

METHYL, ETHYL, AND BUTYL SOYBEAN OIL ESTERS - ALTERNATIVE FUELS
FOR COMPRESSION IGNITION ENGINES

by

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INTRODUCTION

Rapidly rising petroleum prices and fuel shortages during the 1970's has made the agricultural community aware of the importance of a reliable supply of energy. Since many of today's agricultural machines, such as combines and tractors have power requirements met solely through diesel fuel, diesel fuel shortages at critical times such as planting and harvesting, can have a drastic effect upon yields and thus affect total crop production. This evident dependence upon diesel fuel in agriculture, as well as other petroleum based sources of energy, has sparked renewed interest in alternative sources of energy, especially for the internal combustion engine. Vegetable oils have been offered as a possible alternative or supplement to diesel fuel since they have many similar physical properties.

Research and engine testing has been carried out with such vegetable oils as peanut, castor, sunflower, cottonseed, and soybean oil to name only a few. Some of this work dates back to the early 1900's but due to the availability of low cost petroleum, little was done to solve the problems encountered with vegetable oils; namely excessive carbon deposits and lubricating oil thickening.

Due to the sharp increases in petroleum prices and shortages in supplies during the last decade, renewed interest in vegetable oils has prompted new research all around the world. The testing of sunflower oil as a diesel fuel extender has been done in South Africa and Australia. In Canada, canola oil has been tested and Brazil has conducted research on a variety of vegetable oils. Promising results have been obtained, but due to practical problems, these fuels are not ready for widespread use.

The purpose of this study was to establish the potential of soybean oil, in particular, esters of soybean oil, as a replacement for diesel fuel in direct injection diesel engines. This work is to determine which ester, if any, merits further investigation as an alternative fuel. Soybean oil was chosen over other vegetable oils due to the following advantages:

1. Soybeans are the #1 oilseed crop grown in the U.S. with nearly 50% of the crop being exported. Therefore, soybeans are an abundant crop with no new technology involved to produce them.
2. Since soybeans are a legume, fertilizer needs are reduced through symbiotic nitrogen fixation.
3. The oil extraction process yields a high protein meal as the main product.
4. The fuel energy balance in the production process is positive. One hectare of soybeans yields about 400 liters of oil, while it requires about 56 liters to produce it. (Kaufman, 1982)
5. Soybean oil esters have fuel properties similar to #2 diesel fuel.

LITERATURE REVIEW

Soybean Production

Soybeans are by far the number one vegetable oil crop in the U.S. and the world. About 28.3 million hectares of soybeans are grown in the U.S, more than the next ten vegetable oil crops combined. The average yield for the U.S. soybean crop is 2.15 metric tons per hectare which produce 12.3 million tons of protein and fat, more than any other single source. The total annual oil production is 6.4 billion liters.

Goering and Daugherty (1981) found soybeans to be the least energy intensive of the eleven vegetable oils they compared in terms of energy derived from the oil to the portion of energy inputs attributed to the oil. This is primarily due to soybeans having lower energy inputs since the crop is a legume not requiring nitrogen fertilizers and that the high protein meal accounts for nearly two thirds of the energy value of the crop. Consequently, the energy output to energy input ratio is very high, making soybeans a leading candidate as a renewable alternative fuel.

Soybean Oil Extraction

There are basically three types of extraction processes, the mechanical or full-press, the direct solvent, and the pre-press/solvent extraction processes.

The mechanical screw press extraction process requires the least fixed capital investment of the three. It is a continuous process normally using a screw press consisting of a worm shaft rotating within a pressing cylinder or cage, which literally squeezes the oil from the seed. Heating the oilseed

prior to extraction usually increases the amount of oil recovered from the seed, due to the oil's reduced adhesion to the seed fibers at higher temperatures. This process usually yields about 12-13% oil from a soybean seed, or roughly two thirds of the oil available. However, this method is very conducive to small scale systems.

Direct solvent extraction is a continuous process that uses a solvent (usually hexane, a petroleum based product) to separate the oil from the seed. Beans enter a conditioner where they are cracked and dehulled. They are then flaked and dried, after which the solvent is added. The meal is removed from the miscella (oil and solvent) in the extractor after which the solvent and oil are separated through a distilling process. The oil is then filtered and the remaining solvent stripped and recycled through the system. The major advantages of the solvent extraction process is the high extraction efficiency which yields nearly all the oil from the seed and leaves a high quality, high protein meal as the main product since it is nearly oil free. The major disadvantages are the high costs due to the distillation apparatus needed to separate the oil from the solvent and the safety hazards involved with low flash point solvents and the high temperatures necessary for distillation.

The pre-press/solvent process is basically a combination of the first two where a press extracts the bulk of the oil from the seed and the remaining oil is retrieved through the solvent extraction process. The major advantage is reduced size of the expensive solvent extraction equipment with the lower priced press equipment maintaining the high volume capacity of a larger sized solvent extraction process.

The most widely used method of oil extraction is the large scale

counter-current solvent plant which can handle 1000 to 2000 metric tons daily. However, small scale extraction processes could provide the farmer with a greater degree of energy self-sufficiency if economically viable. Research in this area is being conducted.

Billet (1981) reported on the development of an on farm expeller type oil press for sunflower oil production in South Africa. This wheel mounted unit was self contained and capable of delivering 50 liters of oil per hour. Seeds were dehulled, passed over a sieve through a controlled air flow to remove the hulls, and then fed into the expeller. The resulting oil was deposited in a settling tank which allowed the solids to settle out.

Tests with a screw press expeller for sunflower oil were also conducted by Smith, Lovely, and Buchele (1982). Heated air was blown through the seed flow prior to entering the expeller. A peak extraction efficiency of 32.4%, which is about 80% of the oil available in sunflower seed, was obtained at 65°C with a meal flake thickness of 0.75 mm. The operation of the plant was simple. Once the expeller was set, no further adjustments were necessary for an entire day.

Ramsey and Harris (1982) performed tests with a low capacity expeller for soybean oil extraction. The highest oil output of 0.07 liters/kg occurred at a bean temperature of 77°C which gave an extraction efficiency of 6.51% or only about one third of the oil in the beans. This system lended itself well to automation and also functioned smoothly with minimal supervision and daily maintenance.

These low capacity press expellers have been the subject of research in on farm oil extraction due to their simplicity, reliability, and inherent low

cost. However, with the low efficiencies achieved, particularly with marginal oil laden seeds such as soybeans, much of the oil is left in the seed. This high percentage of residual oil left also reduces the palatability, color, and protein content of the meal, which therefore does not make the meal an ideal protein source for livestock. From this standpoint solvent methods will probably need to be employed, especially for low yielding oilseeds, to get high extraction efficiencies. This allows solvent methods to obtain a high protein meal as well as increased oilseed yields from vegetable oil crops. Of course much more research will be needed to develop a reliable, low cost, on farm pre-press/solvent extraction process. Safety will also have to be addressed since low flashpoint solvents are involved.

Alternatives to dangerous low flash point solvents such as hexane used in commercial extraction plants are possible. Beckel et.al. (1948), reported on the use of ethyl alcohol as a solvent and even found it to have these advantages.

1. The fire and explosion hazard for ethanol is less than with hexane.
2. Ethanol can be removed from the oil at a lower temperature than higher alcohols.
3. Ethanol gave better results with respect to the color of the oil and meal protein.
4. Ethanol served as a debittering agent for the meal, making it more palatable to livestock.

Rao and Arnold (1958) found that the purity of the ethanol for oil extraction is also not critical. Another possible advantage of ethanol is

that it can be derived on the farm as well. Other solvents may also have advantages that could enhance the viability of an efficient on-farm solvent oil extraction method.

Engine Tests With Vegetable Oils

The use of vegetable oils as fuels for internal combustion engines is not new. The first investigation on record (R. Martinez de Vedia, 1944) occurred in Buenos Aires University in 1916, when Professor R. J. Gutierrez reported on tests performed on the first diesel engine to arrive in Argentina, using castor oil as a fuel. Another early investigator to attempt use of vegetable oils in diesel engines was the French researcher Gautier. His work was reported in a paper entitled, "The Utilization of Vegetable Oils in Diesel Motors" published in 1928 (Chowhury, 1942). During the next ten years both Gautier and A. W. Schmidt published several articles and papers on the subject.

In 1936 some preliminary work was also done by Chinese investigators on the use of cotton seed oil, but no actual engine tests were carried out. A comprehensive paper was published (Walton, 1938) in which various technical problems associated with the use of many vegetable oils were examined and reported with results from tests performed on a single cylinder engine. R. Martinez de Vedia (1944) published a lengthy report of work being done in Argentina during a period of fuel shortages in that country due to World War II. The engine used was a two cylinder Diesel engine.

In spite of the encouraging results obtained and reported by all these researchers, there is little evidence to show that the investigations were actively pursued. It would appear, since the period from 1945 to 1965 yielded

relatively few papers, that these investigations have been initiated in times of fossil fuel shortages, but were not deemed to be particularly important as long as cheap petroleum fuels were available.

