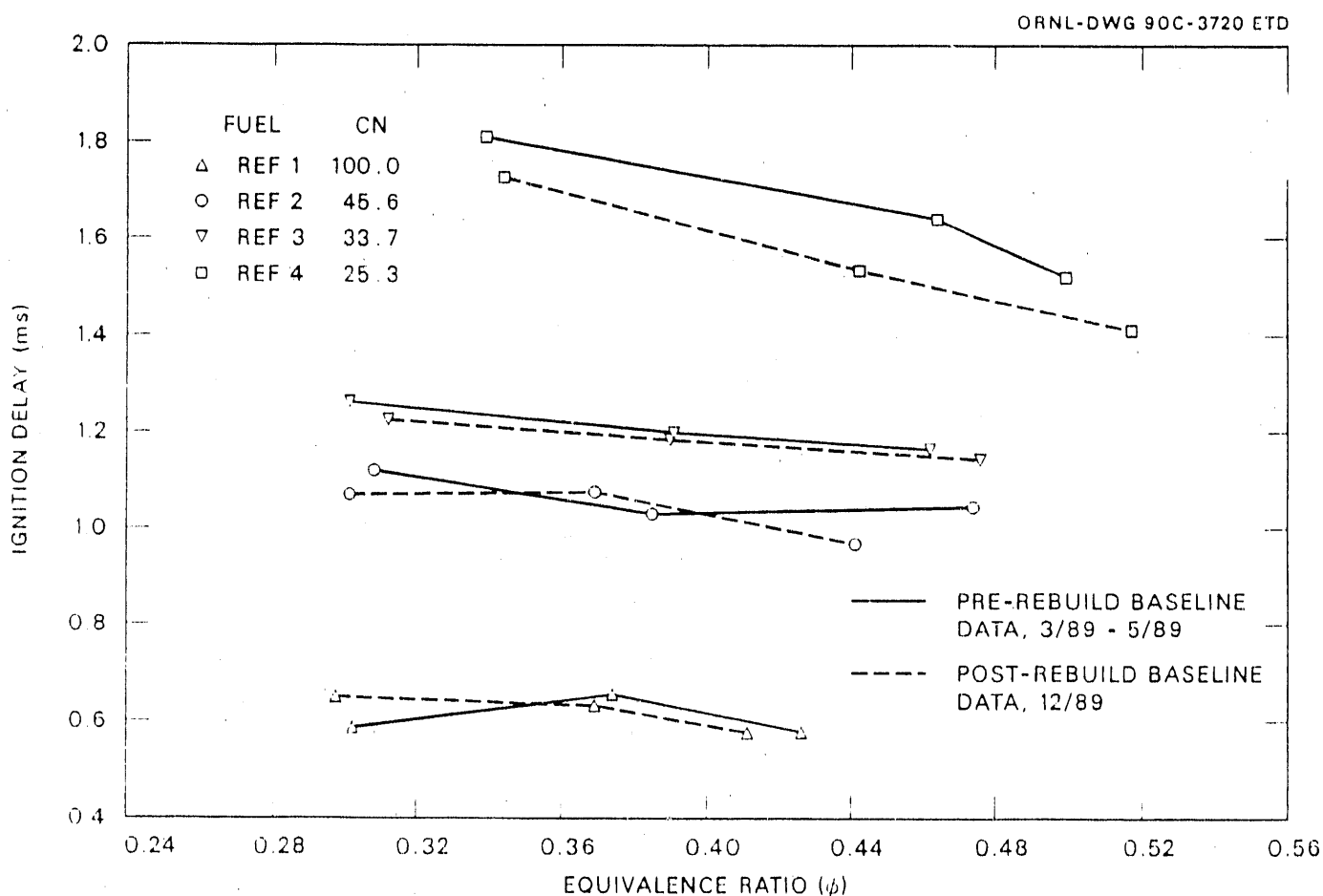

Figure 2. Ignition delay of reference fuels as a function of equivalence ratio.

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In fuel testing, the engine was operated on No. 2 diesel fuel (REF 2) until steady state operating conditions were reached. The experimental set-up included a 50 ml burette which was plumbed into the fuel system via a three-way valve. After the engine reached steady state operating conditions, the valve was switched to allow flow of the test fuel from the burette into the system (and to stop flow of the diesel fuel). Engine data was not monitored interactively (in real time); a finite amount of data (memory size specified by the user) was saved on the operator's command. Several minutes after the three-way valve was switched, a "window" or "snapshot," of data was saved, typically about 10 to 12 engine cycles. About 200 to 250 ml of test fuel was required to ensure that the engine was running on only the test fuel and not a mixture of test fuel and diesel fuel.

The typical loads and speeds used for the reference fuels were about 10, 15 and 20 lb-ft torque at 1950 RPM (1750 RPM). The test fuels were run at the same speed and 12 to 15 lb-ft, if possible. Due to the lower heating values, some had to be run at around 10 lb-ft.

Vapor Lock in Injector Pump. Early in the testing of fuels, some engine stalling was determined to have been caused by vapor lock in the injection pump due to the alcohols' low boiling points. This problem was remedied by installing an automotive type fuel pump upstream of the stock Deutz primary pump, which raised the inlet pressure to the injection pump to about 15 psig, and prevented any further boiling of fuel. Fuels which did not previously perform satisfactorily were retested.

Engine Rebuild during Testing. The Deutz engine used in screening the microemulsion fuels has also been used to exposure test ceramic specimens. In the late fall of 1989 a ceramic specimen fractured in the combustion chamber and caused severe piston, cylinder, and head damage. The engine was rebuilt with some new parts and some refurbished parts. The engine was then rebaselined (recalibrated) on all four of the reference fuels. For the most part, any differences between the pre-rebuild and post-rebuild baseline data were within the experiment's uncertainty. The new data were, of course, used in calculations for subsequently tested fuels. Both the pre and post-rebuild data are shown in Figure 2. Note that the differences were greatest for the lowest cetane fuel (REF 4). Other investigators have reported less repeatable results with decreasing ignition quality (24,28,32,36).