The fuel shortages during the 1970's has again renewed interest in vegetable oils as fuels. A research project involving waste cooking oil as a fuel extender was conducted by Silvis (1977) with a diesel engine. Preliminary work included measurement of some physical properties of the soybean oil-diesel fuel blends and photographing of the different injection spray patterns. All the blends had similar injection spray patterns to diesel fuel, but the pure soybean oil lacked the high degree of atomization. This was improved slightly by heating prior to injection. Full rack settings also displayed better patterns than part load settings for the pure soybean oil. The high viscosity of the soybean cooking oil was cited as responsible for these observations.

The actual engine tests revealed surging with the 60% soybean oil blend. Silvis concluded that this was due to restricted fuel flow through the fuel filter caused by the high viscosity of this blend. In general the blends exhibited superior smoothness of operation to diesel and resulted in better fuel economy and smoke readings.

Strayer et. al. (1980) tested pure canola oil and found a 3% power loss and a 6% specific fuel consumption increase compared to diesel fuel. Starting was not a problem for the turbocharged six cylinder engine on canola oil, either hot or cold. They also noted significantly less smoke than with diesel fuel. No longterm engine tests were conducted but Strayer suspected that the high viscosity of canola oil, roughly comparable to soybean oil, could cause

engine deposit buildup and crankcase oil contamination.

Research on sunflower seed oil conducted by Bruwer et. al. (1980) found results similar to those of Strayer. Maximum power was 3% less than diesel fuel while brake specific fuel consumption was 10% greater. This was explained primarily by the lower heating value of sunflower seed oil compared to diesel fuel. Diesel knock was also found to be substantially less audible.

Initial longterm tests with a direct injection engine confirmed suspicions about engine deposit buildup and crankcase oil contamination. Under prolonged part-load conditions, carbon buildup around injector tips adversely affected combustion to the extent that unburned fuel could be observed in the exhaust system while the engine was idling. Blowby, unburned fuel escaping past the pistons, was also noted where the oxidation of the seed oil depleted the anti-oxidant additives in the lubricating oil, resulting in polymerization. This can cause solidification of the oil and result, ultimately, in total engine failure. Again most of the problems were traced back to the high viscosity of the sunflower seed oil.

Subsequent long term tests with an indirect engine by Bruwer showed that deposit buildup does not occur as easily with an indirect injection engine. Indirect injection engines are used primarily in industry and mining, largely due to their cleaner exhaust emissions. A wider range of fuels can also be used. Ricardo, the inventor of the swirl chamber, stated that the higher surface temperatures in the chamber prevented carbon deposits. This may account for the fact that after 2300 hours of operation on pure sunflower oil, an indirect injection engine showed no abnormal wear or injector tip fouling. Performance was normal throughout the test.

A significant problem with indirect injection engines however, is difficult starting under extremely cold conditions. The cold air, flowing through the throat of the chamber on the compression stroke, is further chilled by a venturi effect, making the use of starting aids such as glow plugs necessary. The poor atomization characteristics of vegetable oils would add to this problem.

From these initial engine tests ran on vegetable oils, the most common problems relate directly to the vegetable oils' high viscosities. A significant reduction in viscosity must be achieved to allow satisfactory use of straight vegetable oils in compression ignition engines. Another solution is to modify the engine to accommodate high viscosity fuels. However, this leads to added expenses and the possibility that the modifications may not allow satisfactory use of standard diesel fuel after they are incorporated into the engine. Therefore, the most logical solution is to modify the oil to match diesel fuel properties so that either fuel may be used in the same engine, which would very possibly be the case if diesel fuel supplies were limited.

Transesterification and Engine Tests with Ester Fuels

One way to lower the viscosity of vegetable oil is by transesterification, a simple and well established process. A vegetable oil is a triglyceride which is a combination of three fatty acids combined to a glycerol molecule. Transesterification is a chemical process which displaces the glycerol from the vegetable oil and replaces it with three alcohol molecules. This allows the fatty acids to separate from one another and produce esters of the original oil with a dramatically reduced viscosity (Figure 1). Thus, this process produces a potential alternative fuel that has physical properties

more similar to diesel fuel than the original vegetable oil.

Preliminary engine tests involving sunflower oil ethyl and methyl esters have been performed by Bruwer (1980). Dynamometer tests revealed that after 100 hours of operation at 80% of maximum power, the ester fuels actually caused less injector tip fouling than diesel fuel. Consequently, higher brake thermal efficiencies and lower smoke values were recorded. No significant differences were observed between the cylinder pressure diagrams of the esters and diesel.

One problem that was experienced though, was that injector needles tended to stick after the engine had cooled off. Long term tests by Hawkins and Fuls (1982) confirmed this problem. They found that the needle sticking was due to the presence of fuel soluble salts of sodium crystalizing on the bearing surfaces. This problem was overcome by using citric acid to adjust the pH, producing an insoluble salt which could easily be stripped from the fuel. However, deposits of sodium carbonates prevented proper valve seating causing exhaust valve burn within 36 hours of operation. The sodium carbonates originated from the catalyst used in the transesterification process and the carbonate group in the citric acid. Using phosphoric acid instead of citric acid to adjust pH solved this problem.

After 1100 hours, inspection of the Perkins 4.236 liter engine revealed that injector tip fouling was comparable to that of diesel fuel with all the orifices unobstructed. Carbon deposits on the cylinder walls above the piston ring travel were evident but within acceptable limits. Performance remained normal throughout the 1300 hour test.

Pischinger et. al. (1982), reported on the use of straight methyl ester of soybean oil. Marginal differences in power and torque were observed between diesel and the methyl esters. Fuel consumption at full rack was greater due to increased fuel delivery by the injection pump (about 7%), but the smoke values were lower. Following a durability run of 1400 hours, the engine was torn down for wear measurement and inspection. No abnormal conditions were noted and combustion chamber deposits were dry, soft, and easily removable. The injection equipment showed no signs of excess wear.

Vehicle testing of straight methyl ester of soybean oil was also done by Pischinger et. al. (1982) with a diesel Passat car which had accumulated 40,500 km at the time of his report. Fuel consumption was, on the average, 5-6% higher than on diesel fuel. CO emissions were significantly lower and NO_x emissions remained much the same as for diesel fuel. A diesel Volkswagon delivery van had also accumulated 5,200 km on a mixture of 23% methyl ester of soybean oil, 9% ethanol, and 68% diesel fuel. Fuel consumption and emissions were similar to the findings of the Passat car, with smoke readings substantially lower than with diesel fuel.

In most cases, fuel dilution of the lubrication oil was observed, but did not cause oil polymerization during the normal oil change interval. Siekman concluded that oil degradation is determined mainly by the amount of unsaturated fatty acids (linoleic and linolenic) in the fuel. To overcome this, oxidation inhibitors such as BHT (butylated hydroxy toluene) can be added. Hydrogenation can also be employed to saturate the double bonds, but this may not be desirable from the standpoint of viscosity as hydrogenated vegetable oils are usually solids.

Fort and Blumberg (1982), conducted tests with cottonseed methyl esters. The test cycle consisted of the 200-hour screening test recommended by the Engine Manufacturer's Association. A slight reduction in power and an increase in fuel flow occurred, while thermal efficiency remained the same as for diesel fuel. NO_x , CO, and HC emissions from the six cylinder, turbo-charged engine were not significantly different for the cottonseed ester compared to diesel fuel. Engine wear was normal with no evidence of piston scuffing. Deposits in the top ring grooves were evident, however, these were soft and easily removed. Analysis of the lubricating oil showed a decrease in viscosity during the 200-hour test.

In light of the promising results obtained with various ester fuels in a variety of engines, it was felt that a suitable basis existed for comprehensive tests involving soybean oil esters, namely methyl, ethyl, and butyl esters of soybean oil.

INVESTIGATION

Objectives

The objectives of this investigation were:

1. To determine how the physical properties of the following fuels compare with #2 diesel fuel.
 - a. ethyl ester of soybean oil
 - b. methyl ester of soybean oil
 - c. butyl ester of soybean oil
2. To perform prescribed medium term tests on a direct injection, turbo-charged diesel engine to compare soybean oil ester fueled engines and a standard diesel fueled engine in regards to:
 - a. amount of internal engine deposits
 - b. degree of engine wear
 - c. engine performance
 - d. exhaust emissions
 - e. crankcase oil deterioration

Theory

Since high fuel viscosity is the main cause of premature failure of most vegetable oil fueled engines (including straight soybean oil), it is of prime concern. High viscosity fuels adversely affect injector spray patterns through increased mean droplet size and greater fuel penetration (Schweitzer, 1937). This decreases the atomization of the fuel and leads to incomplete combustion which causes increased buildup of carbon deposits. Unburned liquid hydrocarbons will also increase, leading to the dilution of the engine lubricating oil. These effects severely reduce engine life.

There are basically two approaches to the problem, either make modifica-

tions to the engine, or alter the fuel. The latter was pursued through a process called transesterification. This process involves the reaction between a triglyceride (soybean oil) and an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters. A significant reduction in fuel viscosity is obtained as represented in Figure 1. An increase in cetane number and heating value are also realized through the transesterification process (Table 1).

Table 1. Properties of #2 Diesel Fuel, Soybean Oil, and Soybean Oil Esters

Property	Reference Diesel Fuel	Soybean Oil	Soybean Oil Esters *
Density kg/m ³ @ 21°C	845	918	881
Kinematic Visc. cSt @ 21°C	3.7	62.3	7.2
Cetane number	45.8	37.0	48.7
Gross Heating Value MJ/kg	45.2	37.1	40.2
MJ/l @21°C	38.2	34.1	35.4

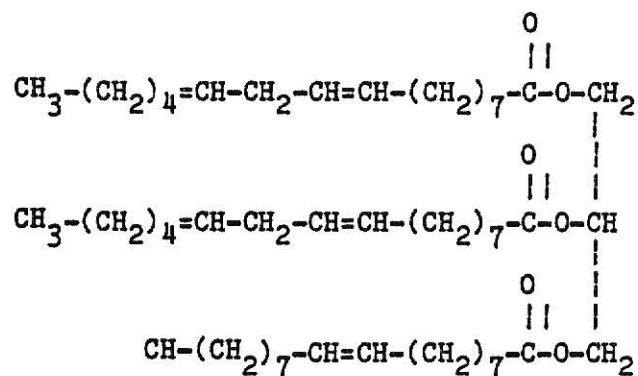
* Average values from ethyl, methyl, and butyl esters of soybean oil

Soybean oil is a member of the triglyceride group of oils typically found in the seeds of peanut, sunflower, castor, cotton, soy, and other common plants. Morrison and Boyd (1973) describe the fatty acid composition of soybean oil as shown in Table 2.

Table 2. Fatty Acid Composition of Soybean Oil

Fatty Acid	Percentage
linoleic	50-60
oleic	22-34
palmitic	7-11
linolenic	2-10
stearic	2-5

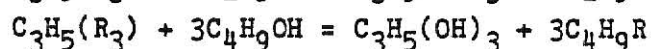
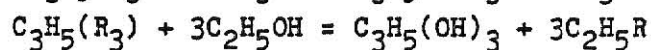
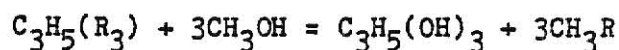
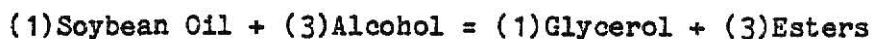
These fatty acids occur in long chains of mainly carbon and hydrogen atoms attached together to form the basic triglyceride molecule. The molecular structure of soybean oil may typically look like this:



The molecular weight of the above molecule is 880.

As mentioned, transesterification is the reacting of a triglyceride with an alcohol in the presence of a catalyst to form fatty acid esters and glycerol as the products. Bradshaw and Meuly (1942) describe this process in detail. A typical reaction consists of mixing 0.5% sodium hydroxide, on the basis of the oil, into 1.6 equivalents of anhydrous ethyl alcohol. The mixture is heated to about 80°C and stirred until homogeneous. The glycerol begins to separate almost immediately and the reaction is usually 98% complete after one hour. The esters are separated from the glycerol and washed with small amounts of warm water to remove unsettled glycerol, unreacted alcohol, and traces of the catalyst. The esters are stable and non-corrosive, therefore the reaction may be carried out in any convenient open tank, usually constructed from carbon steel. Other alcohols such as methanol or butanol may also be used in place of ethyl alcohol.

Typical reactions for each of the esters (methyl, ethyl, and butyl respectively) occurs as follows:



where R represents the particular fatty acid. From this it can be seen that the molecular weight of the esters is about one third that of the original oil, thereby reducing the viscosity as shown in Table 1 and Figure 1. Note that the transesterification process does not change the fatty acid composition of the vegetable oil as shown in Table 3, but merely separates the fatty acids from the glycerol molecule to form smaller individual molecules.

Wright (1944) found that the materials used in this process should meet certain qualifications for best results. Both the oil and the alcohol must be substantially anhydrous because any presence of water causes soap formation.

The acid value of the oil, which is an indication of the amount of free organic acid in any vegetable oil, must be below one for the reaction to take place as described. Soybean oil has an acid value of about two, therefore, in order to neutralize the acids, an excess amount of sodium hydroxide must be added. Because of the resulting soap formation, the reaction mixture becomes viscous, preventing the gravity separation of the glycerol.

A similar problem occurs when there is water present in the reaction mixture. Acidification is consequently necessary to promote separation of the layers.

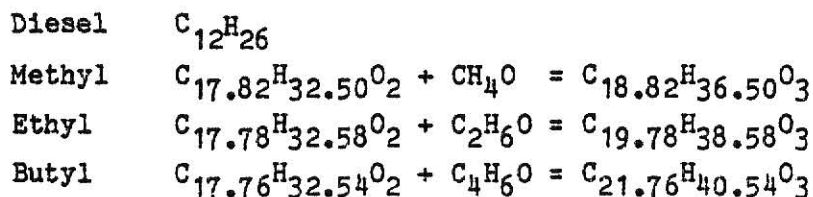
The resulting esters formed from the transesterification process, performed by Emery Industries, have the following fatty acid compositions as shown in Table 3.

Table 3. Fatty Acid Composition (molar %) of Soybean Oil and Soybean Oil Esters

Fatty Acid	Formula	Abbrev.	Degummed Oil #	Methyl	Ethyl	Butyl
Myristic	$C_{14}H_{28}O_2$	C14	0.1	0.05	0.4	0.0
Palmitic	$C_{16}H_{32}O_2$	C16	10.76	9.6	10.1	12.2
Margariz	$C_{17}H_{34}O_2$	C17	0.17	0.0	0.0	0.0
Stearic	$C_{18}H_{36}O_2$	C18	4.13	4.5	5.7	4.6
Iso-Stearic	$C_{18}H_{36}O_2$	ISO-C18	0.1	0.0	0.6	0.0
Arachidic	$C_{20}H_{40}O_2$	C20	0.33	0.3	0.0	0.3
Behenic	$C_{22}H_{44}O_2$	C22	0.07	0.0	0.2	0.0
Palmitoleic	$C_{16}H_{30}O_2$	C16:1	0.23	0.1	0.8	0.1
Oleic	$C_{18}H_{34}O_2$	C18:1	23.03	22.35	22.2	22.9
Gadoleic	$C_{20}H_{32}O_2$	C20:1	0.07	0.0	0.2	0.0
Linoleic	$C_{18}H_{30}O_2$	C18:2	52.67	54.35	51.2	52.7
Linolenic	$C_{18}H_{30}O_2$	C18:3	7.6	8.35	6.5	7.1

* The average value is given for all three lots of crude degummed soybean oil which was used to make the esters.

The "average" molecular constituents of diesel fuel are given with the "average" molar constituents of carbon, hydrogen, and oxygen as derived from their respective fatty acid components for each of the soyates are:



Unlike the structures of the compounds of petroleum oil, soybean oil and the soybean oil esters are not pure hydrocarbons but are partially oxygenated hydrocarbons.

The presence of double bonds in the fatty acids causes a high degree of unsaturation and reaction with oxygen occurs readily to form a gummy substance. The iodine value, defined as the number of grams of Iodine absorbed under standard conditions by 100 grams of fat, is a measure of the degree of unsaturation; the higher the value, the higher the degree of unsaturation. Unsaturation is a desirable property to maintain liquidity of vegetable oils at low temperature, but is undesirable with respect to oxidative stability. Linseed oil for example, has an iodine number of 177 and is classed as a varnish-forming rapid drying oil. Soybean oil is classed as semi-drying with an iodine number between 130 and 135. The saponification value is defined as the number of milligrams of potassium hydroxide required to saponify one gram of fat. It is a measure of the average molecular weight of fatty materials. The iodine and saponification values for the ethyl and butyl soyates were somewhat lower than pure soybean oil as shown in Table 4, indicating that the transesterification process may lower the degree of unsaturation and average molecular weight of their fatty acid constituents.

Table 4. Other Physical Properties of Soybean Oil and Soybean Oil Esters

	Soybean Oil	Methyl Ester	Ethyl Ester	Butyl Ester
Acid Value (mg KOH/g)	2	0.9	<0.1	0.1
Moisture Content (%)	-	0.2	0.073	0.05
Appearance	-	clear	clear	clear
Iodine No. (cg I ₂ /g)	130-135	135.1	123.0	116.0
Saponification No. (mg KOH/g)	188-195	190.8	182.8	168.0

Materials and Experimental Equipment

Test Fuels

The test fuels consisting of a #2 reference diesel fuel purchased from Phillips Petroleum, and ethyl, methyl, and butyl esters of soybean oil (trade name ethyl, methyl, and butyl soyate respectively) purchased from Emery Industries.