Emissions Measurements. Nitric oxide (NO) emissions were measured on a select few fuels using a Beckman 951 NO/NOₓ analyzer, mounted inside a Beckman cabinet with sample pump, dryer, and filters. NO_x emissions are not reported as this portion of the instrument was not operational. During engine testing the Beckman analyzer provided NO concentration in ppm (parts per million). The exhaust gas was assumed to consist only of CO_2, H_2O, and O_2 (the H_2O is removed by the dryer before measurement). The concentrations of CO_2, H_2O, and O_2 were calculated knowing the fuel formulation, and A/F ratio, and mass of NO was then calculated knowing the molecular weight of the exhaust

RESULTS

Less than 10% of the fuels tested had ignition quality so poor that the engine would not run at the specified speed (1950 RPM), and apparent cetane numbers could not be determined. Figure 3 shows the apparent cetane number plotted as a function of diesel fuel content for those fuels for which the apparent cetane number could be determined. The diagonal line in the figure represents the cetane number which, based on the ASTM D 613 definition, would be obtained by blending No. 2 diesel fuel (CN 45.6) in varying proportions with alphamethylnaphthalene (CN 0.0). The significance of the line is that over 90 percent of the fuels tested reside above the line. Despite poor ignition quality of some of the additives, some of the cosolvents and surfactants used were able to maintain the apparent cetane number of the test fuels. Obviously, some of the fuel additives have cetane numbers greater than zero. The individual fuels are discussed in more detail in the sections that follow, and some of the data in Figure 3 is presented again in several other figures, classed by additive type.

UNSATURATED FATTY ACID SUPPLEMENTED FUELS. The compositions and performance of eleven fuel blends using unsaturated fatty acids or fatty acid blends are shown in Table 3. Surfactant concentrations in these fuels ranged between 9% and 26%. Diesel fuel concentrations ranged between 30 and 76%. Four of the fuels contained water. Densities of these fuels ranged between 0.83 and 0.87 g/ml. Fuel heat of combustion varied between 7.9 and 9.5 kcal/g, and stoichiometric A/F varied from 11.2 to 13.6. This considerable variation was due to the large amount of alcohol and water in the fuels. Except for fuel 12, for which an apparent CN could not be determined, apparent CNs for these fuels ranged between 28 and 55. Note in Figure 4 that, in general, apparent CN increases with increasing diesel fuel content, as might be expected. Note also, however, that the apparent CNs of several of the fuels are higher than that of neat diesel fuel.

FATTY ACID ESTER SUPPLEMENTED FUELS. The compositions and performance of five fuel blends using fatty acid esters and three fatty acid ester - fatty acid blends are shown in Table 4. Two of the fuels contained no diesel fuel, while the concentration of diesel fuel in the other four fuels was 40 to 62%. The densities of these fuels ranged between 0.82 and 0.88 g/ml. Due to the high concentration of oxygenates, the heats of combustion and stoichiometric A/F ratios of these materials showed considerable variation. Apparent cetane numbers of test fuels ranged between 27 and 78, except for fuel 5, whose apparent CN could not be determined. Methyl dodecanate (fuel 1), a fatty acid monoester with an average chain length roughly equivalent to that of soy bean oil fatty acid, had the
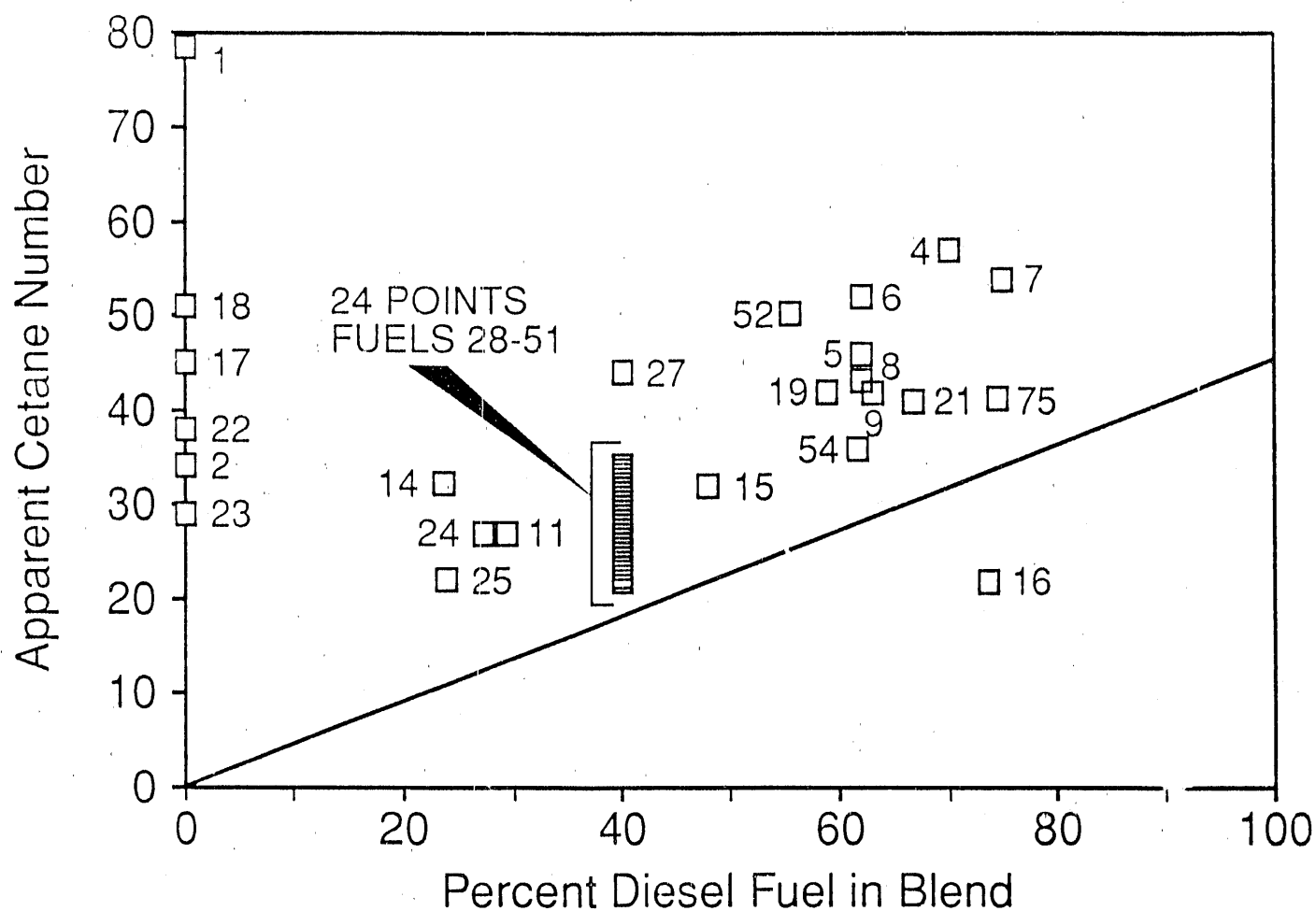
Figure 3. Apparent cetane number of fuel blends as a function of diesel fuel content.