To evaluate the test fuels and to more accurately compare them to #2 diesel fuel, an additive package was added to the ester fuels to improve some of the fuel properties. These additives were supplied by Ethyl Corporation and consisted of Ethyl Diesel Additive-2 (EDA-2), Distillate Ignition Improver-3 (DII-3), and Cold Flow Improver-42 (CFI-42). The EDA-2 contains an antioxidant, a detergent dispersant, metal deactivator, corrosion inhibitor, and an emulsification agent. The DII-3 provides a gain in cetane number of about 5 in diesel fuels. The CFI-42 acts as a pour point depressant. The following treatment rates suggested by Ethyl Corporation were used:

1. EDA-2: 0.02% by weight
2. DII-42: 0.1% by volume
3. CFI-42: 0.1% by weight

All these additives are currently used in commercial diesel fuel.

Test Equipment

Test Engine The test engine was a John Deere 4239TF, direct injection, turbo-charged diesel engine. This model was used since it represented the typical diesel engine used in agriculture today, yet was small enough to keep fuel

expenses down. The engine was equipped with a Roosa Master model DM distributor type pump and Roosa Master 9.5 mm (22044-AR88241) injection nozzles. The engine specifications are given in Table 5.

Table 5. J.D. 4239TF Test Engine Specifications

Specification	Value	Units
Cylinders	4	-
Bore	106	mm
Stroke	110	mm
Displacement	3.917	liters
Compression Ratio	16.2:1	-
Rated Speed	2500	rpm
Power(intermittent @ 2500 rpm)	70.1	kW
Power(continuous @ 2200 rpm)	57.4	kW
Torque(maximum @ 1600 rpm)	306	Nm
Injector Nozzles	9.5	mm

The engine came equipped with an alternator, starter and oil cooler. A Rockwell power take-off clutch and an instrument panel were installed. The panel consisted of a starter key switch, vernier type throttle control, ammeter, oil pressure gauge, water temperature gauge, and an hourmeter. Engine safety features included engine shut-off for low oil pressure and high water temperature. Engine cooling was provided by a water to water heat exchanger.

To facilitate periodic removal of the engine from the test facility, it was mounted on a two-piece stand, constructed of 100 mm channel iron. The lower half remained in place, while the upper half provided a stable platform for transportation. Rubber pillow blocks mounted between the upper frame and the engine mounting brackets dampened vibrations.

Dynamometer and Instrumentation A 130 kW model 1014A Mid-West eddy current dynamometer was used throughout the tests. The dynamometer, equipped with a Control Engineering CE229 controller, allowed automatic control in either constant load or constant speed modes. A dual bridge load cell, Transducers Inc.

Model T63H-200, installed in the dynamometer scale linkage provided an electronic as well as a visual indication of torque. The load cell signal was received by a Daytronic 3270 strain gage conditioner and indicator. Engine speed was determined by a 60-tooth gear and an Electro 3010AN magnetic pick-up, with the signal being received by a Daytronic 3240 frequency conditioner and indicator.

Copper-constantan thermocouples were used to measure the temperatures of the oil, fuel (at the injector pump), water inlet and outlet, ambient intake air, and manifold inlet air. The exhaust gas temperature was measured by an iron-constantan thermocouple.

Turbocharger boost pressure, inlet pressure and the atmospheric air pressure were measured by Setra Systems Inc. Model 204 variable capacitance absolute pressure transducers. These pressure transducers were calibrated daily according to the barometric pressure.

Air flow measurement was done by using a 62.5 mm diameter ASME nozzle mounted in a 200 liter fuel drum in series with a 160 liter oil drum which acted as plenum chambers. The pressure drop across the nozzle was measured with a Setra Systems Inc. Model 239 variable capacitance differential pressure transducer. The differential pressure transducer was calibrated against a Meriam Model 34FB2 micromanometer. The discharge coefficient for the flow nozzle was determined by using a relationship proposed by Benedict (1966), relating the most probable discharge coefficient to the Reynold's number. Air filtering was achieved via an automotive type air filter located at the exit port of the larger plenum chamber. The air was ducted with 75 mm diameter plastic pipe.

Fuel flow measurement was determined by weighing the fuel used over a given time period. The fuel supply system consisted of two three way valves, two small 12 volt electric fuel pumps, a measuring stand, and a fuel bucket. All plumbing was done with 9.5 mm copper and 6.4 mm plastic tubing. This system allowed easy switching from the fuel barrels to the fuel weighing bucket for testing and back again. The measuring stand consisted of a bucket suspended from an Ametec Controls Model BA25-LB load cell connected to a Calex Mfg. Co., Inc. Model 166 Bridgesensor. The load cell output was calibrated to provide the desired linear relationship between the output voltage and the weight of the fuel in the bucket. The bucket was filled from the fuel supply barrel using two small electric fuel pumps. The excess fuel in the return line from the injectors was passed through a heat exchanger before returning to the bucket to maintain a constant fuel temperature during testing.

An ADAC System 1000 Series data acquisition system incorporating a DEC LSI 11/23 computer and DEC VT100 terminal was used to collect, process, and store data online. The computer contained 256K of memory, a 5 megabyte 880 Data Systems Winchester hard disk, and 8 inch floppy disk drive.

A 32 channel 12 bit resolution ADAC 1023AD and 1023EX analog to digital cards with programmable gain selection collected analog voltage signals from the fuel scale Calex Bridgesensor, the dynamometer's Daytronic 3270 strain gage conditioner and Daytronic 3240 frequency conditioner (for dyno load and engine rpm respectively), and the Setra Systems 239 and 204 pressure transducers for pressure measurement. A 12 bit resolution ADAC 1113AD and 1113EX low level analog to digital cards were used to collect all the thermocouple voltages. A software programmable gain and cold junction compensation circuit allowed direct reading of the different thermocouple types. A 16 bit ADAC

1601GPT general purpose timer card was used as a software programmable clock that controlled the data collection timing process.

Software programs written in Fortran controlled the interrupts for data collection and performed the necessary calculations. Data could be sent to the terminal screen for immediate analysis or stored on disk files for permanent storage. Actual data collection was set to occur every 10 seconds and averaged over the last 3 minutes continuously.

Exhaust Gas Analysis Equipment Emissions measurements were done with the following instruments:

1. Beckman 865 infrared carbon monoxide analyzer with two ranges (0-2% and 0-10%)
2. Beckman 864 infrared carbon dioxide analyzer with two ranges (0-5% and 0-10%)
3. Beckman 402 flame ionization hydrocarbon analyzer with eight ranges (0-10, 0-50, 0-100, 0-500, 0-1000, 0-5000ppm, 0-1%, and 0-5%)
4. Beckman 955 Chemiluminescence nitrous oxides analyzer with seven ranges (0-10, 0-25, 0-100, 0-250, 0-1000, 0-2500ppm, and 0-1%)
5. Beckman OM-11 polarographic oxygen analyzer with three ranges (0-5%, 0-10%, and 0-25%)

The instruments are mounted in a portable equipment console according to Beckman specifications and are plumbed so that the appropriate zero and span gases can be passed to their respective analyzers for calibration purposes. The exhaust gas analysis unit contains a refrigerated water bath, filters, low volume pumps, and electrical service. A furnace and heated sampling hose are also used to keep the exhaust gas temperature high enough to prevent chemical decomposition of the exhaust gas constituents which is necessary for accurate hydrocarbon and nitrous oxides measurements.

Probes in the engine's exhaust system facilitated sampling for individual cylinders or for the composite gas of all four cylinders.

Oil Viscosity Measurement Equipment Crankcase oil kinematic viscosity was checked frequently with Ubbelohde type viscometers. A precision Lauda Model B-1 immersion circulator kept the water bath at the desired temperature.

Test Procedures

Before the start of the engine tests, the engine was "blueprinted" by the Petroleum Research Division of Farmland Industries at Kansas City, Missouri. The engine was also torn down and overhauled after each engine test and the "blueprinting" repeated to give an accurate indication of engine wear from each of the tests. The following outline contains the blueprinting and overhaul procedure conducted:

- A. Engine measurements taken:
 1. Crankshaft journals
 - a. Main journals miked parallel and perpendicular to the crankshaft gear's woodruff key
 - b. Rod journals miked parallel and perpendicular
 2. Rod bearing weight
 - a. Bearings weighed in milligrams and all journals plastigaged on final installation
 3. Camshaft lobe height, maximum in inches
 4. Cylinder liners
 - a. Measurements taken 1.25", 2.5", 4", and 7" from top of liner parallel and perpendicular to the crankshaft
 5. Pistons
 - a. Measurements taken at four positions
 - (1) Position A--O.D. at top of skirt, right angle to pin
 - (2) Position B--O.D. at bottom of skirt, right angle to pin
 - (3) Position C--O.D. at top of skirt, parallel to pin
 - (4) Position D--O.D. at bottom of skirt, parallel to pin
 6. Piston pins
 - a. Measurement taken at both ends and the middle, parallel, and perpendicular to each other
 7. Piston ring end gap in a standard liner
 8. Valve guides
 - a. Measurements taken at the top, middle, and bottom of guides
 9. Valve stems
 - a. Measurements taken 1.5", 2.5", 4.5" from the valve head

B. Fuel System

1. Injection pump calibrated by Electrical and Magneto Service Company
2. Injectors tested for leakage, chatter, cracking pressure, and spray pattern on a Bacharach test pump

C. Engine overhaul

1. Overhaul accomplished in accordance with 300 Series OEM Technical Manual TM-1190
2. New gaskets were installed as needed
3. Rod and main bearings were etched per installed position
4. Cylinder liners were etched to show the front of the liner
5. Oil pump gears visually inspected
6. Valves were cleaned in stoddard solvent and relapped in originally installed position
7. Valve lash was set cold
8. Fuel injection pump was statically timed

A break-in period of 50 hours succeeded each engine rebuild following the 90 minute break-in cycle proposed by the Engine Manufacturer's Association (EMA) to the United States Department of Agriculture. Commercial diesel fuel was used during the break-in cycle, which was as follows:

1. 10 minutes at low idle
2. 10 minutes at 1/2 rated speed and no power
3. 15 minutes at 3/4 rated speed and 1/2 rated power
4. 55 minutes at rated speed and rated power

The actual engine tests consisted of a 200-hour cycle also recommended by EMA. The test cycle was as follows:

1. 30 minutes at low idle
2. 60 minutes at rated speed and rated power
3. 60 minutes at peak torque
4. 30 minutes at 80% speed and 25% rated power

Five of the above cycles were run, after which the engine was shut down for 9 hours. Maximum performance was checked at the beginning, middle, and end of the 200-hour test. This was done by applying full rack, and progressively loading the engine using the constant speed control on the dynamometer.

Data was taken at 50 rpm intervals.

Lubricating oil viscosity was measured daily and samples were sent to Farmland Industries to monitor wear metal levels and oil deterioration.

Exhaust gas emissions measurements including hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen, and oxygen were taken at the beginning, middle, and end of the 200-hour test. The measurements were made according to SAE J1003, which specifies the following 13 mode test sequence:

Mode	Engine Speed	Percent Load
1	Low Idle	0
2	Intermediate	2
3	Intermediate	25
4	Intermediate	50
5	Intermediate	75
6	Intermediate	100
7	Low Idle	0
8	Rated	100
9	Rated	75
10	Rated	50
11	Rated	25
12	Rated	2
13	Low Idle	0

At each mode the emissions were recorded every two minutes for ten minutes. Before and after each test, the instruments were calibrated using the appropriate zero and span gases.

DISCUSSION and RESULTS

Fuel Properties

In order to fully evaluate the potential of the soyates, complete ASTM tests were performed. A brief description of each test and the relevant results of each are presented. A summary of all test results are provided in Table 6.

The viscosity of a fuel (ASTM D445) has a strong influence on the shape of the fuel spray. High viscosities cause low atomization due to larger sized droplets, and higher penetration of the spray jet. Low atomization can cause incomplete combustion which increases piston, combustion chamber, intake valve and injector tip deposits. High viscosity fuels also can inhibit fuel flow through intake lines and filters, especially in cold weather. If fuel viscosity is too low, leakage past the piston in the fuel injection pump will be greater, especially after wear has occurred. Also, the lubricating qualities, necessary for pump lubrication, of low viscosity fuels are generally poorer. These effects of viscosity can be critical not only to engine performance, but engine life as well. Viscosity is determined by measuring the time differential for a given volume of liquid to drain through a capillary, and multiplying that time in seconds by the calibration constant for the viscometer.

The viscosity of the soyates, graphically represented in Figure 2, compare favorably with diesel fuel. The viscosities of the esters matched the order of the molecular weights of the alcohols used in the transesterification process, giving the methyl ester the lowest viscosity and the butyl ester the highest viscosity. No significant change was evident due to the use of fuel additives.

Table 6. ASTM Fuel Properties for #2 Diesel Fuel and Soybean Oil Esters

Test Property	ASTM NO.	#2 Ref. Diesel Fuel	Methyl Soyate	Methyl Soyate with additives	Ethyl Soyate	Ethyl Soyate with additives	Butyl Soyate	Butyl Soyate with additives
Visc. @ 40°C (cSt)	D445	2.39	4.08	4.14	4.41	4.40	5.24	5.21
Cetane No. *	D613	45.8	46.2	48.7	48.2	49.0	51.7	54.0
Cetane Index	D976	46.0	**	**	**	**	**	**
Gross Heating Value (MJ/kg)	D240	45.2	39.8	39.9	40.0	40.0	40.7	40.6
(MJ/l)@15.6°C		38.3	34.6	35.3	35.2	35.3	35.6	35.6
@ 15.6/15.6°C Specific Grav.		.847	.884	.887	.881	.882	.876	.876
API Grav.	D287	35.5	28.4	28.1	29.1	29.0	30.1	30.0
Distillation 50% pt°C	D86	258	336	336	336	337	352	353
90% pt°C		296	342	347	344	351	364	369
Cloud pt. °C	D2500	-19	2	1	1	-2	-3	-4
Pour pt. °C	D97	-23	-1	-4	-4	-7	-7	-7
Flash pt. °C								
Clev Open Cup	D92	92	171	166	174	163	185	179
PM Closed Cup	D93	78	141	135	160	157	157	121
H ₂ O & Sediment (% vol)	D1796	trace	trace	trace	trace	trace	trace	trace
Sulfur(% mass)	D129	.25	.01	.01	.01	.01	.01	.01
Cu. Corrosion 98.9°C	D130	1-a	1-a	1-a	1-a	1-a	1-a	1-a
Ash(% mass)	D482	.025	<.01	.01	.01	.01	.01	<.01
% Ramsbottom Carbon Residue	D524	.14	.30	-	.69	-	2.21	-
Gum No.(cg/l)	D2274	6.6	16400	15500	19200	18400	17900	13400
Color(ASTM code)	D2274	L3.0	L1.5	L1.5	L1.0	L1.5	L1.0	L1.0
Color(ASTM code)	D1500	L2.0	L2.0	L2.0	L2.0	L2.0	L3.0	L2.5

* Cetane tests ran by Waukesha, all others by Farmland Industries

** off scale

Cetane number is a measure of ignition quality of the fuel and influences engine operating roughness due to the rate of pressure rise in the cylinder. The severity of the pressure rise at ignition will depend upon the length of ignition delay (first stage of combustion in CI engine). The ignition delay period is usually divided into two processes: physical and chemical.

The physical processes include spray disintegration, droplet formation, heating of the liquid fuel, evaporation of the fuel, and diffusion of the vapor into the air to form a combustible mixture. The chemical processes include the decomposition of the heavy hydrocarbons into lighter components, and pre-ignition chemical reactions between the decomposed components and oxygen. The physical processes begin first, with the chemical processes beginning after the fuel vapor comes into contact with the air. Thus, both processes do overlap, however, during the early stages of combustion, the mass of fuel vapor which undergoes chemical reaction is very small compared to the mass necessary to cause a detectable pressure rise in the cylinder. Therefore, the first part of the ignition delay is considered to be dominated by the physical processes which result in the formation of a combustible mixture. The second part of the ignition delay is then considered to be dominated by the chemical changes which leads to auto-ignition.

The explosive combustion or self-ignition of the homogeneous mixture (second stage of combustion in a CI engine) produces a rapid pressure rise in the cylinder. Therefore, a shorter ignition delay means less fuel has a chance to evaporate and mix to become part of the initial homogeneous mixture before ignition. Thus, the rapid pressure rise will be less severe due to less fuel burning under a homogeneous condition and therefore reducing engine "knock". Of course the remainder of the fuel burns as it vaporizes and mixes

with air under the more controlled heterogeneous combustion of the fuel droplet (third stage of combustion in a CI engine). A high cetane fuel has a shorter ignition delay than a low cetane fuel. Therefore, a high cetane fuel will naturally reduce high stresses and severe vibration on the engine from the effects of the rapid load applied due to the initial pressure rise in the combustion chamber.

The cetane number can be determined directly by using a CFR engine (ASTM D613) and measuring the percentage of cetane necessary to give the same knock characteristics as the test fuel. Alternatively a cetane index can be determined (ASTM D976) by using an equation which includes the fuel's API gravity and the midpoint temperature in the distillation of the fuel. A high cetane number does not necessarily mean better performance, only easier starting, faster warmup, less diesel knock, and reduced carbon and varnish deposits.

The cetane rating of the soyates are markedly higher than the reference diesel fuel as shown in Table 6. This implies better ignition quality and smoother engine operation for the soyate fuels. No indication was observed during any of the tests to dispute that implication. The high cetane numbers reported for the soyates are possibly due to the initial cleavage of the weaker bonded alcohol radicals (CH_3 , C_2H_5 , C_4H_9 for methyl, ethyl, and butyl respectively) from the soyate molecules. The presence of these radicals may be reducing ignition delay by lowering the self-ignition temperature of the homogeneous mixture. This would decrease ignition delay by affecting the rate of the chemical processes present. However, the delay incurred from the physical processes are usually greater than the delay created by the chemical processes in a CI engine. Therefore the fatty acid molecules of the soybean oil esters may also have a faster vaporization rate than diesel fuel.