Table 3. Compositions by weight and performance of unsaturated fatty acid supplemented test fuels

Fuel	Surfactants				Alcohols				Density, g/ml	Stoichiometric air/fuel ratio	Heat of combustion kcal/g	Apparent cetane number
	Surfactant	%	Surfactant	%	% Methanol	% t-Butanol	% Diesel	% H$_2$O				
4	E-315	10.0			10.0	10.0	70.0		0.842	13.5	9.485	56.1
5	E-315	18.0			14.0	6.0	62.0		0.846	13.1	9.223	44.1
7	E-315n[a]	9.0				10.0	76.0	5.0	0.855	13.6	9.483	52.5
6	E-315n	8.0	MDD	10.0	14.0	6.0	62.0		0.843	13.1	9.191	
8	E-315n	18.0				10.0	62.0	10.0	0.867	12.6	8.734	42.3
9	E-315n	18.0			5.0	10.0	62.0	5.0	0.857	12.9	9.002	41.5
12	OA	20.0			30.0	20.0	30.0		0.826	11.2	7.901	
33	SFA[b]	20.0			20.0	20.0	40.0		0.832	12.1	8.454	31.1
43	OA	20.0			20.0	20.0	40.0		0.832	12.1	8.475	28.0
44	OA	20.0			20.0	20.0	40.0		0.832	12.1	8.475	29.7
52	E-315	16.2	MDD	10.0		9.0	55.8	9	0.865	12.3	9.205	50.4

[a]Neutralized. [b]Fatty acid blend containing substantial amounts of unsaturated acids.

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Figure 4. Apparent cetane number of unsaturated fatty acid supplemented fuels as a function of diesel fuel content.

Table 4. Compositions by weight and performance of fatty acid ester supplemented test fuels

	Surfactants				Alcohols						Stoichiometric	Heat of	Apparent
Fuel	Surfactant	%	Surfactant	%	% Methanol	% n-Butanol	% t-Butanol	% H₂O	% Diesel	Density, g/ml	air/fuel ratio	combustion kcal/g	cetane number
1	MDD	100.								0.875	12.0	8.432	78.5
2	MDD	66.5			33.5					0.842	10.2	7.203	34.1
3	MDD	33.5			66.5					0.816	8.3	5.992	--
6	E-315	8.0	MDD	10.0	14.0		6.0		62.0	0.843	13.1	9.191	52.2
40	MOL	20.0			20.0		20.0		40.0	0.830	12.1	8.493	29.9
41	BES	20.0			20.0		20.0		40.0	0.849	12.1	8.489	27.0
52	E-315	16.2	MDD	10.0			9.0	9.0	55.8	0.865	12.3	9.205	50.4
54	792	8.4	MDD	8.4		20.9			62.4	0.854	13.3	9.961	36.1

highest apparent cetane number. Figure 5 shows the apparent cetane numbers of these fuels as a function of diesel fuel content. It is interesting to note that while fuel 1 has an apparent cetane of 78, adding 33.5% methanol pulls fuel 2's apparent cetane down to 34. Also note that while several fuels' apparent cetanes increase with increasing diesel fuel content, the apparent CN of fuels 6 and 52 are 5 to 7 points higher than that of neat diesel fuel.

ETHYLENE GLYCOL FATTY ACID ESTER SUPPLEMENTED FUELS. Compositions and performance of fifteen fuel blends using ethylene glycol esters of saturated, unsaturated, and branched saturated fatty acids are shown in Table 5. Diesel fuel concentration in the fuels tested ranged from 0 to 67%. Although there was little variation in fuel density, ranging from 0.83 to 0.89 g/ml, the substantial oxygenate concentrations of the fuels caused significant variations in stoichiometric A/F ratios and in heats of combustion. The stoichiometric A/Fs ranged from 7.6 to 13.3 and the heating values from 5.9 to 9.5 kcal/g. Apparent cetane numbers for these fuels ranged between 22 and 51, with that of fuel 26 being undeterminable. Apparent cetanes are plotted as a function of diesel fuel content in Figure 6. Note that several of the monoesters of unsaturated fatty acid supplemented fuels' apparent cetanes increase with increasing diesel fuel content, while fuels supplemented with the diesters of unsaturated fatty acids follow no such trend. Fuel 18 has the lowest diesel fuel content and yet the highest apparent cetane number. Many of these fuels look promising, with 5 of them having apparent cetanes greater than 40. Fuels 18 and 17 have no diesel fuel and the highest apparent cetane numbers, but heating values which are only about 60% of that of diesel fuel. On the other hand, fuels 19 and 27 have good apparent cetanes (over 40), contain only 40 to 55% diesel fuel, and have heating values that are 82 to 90% of that of diesel fuel.