The esters also showed an increase in cetane rating according to the molecular weight of the alcohol used in the transesterification process. This again may be due to the differences in the self-ignition temperatures of the alcohol radicals of the fuels. A slight improvement in cetane numbers was achieved in all the soyates with fuel additives, however, not a gain of 5 as reported for diesel fuels at this treatment rate by Ethyl Corporation. The indirect method of obtaining a cetane index gave values that were off-scale suggesting that this method is not a valid fuel test for soybean oil esters and probably not for vegetable oils in general. This was expected since the test was derived from data with diesel fuels, however a similar method may possibly be constructed that would give a strong correlation to the cetane number that takes into account the different composition and properties of the soyates.

The higher or gross heating value of a fuel (ASTM D240) is determined by combusting it in a bomb calorimeter. With the water left as vapor the lower or net heating value is obtained, while the higher or gross heating value is obtained when the water vapor is condensed. Heating values indicate the energy content of the fuel in either a mass or volume basis. Therefore, a fuel with a higher energy content is capable of producing more work than the same amount of a fuel with a lower energy content if the thermal efficiency is the same for both fuels.

The higher or gross heating values of the esters were approximately 11% lower on a mass basis than the reference diesel fuel as shown in Table 6. The butyl soyate had the highest energy content of the esters with the ethyl soyate next, followed closely by the methyl soyate. This trend is due to the butyl ester molecule having three more carbon atoms and six more hydrogen

atoms to burn than a molecule of methyl ester while the ethyl ester has one more carbon and two more hydrogen atoms than the methyl ester. The fuel additives provided no significant change in the heating value of the soyates as expected. The soyates do have a slightly higher specific gravity than diesel fuel so the energy content of the soyates on a volume basis is somewhat closer to diesel fuel than on a mass basis. Since the injection pump meters fuel on a volume basis and since a higher specific gravity fuel contains a higher energy content on a volume basis than a fuel with a lower specific gravity if the two fuels have the same heating value on a mass basis, the denser fuel will provide more energy at the same rack setting if all other factors are equal. Of course fuel flow and engine performance is affected by many factors such as fuel viscosity. Also noted is that commercial diesel fuels are sold on a volume basis, thus, it is important to compare fuel heating values on a volume basis as well as a mass basis.

The gravity of a fuel is an indication of its density. Specific gravity is the ratio of a unit volume mass of fuel to the mass of the same volume of water. The American Petroleum Institute (API) gravity is defined using the specific gravity (ASTM D287). The API gravity of a fuel can give the following general relationships (Obert, 1973 and SAE Handbook, 1983):

1. The lower the API gravity, the more viscous the fuel, the higher the carbon residue, and the heavier in weight. The higher the API gravity (less mass per unit volume of fuel), the lower the heating value per volume, but the greater the heating value on a mass basis.
2. High API gravities imply high cetane numbers.

The specific gravities of the soyates are greater than the diesel fuel, indicating that they are denser. The API gravity of the soyates are lower than the reference fuel. Thus, the general relationships inferred by a low API gravity is that the fuel will be more viscous, show a higher carbon residue, be heavier in weight, have a lower mass heating value, a higher heating value on a volume basis, and have low cetane numbers. All of the general relationships listed above hold between the reference diesel fuel and the soyates, as shown in Table 6, except the prediction of low cetane numbers and a higher heating value on a volume basis for the soyates. The only generalizations inferred by API gravities that hold for comparisons between the soyate fuels themselves are that higher API gravities yield a greater heating value on a mass basis and that the cetane number will increase. The trend among the esters is that the API gravity increases with the increasing molecular weight of the alcohols used in the transesterification process. A slight decrease in API gravity is noted from the use of fuel additives in the soybean oil esters.

The distillation of a fuel (ASTM D86) reveals the volatility of the fuel. A low distillation range is desirable with the most important characteristics being a low 50% distillation temperature (more volatile fuel) to prevent smoke and a low 90% and endpoint temperatures to ensure low carbon residuals. The distillation of a fuel is also an important factor for engine design when size, speed, and load variations are considered. Low volatility fuels can, under certain engine operating conditions, result in incomplete combustion since evaporation of the fuel is more difficult. The part of the unburned fuel can cause high dilution of the lubricating oil. Therefore, for engines operating in rapidly fluctuating load and speed situations, a more volatile fuel is usually desirable.

The distillation curves for the reference fuel, and soyates with and without additives are represented in Figure 3. The esters, consisting of similar sized hydrocarbons (fatty acids), tend to exhibit more of a boiling point phenomena rather than a distillation curve as with diesel fuel. The soybean esters have higher 50% and 90% distillation temperatures revealing less volatility than the diesel fuel. The esters again follow the molecular weight of the alcohols with respect to distillation temperatures. The butyl soyate engine tests revealed more visible smoke under full rack than the other two esters and did not have as distinct an odor of deep fat frying as did the methyl soyate. This corresponds with the butyl ester being the least volatile fuel. Apparent decomposition (pyrolysis) began before the actual endpoint was reached in all of the esters. The additives improved the volatility of the soyate fuels very little.

The pour point (ASTM D97) is the lowest temperature at which a fuel flows. The pour point is important when the engine is operated at low temperatures, since it is an indication of the temperature below which gravity feeding of the fuel may not be possible. This corresponds with the cloud point (ASTM D2500) which is the temperature at which some component of the fuel first becomes visibly insoluble under specified conditions of the test. It may indicate a tendency toward filter plugging with some fuel system designs. These two properties indicate the fuel's cold weather characteristics.

The pour points and cloud points of the soyates are much higher than the reference fuel. The additives lowered the cloud points for each of the esters but only lowered the pour point for the methyl and ethyl soyates. Higher treatment levels than those required for diesel fuel, on the other hand, may

cause the soyate fuel's pour points to respond better to the additives. These tests indicate that the soyates would be much more susceptible to cold weather problems if substituted for diesel fuel.

The flash point of a fuel (ASTM D92 for Cleveland open cup & ASTM D93 for Pensky-Marten closed cup) is the temperature at which the fuel vapors will flash when ignited by an external flame. While not directly related to engine performance, the flash point is important with regard to safety precautions and legal requirements concerning fuel handling and storage.

The flash points are significantly higher for the soyates. The fuel additives lowered the flash points on all the esters. This suggests that the soybean esters are not as flammable as diesel fuel and are therefore safer fuels to handle. The flash points of the esters correspond with their respective distillation curves where the esters with a higher volatility have lower flash points. These high flash points will not occur though if all the excess alcohol is not removed after the transesterification process.

A centrifuge is used to detect the water and sediment (ASTM D1796) present in a fuel which is objectionable due to increased injection equipment wear. Since more engines have been damaged by dirt and water than from any other deviation from fuel standards, fuel cleanliness is very important. There was only a trace of water and sediment in all the test fuels.

The sulfur content of a fuel (ASTM D129) is of importance due to its corroding effects upon fuel lines and injection equipment. A direct method of evaluating corrosion (ASTM D130) is used where polished copper strips are immersed in the fuel for a specified time, then washed and compared to the ASTM Copper Strip Corrosion Standards. All fuels scored 1-a (slight tarnish -

light orange, almost the same as a freshly polished strip). Thus, all fuels passed the test.

Ash forming materials (ASTM D482) such as abrasive solids or soluble metallic soaps may be present in fuels. The abrasive solids can cause excessive wear in the injector pump, injectors, pistons, and rings, while the soaps may contribute to engine deposits. All the soyate fuels contained less ash than the reference diesel fuel.

The amount of carbon residue left after evaporation and pyrolysis of a fuel is determined by the Ramsbottom Carbon Residue method (ASTM D524). This method is generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure. Since the soyates reveal decomposition phenomena during distillation it was included in the list of fuel property tests. However, this test can present erroneously high values if amyl nitrates or alkyl nitrates are present and is also difficult to replicate accurately. The additives used in the soyates do contain nitrate compounds, therefore, the results for the soyates with additives were excluded. The high values for the butyl soyate without additives compared to the other soyate fuels without additives indicate that the butyl soyate could cause greater carbon deposits. This was indeed the case as revealed in the engine deposit ratings discussed later.

The gum number and color (ASTM D2274) give the gum content of the fuel in milligrams of gum per 100 milliliters of fuel and discoloration due to oxidation after the accelerated 16 hour oxidation test. These tests give an indication of the longterm storage ability of a fuel. Excess gum content in a fuel can inhibit fuel flow by plugging fuel filters, and also cause injector

needle sticking.

The rate of gum formation for all of the soyates under the test conditions were very high compared to the reference diesel fuel. The gum content created from the test conditions for the soyates ranged between 13 and 20% of the fuel, over 2,000 times the value for the reference diesel fuel. The maximum value for standard commercial diesel fuel is 50 which is still much lower than the esters. The large numbers were attributed to the high percentage of unsaturated hydrocarbons in the fatty acid composition of the soyates. These unsaturated double bonds are unstable and easily oxidize, resulting in gum formation. Oxidation therefore reduces the longterm storage capability of the soyates. All the soyates did show a reduction in gum number with the additives but the accuracy of the test must be considered in any conclusion derived from this fact. This test was designed to be used for values less than 1000, nearly one twentieth the highest value reported for the soyates.