POLYETHYLENE AND POLYPROPYLENE GLYCOL SUPPLEMENTED FUELS. Compositions and performance of seven fuels using polyethylene and polypropylene glycols as both surfactant and cetane enhancer are shown in Table 6. These materials were tested in blends containing 40% diesel fuel and 20% each glycol, methanol, and butanol. Properties of these fuels are, as might be expected, tightly clustered. The densities are all around 0.84 to 0.85 g/ml, and the stoichiometric A/F ratios only range from 11.4 to 11.8. Heats of combustion are all between 8.2-8.3 kcal/g, except for fuel 42 which has a heating value of 7.5. The apparent cetanes of these fuels fell between 29 and 32. It is probable that the variation in these values is due to small errors in measurement, rather than to any discernible trend related to surfactant structure.

INDUSTRIAL SOLVENT SUPPLEMENTED FUELS. Table 7 shows the compositions and performance of eight fuels supplemented with common industrial solvents. Fuel 36 was formulated with dibutyl carbitol, a solvent with predominantly ether linkages. Four fuels were blended with solvents in which alcohol and ester chain endings and linkages predominated and

three fuels were simple blends of n-butanol and diesel fuel. Densities and heats of combustion for fuels with the general formula of 40% diesel fuel, and 20% each of methanol, butanol, and surfactant show little variation. The densities range from 0.82 to 0.85 g/ml, and the stoichiometric A/F ratios range from 11.3 to 11.9. The heating values are also tightly clustered, ranging between 7.98 and 8.38 kcal/g. Apparent cetane number was significantly increased by the dibutyl carbitol in fuel 36, and to a lesser extent by by butyl carbitol in fuel 35. Densities, heats of combustion, and cetanes for diesel fuel -- n-butanol blends decreased with decreasing diesel fuel content.

MISCELLANEOUS INDUSTRIAL COMPOUNDS. Compositions and performance of seven fuels supplemented by a variety of industrial compounds are shown in Table 8. The compounds included n-butyl alcohol, acrylic acid, propyl nitrate, triacetin, and two alkylphenyl ethoxylates. Diesel fuel concentrations in these fuels ranged between 19 and 40%. Fuel densities ranged between 0.82 and 0.86 g/ml. Stoichiometric A/F ratios ranged between 10.2 and 12.2. Heats of combustion ranged between 7.2 and 8.5 kcal/g. The apparent cetane numbers of these fuels ranged from indeterminable to 33.7. The fuels with the best apparent cetanes were fuels 31 and 32, supplemented by only 40% diesel fuel and the alkylphenyl ethoxylates.

EMISSIONS MEASUREMENTS FOR SELECTED FUELS. Nitric oxide (NO) emissions were measured for selected fuels over various loads and speeds. The emissions for all of the fuels decrease with increasing equivalence ratio, as shown in Figure 7. Note that as much as a 20 percent decrease in NO emiss is realized by switching from diesel fuel. Note also that fuels 4 and 52 have 56 to 70% diesel fuel content, and fuel 27, the lowest NO producer, has only 40% diesel with 40% alcohols, an apparent cetane number greater than 40, and an energy density that is 82% that of No. 2 diesel fuel (8.2 kcal/g). Regression analysis (22) indicates that even more remarkable reductions in particulate emissions would be evident with these fuels, especially those high in alcohol content. Unfortunately, particulate measurements were precluded by a lack of resources in this preliminary study.

DISCUSSION

VAPOR PRESSURE PROBLEMS WITH METHANOL FUELS. Due to methanol's low boiling point (65 °C), some problems were experienced with fuel starvation due to vapor lock in the injector pump. This was easily remedied on the test engine by installing a fuel pump upstream of the injector pump, increasing the gauge pressure in the fuel line to about one atmosphere. This would not necessarily be required on a commercial in-service engine, unless fuel temperature was high enough, and fuel pressure and flow rate were low enough to allow boiling of the fuel.

FUEL ECONOMY AND POWER OUTPUT. The specific heating values of all of the fuels tested were 60 to 95% of that of conventional diesel fuel. It is an

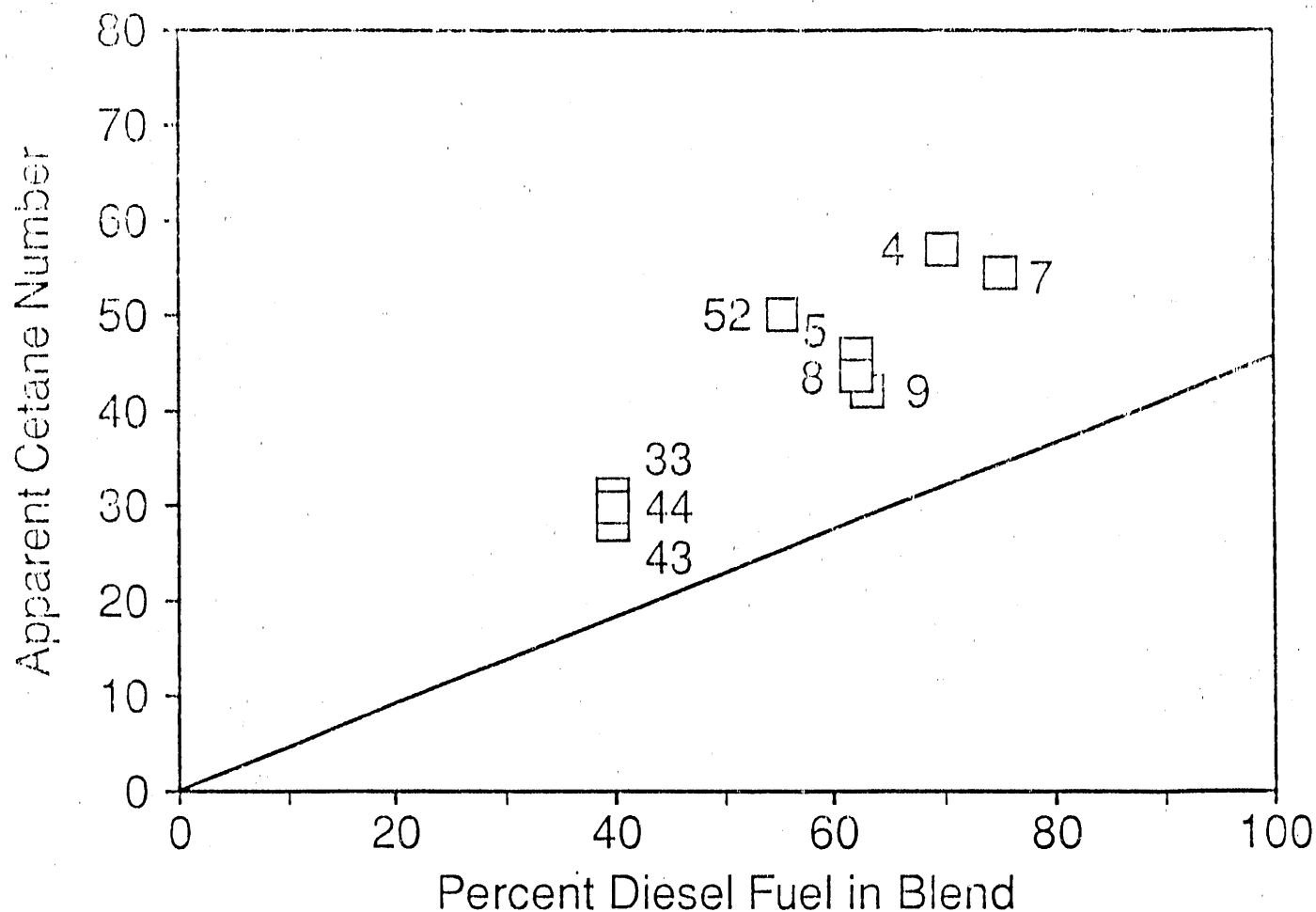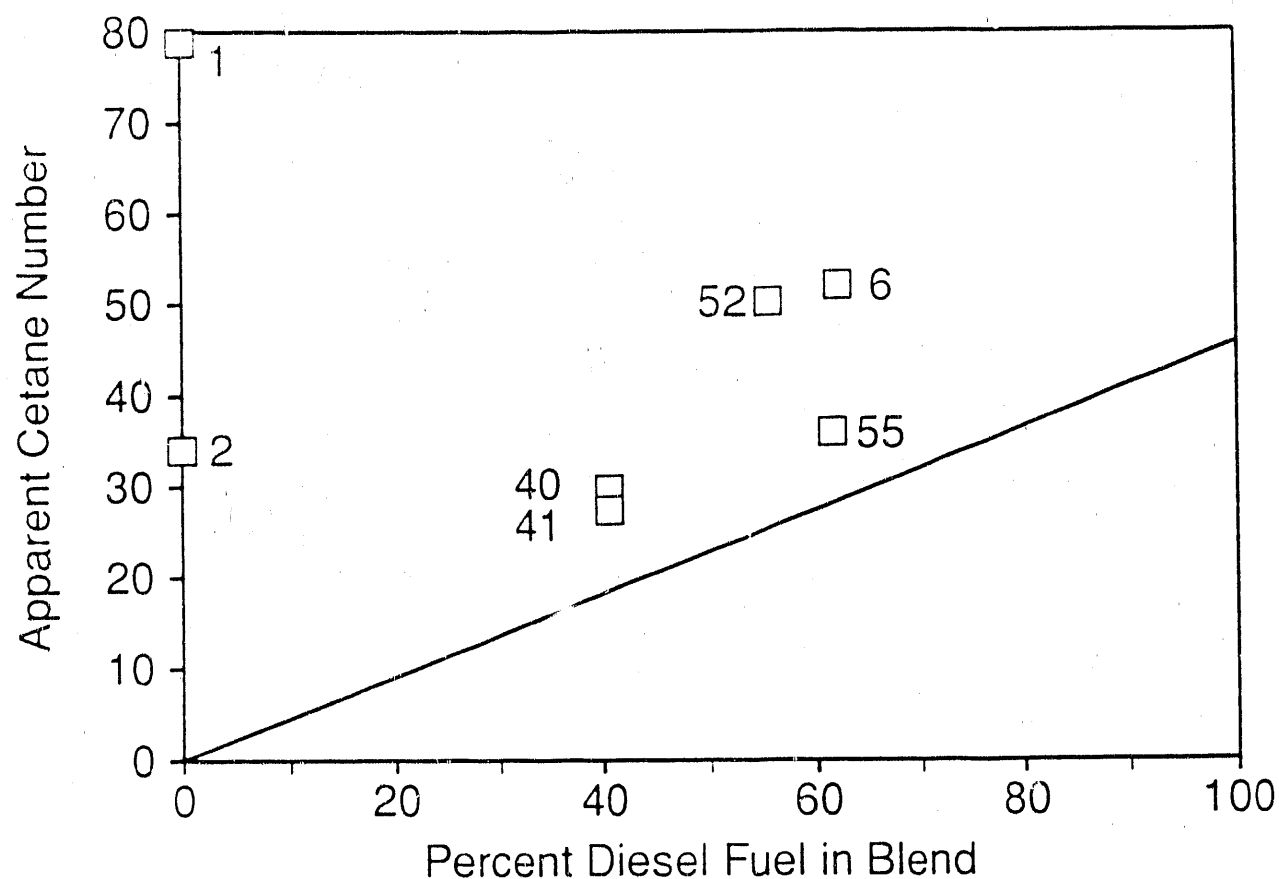**Figure 5. Apparent cetane number of fatty acid ester supplemented fuels as a function of diese¹ content.**