The color of the fuel (ASTM D1500) does not have any effect on engine performance and only serves as a comparison between the different fuels. The ASTM D2274 color test is performed after the gum formation oxidation test, therefore a comparison can be made before and after oxidation. The reference diesel fuel is darker than the soyates before oxidation and gets lighter in color after oxidation which is typical for diesel fuels, however the soyates show a reversed trend. The reason for this is probably tied into the presence of unsaturated double bonds in the soyates.

Engine Oil Analysis

Lubricating oil viscosity was checked daily and samples were sent to

Farmland Industries for an oil wear metal analysis at 45 hours, 90 hours, 142 hours and 200 hours for the base line test. The sampling frequency was increased to every 15 hours for the soyates to get an earlier indication of any problems. The type of lubricating oil used was Farmland Industries' Multi-Grade, SAE 15W-40, A.P.I. Service SF-CD, Diesel Engine Oil. The oil analysis measured viscosity, and the amounts of fuel dilution, water, and total solids in the oil. Metal concentrations in ppm were determined for iron, chromium, aluminum, copper, lead, tin, silver, nickel, silicon, sodium, boron, phosphorous, and zinc. A check for antifreeze, oil oxidation, and total acid number were also made. Table 7 shows the concentration levels of the most important metals for the test fuels.

Table 7. J.D. 4239TF Engine Oil Wear Metal Analysis

Fuel	Hours	Iron	Chromium	Aluminum	Copper	Lead
Reference Fuel	45	12	0	0	3	9
	90	28	0	2	3	12
	142	12	0	0	2	5
	200	38	1	2	4	10
Methyl Soyate	45	8	0	4	2	29
	90	2	0	0	4	39
	145	7	0	6	2	13
	200	18	1	2	3	16
Ethyl Soyate	45	18	0	7	1	37
	92	31	1	2	3	46
	144	13	0	0	2	9
	200	30	0	7	4	16
Butyl Soyate	45	11	0	0	3	10
	90	27	1	0	4	13
	145	14	0	0	2	5
	200	60	1	0	4	9

Wear metal levels for the soyate fuels were considered to be normal throughout the 200-hour test. Of interest were the initial high levels of lead for the ethyl soyate, suggesting that abnormally high wear was taking place on the bearings. Following the oil change at 100 hours however, the lead concentration returned to normal. It may be that a slightly different alloy was used on the surfaces of the replacement bearings, containing a

higher percentage of lead, or that the bearings were still "breaking in" after the 50 hour break-in cycle. Also noted were slightly higher concentrations of iron reported for the butyl soyate near the end of the test cycle compared to the other test fuels. Again these levels were not serious and were probably due to the differences in the engine since each test was run with new internal engine parts. The actual engine wear measurements discussed later detected no significant differences between the test fuels which directly support the oil analysis conclusions of no abnormal engine wear problems.

The lubricating oil viscosity, monitored over the 100 hour oil change interval, is shown in Figure 4. For all the fuels, the shearing forces acting on the oil caused an initial rapid drop in oil viscosity during the first 10-20 hours. In the case of the reference fuel, the viscosity then stabilized at about 103 cSt. For the methyl, ethyl, and butyl soyates however, the viscosity continued to drop for the entire 100 hours, which suggests that more oil dilution was taking place. This decrease in viscosity is contrary to the results of others, such as Bruwer (1980), where crankcase oil polymerization was experienced with straight vegetable oils. Pischinger (1982) and Fort and Blumberg (1982), however, observed fuel dilution of the lubrication oil without oil polymerization occurring for transesterified soybean oil and cottonseed oils respectively. The different responses by the lubricating oil to vegetable oil fuel dilution could be due to differences in the lubricating oils themselves such as multi-grade vs. single grade oils or due to the transesterification process. Continued fuel dilution could eventually lead to oil thickening, though, as the antioxidant additives in the oil become depleted. However, this did not occur during the normal oil service interval.

By adhering to the manufacturer's recommended oil change interval, no problems with oil polymerization should occur, at least not on the short term basis. On the long term, deposits might increase to the point where combustion of the ester fuels will deteriorate, resulting in more unburned fuel in the cylinder. This would in turn accelerate oil dilution, so that the oil change interval may need to be shortened. In an engine with more hours on it (thus more wear), more blowby will occur. This would also accelerate oil dilution.

Internal Engine Wear Measurements

Conclusive evidence of engine wear can only be established from physical measurement of various parts. Thus, measurements in key wear areas of the engine were taken to determine the actual engine wear after each of the engine tests.

In Table 8 the average condition for the four cylinders are presented for the base line test, the methyl soyate test, the ethyl soyate test, and the butyl soyate test, respectively.

From this table it is apparent that there was no notable difference in the wear patterns of the four fuels. In all cases the honing marks in the liners were still clearly visible, as were the machining marks on the pistons. The valve stems had faint polishing marks on them, with the valve seat interference angle barely starting to show. Bearing discoloration was only evident on the thrust side of the bearings.

Table 8. J.D. 4239TF Engine Wear Rate Data for each 200-hr Test

	Diesel	Methyl	Ethyl	Butyl
1. Cylinder Walls (Liners)				
Inches of Wear (Ave)	Nil	Nil	Nil	Nil
2. Pistons (Ave)				
Wear	Nil	Nil	Nil	Nil
3. Rings (Ave)				
Number Stuck or Sluggish	None	None	None	None
Face Condition	OK	OK	OK	OK
Gap Increase, Inches				
First	0.00320	0.00225	0.00375	0.00200
Second	0.00150	0.00100	0.00125	0.00125
Oil Control	0.00250	0.00200	0.00200	0.00200
4. Wrist Pin Wear (Ave)	Nil	Nil	Nil	Nil
5. Bearings (Ave)				
Rods--Upper (Mg. BWL)	8.63	8.38	6.5	5.78
Lower (Mg. BWL)	9.58	5.45	6.9	4.95
Mains--Upper (Mg. BWL)	OK	OK	OK	OK
Lower (Mg. BWL)	OK	OK	OK	OK
6. Camshaft Lobe Wear (Ave)				
Average (in.)	0.0010	0.0001	0.0001	0.0004
Maximum (in.)	0.0016	0.0003	0.0002	0.0007
7. Lifter Condition (Ave)				
Face	OK	OK	OK	OK
Body	OK	OK	OK	OK
8. Valves (Ave)				
Caps				
Intake	OK	OK	OK	OK
Exhaust	OK	OK	OK	OK
Stems				
Intake	Nil	Nil	Nil	Nil
Exhaust	Nil	Nil	Nil	Nil
Seat Condition				
Intake	OK	OK	OK	OK
Exhaust	OK	OK	OK	OK

Internal Engine Deposit Ratings

Engine deposits for the test fuels were rated by the Petroleum Research Division of Farmland Industries and are summarized in Table 9. Their report indicated that deposits for the ethyl soyate were the same as for diesel, with

the exception of the color of the exhaust valve deposits. These deposits were light brown for the ethyl soyate, compared to black in the diesel tests. The ethyl ester carbon deposits were relatively dry and soft, except around the injector bodies. In this area, gum-like deposits made removal of the injectors more difficult. This was not the case for the methyl and butyl esters. However piston deposits were significantly greater for the methyl and butyl esters.

The methyl soyate engine test revealed two pistons containing carbon deposits in the top ring groove space with an overall four piston average top ring groove fill of 17.5%. Top ring groove filling was also evident, but on all four pistons, for the butyl soyate engine test with an overall average of 75% top ring groove area containing some carbon deposition. No carbon deposits were below the first ring in any of the soyates. However, carbon deposits would eventually migrate down the piston and collect in the lower rings and on the lands (piston surface area between the rings) if more hours were accumulated. Continued filling of ring grooves would eventually cause stuck and broken rings with severe carbon deposition eventually leading to complete engine failure. The CRC Weighted Total Demerits (WTD) deposit rating for pistons uses a comparison scale where the more severe the piston deposits, the greater the score. The average WTD scores take into account the amount and type of deposits as well as their specific location on the piston. Thus, a piston with an abundance of heavy carbon deposits below the first ring would receive a higher rating than a piston having a few traces of laquer above the first ring groove. The piston WTD scores thus indicate that the butyl soyate engine has the greatest susceptibility to piston carbon deposit buildup that could reduce engine life and that the ethyl soyate fueled engine the least

susceptible of the esters. However, only longer term engine tests can substantiate these initial indications.

The CRC sludge and varnish ratings as well as the valve deposit ratings use a scale of 0-10 with a score of ten equal to a new part. The sludge and varnish ratings were excellent with no unusual depositions. The intake valve deposit ratings showed all the soyates to be slightly better than diesel fuel, however, these could change dramatically if more hours were accumulated. The exhaust valve deposit ratings showed excellent results for all fuels as expected since the higher temperatures at the exhaust ports tend to keep the valves clean unless severe deposition is occurring.