Table 5. Compositions by weight and performance of ethylene glycol fatty acid ester supplemented test fuels

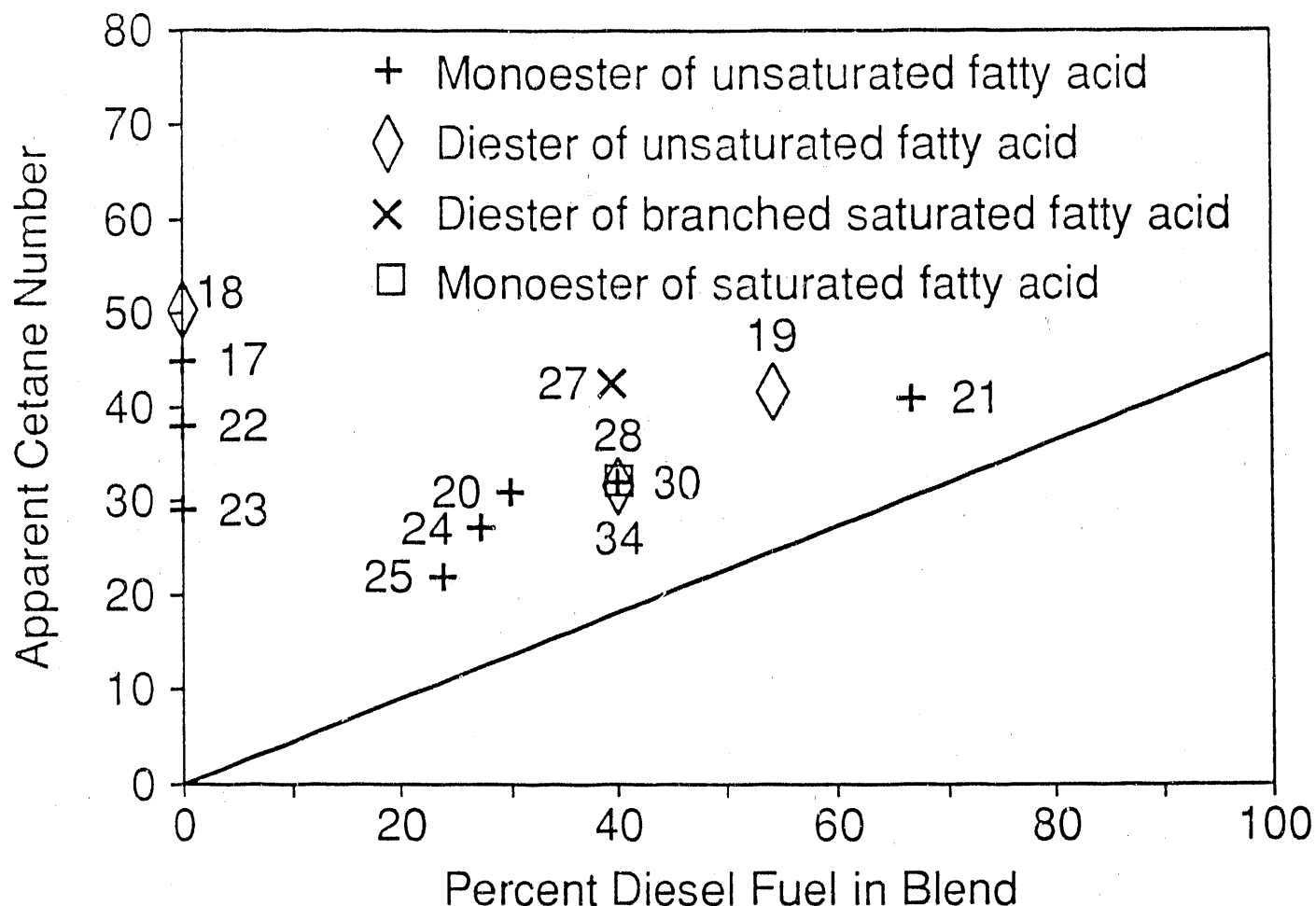|	Surfactants				Alcohols				Density, g/ml	Stoichiometric air/fuel ratio	Heat of combustion kcal/g	Apparent cetane number
Fuel	Surfactant	%	Surfactant	%	% Methanol	% n-Butanol	% t-Butanol	% Diesel				
					Monoester of saturated fatty acid							
34	P200MS	20.0			20.0		20.0	40.0	0.849	11.7	8.242	32.0
					Monoester of unsaturated fatty acid							
17	P400MO	33.5			66.5				0.854	7.6	5.937	44.8
20	P200DL	20.0			30.0	20.0		30.0	0.841	10.9	7.842	31.0
21	P200DL	9.52			9.52	14.29		66.67	0.847	13.3	9.386	40.8
22	P400MO	50.0			50.0				0.889	8.2	6.515	37.9
23	P400MO	33.33			33.33	33.33			0.861	9.2	6.984	28.7
24	P400MO	13.64			29.55	29.55		27.27	0.838	10.7	7.739	27.2
25	P400MO	9.52			28.57	38.10		23.81	0.829	10.7	7.667	22.2
30	P400MO	20.0			20.0		20.0	40.0	0.851	11.5	8.370	31.7
					Diester of unsaturated fatty acid							
18	P400DO	33.5			66.5				0.845	8.0	6.052	51.4
19	P400DO	7.02 MOL	8.77		12.28	17.54		54.39	0.845	12.8	9.070	42.2
26	P200DL	9.52			28.57	38.10		23.81	0.825	10.8	7.679	—
28	0.15	20.0			20.0		20.0	40.0	0.849	11.8	8.367	31.8
					Diester of branched saturated fatty acid							
27	792	20.0			20.0		20.0	40.0	0.849	11.7	8.213	43.5
24	792	34 MDD	8.4			20.9		62.4	0.854	13.3	9.961	36.1

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Figure 6. Apparent cetane number of ethylene glycol fatty acid ester supplemented fuels as a function of diesel fuel content.

Table 6. Compositions by weight and performance of polyethylene and polypropylene glycol supplemented test fuels

Fuel	Surfactants				Alcohols			Density, g/ml	Stoichiometric Air/Fuel Ratio	Heat of Combustion kcal/g	Apparent cetane number
	Surfactant	%	Surfactant	%	% Methanol	% t-Butanol	% Diesel				
42	P425	20.0			20.0	20.0	40.0	0.854	11.4	7.479	29.4
46	SFA*	10.0	T701	10.	20.0	20.0	40.0	0.842	11.8	8.277	31.7
47	SFA	10.0	L42	10.	20.0	20.0	40.0	0.842	11.7	8.276	30.7
48	SFA	10.0	L43	10.	20.0	20.0	40.0	0.843	11.7	8.242	30.0
49	SFA	10.0	L44	10.	20.0	20.0	40.0	0.844	11.7	8.257	30.3
50	SFA	10.0	L35	10.	20.0	20.0	40.0	0.844	11.7	8.248	31.0
51	SFA	10.0	F77	10.	20.0	20.0	40.0	0.843	11.7	8.224	30.7

*Fatty acid blend containing substantial amounts of unsaturated acids.

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Table 7. Compositions by weight and performance of industrial solvent supplemented test fuels

Fuel	Surfactant	%	% Methanol	n-Butanol	% t-Butanol	% Diesel	Density, g/ml	Stoichiometric air/fuel ratio	Heat of combustion kcal/g	Apparent cetane number
					Predominantly ether					
36	DBC	20.0	20.0		20.0	40.0	0.822	11.9	8.381	33.4
					Predominantly alcohol					
15				48.8		51.2	0.830	8.7	6.452	31.9
16				74.1		25.9	0.820	9.9	7.532	23.9
53				25.1		74.9	0.840	13.7	10.241	41.5
					Alcohol and ether mixtures					
35	BCA	20.0	20.0		20.0	40.0	0.844	11.5	8.118	26.4
37	BCU	20.0	20.0		20.0	40.0	0.838	11.3	7.982	24.8
38	BCU	20.0	20.0		20.0	40.0	0.834	11.6	8.178	22.6
39	CUA	20.0	20.0		20.0	40.0	0.846	11.3	8.013	22.3

Table 8. Compositions by weight and performance of selected test fuels

| Fuel	Surfactant	%	Cosurfactant	%	% Methanol	% t-Butanol	% Diesel	Density, g/ml	Stoichiometric air/fuel ratio	Heat of combustion kcal/g	Apparent cetane number
						Acrylic acid					
10	D-315	19.51	AA	2.44	39.02	19.51	19.51	0.826	10.2	7.245	—
13	OA	19.51	AA	2.44	29.27	19.51	29.27	0.830	11.1	7.811	—
						Alkyl nitrate					
11	OA	19.51	PNO3	2.44	29.27	19.51	29.27	0.830	11.1	7.809	26.8
						Fatty acid amine					
29	ODA	20.0			20.0	20.0	40.0	0.849	12.2	8.530	22.8
						Triglyceride					
45	SFA	10.0	TA	10.	20.0	20.0	40.0	0.850	11.4	8.014	21.5
						Alkylphenyl ethoxylates					
31	15-S-5	20.0			20.0	20.0	40.0	0.837	11.7	8.405	33.7
32	CO-630	20.0			20.0	20.0	40.0	0.857	11.5	8.137	31.2

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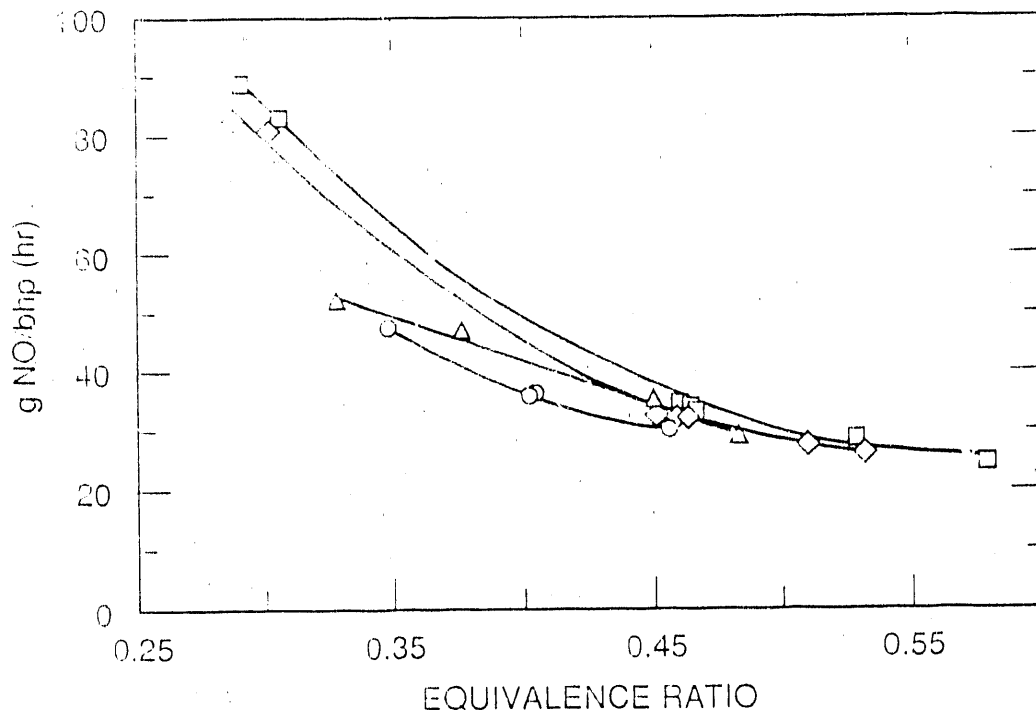
Figure 7. Nitric oxide (NO) emissions as a function of equivalence ratio for four fuels: Phillips No. 2 diesel (□); fuel 4 (◇); fuel 27 (○); and fuel 52 (△).

important advantage that many of these fuels can function in the conventional diesel engine with little or no modification, however, the tradeoff for lowered emissions and petroleum conservation might be reduced power output and fuel economy (miles per gallon). Provided that these fuels are compatible with engines (i.e., no injector fouling, plunger scoring, etc.), then the one time cost of a higher flow capacity fuel system could be justified, and power output could be largely restored. The modification may be as simple as injector and injector pump replacement or modification.

Figure 8 shows the brake thermal efficiency as a function of fuel energy input for those fuels for which NO emissions data has been presented. The lines in the figure are quadratic least squares regressions. Operating on No. 2 diesel fuel, the Deutz single cylinder engine appears to reach its peak efficiency of about 31 percent at a fuel energy input of 25 hp. At the same fuel input horsepower, the peak thermal efficiency decreases with decreasing fuel heating value for the test fuels. This is probably due to the higher equivalence ratio required for the fuels with lower heats of combustion. It is not known what effect a higher flow fuel system would have on the thermal efficiency of the diesel engine running on microemulsion fuels.

CONCLUSIONS AND RECOMMENDATIONS

Results of the screening tests were very good. Of the fifty-four fuels tested, the apparent cetane numbers of

thirty fuels was greater than 30, and thirteen peaked the 40 mark. Six of the fuels had apparent cetanes greater than diesel fuel. Preliminary emissions testing indicates that high alcohol microemulsion fuels could provide small but significant reductions in nitric oxide emissions. It appears that functional diesel fuels with apparent cetane numbers around 40 can be blended which contain as much as 70 percent, or as little as 30 to 40 percent diesel fuel.

Given that microemulsion and micellar fuels *can* be blended with sufficient ignition quality to *run* in a diesel engine, it is important to identify areas of further research. The authors recommend further testing of the higher apparent cetane number fuels to include:

Measurement of particulate, hydrocarbon, carbon monoxide, and oxides of nitrogen emissions

Calorimeter tests to verify heating values of selected fuels

Testing in different engine type with different compression ratio and/or combustion system (such as direct injection)

Injector pump and injector durability testing

Viscosity and lubricity measurements

Cold-start testing

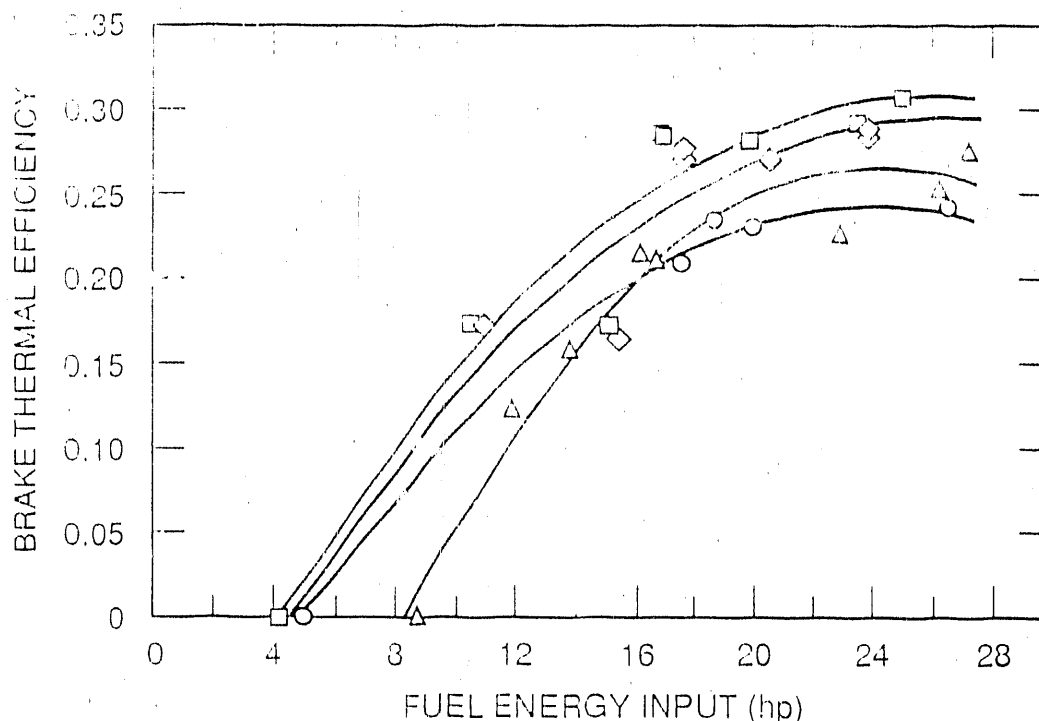West, Compere, and Griffith

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Figure 8. Brake thermal efficiency as a function of fuel input horsepower for four fuels: Phillips No. 2 diesel (□); fuel 4 (◇); fuel 27 (○); and fuel 52 (△).

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