Table 9. J.D. 4239TF Engine Deposit Inspection for each 200-hr Test

Pistons -CRC Weighted Demerit Rating-*	Diesel	Methyl	Ethyl	Butyl
% Top Groove Fill	0.0	17.5	0.0	75.0
2nd Groove, % Carbon Fill	0.0	0.0	0.0	0.0
Oil Groove, & Cover (% clean)	100.0	33.8	100.0	86.3
very light amber laquer (%)	0.0	66.2	0.0	2.5
light amber laquer (%)	0.0	0.0	0.0	11.2
Top Land % Med. Carbon	7.0	0.0	0.0	0.0
2nd Land % Carbon + Black Laq.	0.0	0.0	0.0	0.0
Wtd. Total Demerits (Grooves)	42.4	56.6	45.3	71.5
Wtd. Total Demerits (Lands)	4.8	7.8	5.2	8.8
Total Piston WTD (4 piston Avg.)	47.2	64.4	50.5	80.3
Sludge -CRC Rating-*				
Rocker Arm Cover	9.5	9.6	9.5	9.4
Valve Deck	9.5	9.5	9.6	9.5
Oil Pan	9.2	9.5	9.2	9.5
Timing Gear Cover	9.5	9.6	9.5	9.5
Rocker Arms	9.5	9.6	9.5	9.7
Average Sludge	9.44	9.58	9.44	9.58
Total Sludge	47.2	47.9	47.2	47.9
Varnish -CRC Rating-*				
Rocker Arm Cover	9.9	9.9	9.9	9.95
Rocker Arm Assy.	9.9	9.9	9.9	9.9
Piston Skirt	10.0	10.0	10.0	10.0
Cylinder Walls	9.9	9.9	9.9	9.9
Push Rods	9.9	9.9	9.9	9.9
Lifter Bodies	9.9	9.9	9.9	9.9
Oil Pan	9.8	9.8	9.8	9.8
Average Varnish	9.9	9.9	9.9	9.9
Total Varnish	69.3	69.3	69.3	69.3
Valves -CRC Rating-*				
Exhaust Valves	9.0	9.2	9.5	9.2
Intake Valves	7.2	7.8	8.4	8.7

* Piston WTD rating increases with increased deposits while sludge, varnish, and valve deposit CRC ratings decrease with increased deposits

The injector tips were as deposit free as in the diesel test for all the soyate fuels. There were no obstructed orifices and the spray patterns were unaffected. Cracking pressures, as shown in Table 10, declined by an average of 603 kPa for the ethyl soyate as opposed to 1535 kPa for the reference fuel test and 1078 kPa and 819 kPa for the methyl soyate and butyl soyate respectively. The lower cracking pressure decrease for the ethyl soyate was not an abnormal condition, as injectors tend to wear less rapidly as hours are accumulated (injectors were not replaced before the ethyl soyate test following the 200-hour diesel fuel baseline test).

Table 10. Roosa Master 9.5 mm (22044-AR88241) Injection Nozzle Tests for each 200-hr Test

Test	Diesel	Ethyl	Methyl	Butyl
Leakage (Ave) *				
Start	OK	OK	OK	OK
Stop	OK	OK	OK	OK
Chatter (Ave)				
Start	OK	OK	OK	OK
Stop	OK	OK	OK	OK
Cracking Press. (Ave)				
Start (kPa)	25457	24098	25133	25733
Stop (kPa)	23926	23491	24057	24919
Press. drop (kPa)	1535	603 **	1078	819
Spray Pattern (Ave)				
Start	OK	OK	OK	OK
Stop	OK	OK	OK	OK

Note: New injectors for Diesel, Methyl, and Butyl tests.

Same injectors used in Diesel and Ethyl tests.

Note: Nozzle opening pressure (Manufacturing Specifications)

new: 25200-25900 kPa; used: 23800-24500 kPa

* Leak test run at approx. 90 kg below cracking press. for 30 sec.

** Lower pressure losses normal in used injectors

The injector pump calibration, shown in Table 11, was checked before any engine tests and after each of the soyate tests. The pump delivery did not change significantly and was not below the manufacturer's recommendations, indicating that no abnormal wear had taken place.

Table 11. Roosa Master Model DM4427 Injector Pump Calibration Tests for each 200-hr Test

RPM	Pump Strokes	Mfg. Recommend	Delivery Range in cc/1,000 strokes *			
			Before Diesel	After Ethyl	After Methyl	After Butyl
2500	1000	76-79	82.25	82.75	84.25	83.50
1500	1000	80-84	84.50	84.75	86.50	84.80
1000	1000	62-66	65.00	63.90	75.25	71.50
Start * (150)	500	14.00 min	16.93	16.33	16.85	16.10

* Fuel delivery on the start mode is reported as cc/500 strokes

Engine Performance

The brake power output at full rack for all four test fuels is shown in Figure 5. The maximum engine power output of each fuel was obtained between 2450 and 2500 rpm. The power output for the reference fuel and the butyl soyate were nearly identical at 2200 rpm as shown in Table 12. The methyl soyate showed only a 2% difference in maximum power output at 2200 rpm. The ethyl soyate fuel displayed the lowest maximum power output with a 6% difference compared to the reference diesel fuel at 2200 rpm.

Table 12. J.D. 4239TF Power and Torque Comparisons at Full Rack

	Diesel	Methyl Soyate	Ethyl Soyate	Butyl Soyate
Power in kW				
@ 2200 rpm	66.3	65.8	64.1	66.9
Difference		2.0%	4.0%	0.0%
Torque in N-m				
@ 1600 rpm	315.9	315.7	296.1	306.7
Difference		0.0%	6.0%	3.0%

Figure 6 shows the torque output at full rack. Also, shown in Table 12, are the maximum torques generated at 1600 rpm. The reference fuel and the methyl soyate were nearly identical while the butyl soyate and ethyl soyate developed about 3% and 6% less torque respectively than the diesel fuel.

Assuming that the injection pump metered fuel equally on a volume basis at the same rack position for all the test fuels, the differences between the gross heating values of the fuels and the differences in engine power output at full rack should be similar. However, this was not the case as seen when these differences, shown in Tables 12 and 13, are compared to each other. The methyl and ethyl soyates had about a 12% lower heating value than the diesel fuel on a mass basis, while the butyl soyate was about 10% less. Since the brake thermal efficiencies (Figure 9) are very similar for all four test fuels, thermal efficiency does not help explain these differences.

Table 13. Gross Heating Value Comparisons of Test Fuels

	Diesel	Methyl Soyate	Ethyl Soyate	Butyl Soyate
Gross Heating Value (mass basis)				
MJ/kg	45.2	39.9	40.0	40.6
Difference		11.7%	11.5%	10.2%
Gross Heating Value (volumetric basis)				
MJ/kg @15.6°C	38.3	35.3	35.3	35.6
Difference		7.8%	7.8%	7.0%

Since the soyate fuels are denser than diesel fuel and since the injection pump meters fuel on a volumetric basis, the heating values of the fuels should be compared on a volume basis to determine the actual influence of the fuel's heating value on the engine power output tests. Comparisons now show only an 8% difference in heating value on a volume basis at 15.6°C for the methyl and ethyl soyates compared to the reference diesel fuel. The butyl soyate now shows a 7% difference.

Thus, increased fuel consumption on a mass basis by the soyate fuels, due to their greater relative density compared to the reference diesel fuel, explains only a portion of the discrepancy between the heating value and power differences. Therefore, either the engine tests for the soyate fuels were run

at much lower fuel temperatures than the baseline diesel fuel test which increased fuel flow on a mass basis by increasing the specific gravity of the soyate fuels, or the injection fuel pump actually metered more fuel on a volume basis for the ester fuels. The average fuel temperatures for all four fuels at full rack, shown in Table 14, clearly indicate that the full rack tests for the soyate fuels were not run at lower fuel temperatures. Thus, the fuel injection pump did seem to meter more fuel on a volume basis at the same rack position for the soyate fuels than for diesel fuel. This can be explained due to the fact that the soyate fuels have a higher viscosity than diesel fuel and that a more viscous fuel could cause less leakage past the injection pump pistons.

Table 14. Average Fuel Temperature Comparisons

	Temperature in degrees Centigrade			
	Diesel	Methyl Soyate	Ethyl Soyate	Butyl Soyate
Full Rack Tests	32.6	42.9	38.0	46.3
Difference		10.3	5.4	13.7
Emission Tests	31.8	38.1	37.9	44.5
Difference		6.4	6.1	12.7
Average Diff.		8.4	5.8	13.2

Brake specific fuel consumption, shown in Figure 7, is about 12% higher for all the soyates over the 1500 to 2500 rpm range than the reference diesel fuel. This again is due to the soyates being a denser fuel and to a slightly higher volumetric fuel flow since the soyates are more viscous and do not allow as much fuel leakage past the injection pump pistons.

Figure 8 shows a richer fuel-air ratio for all the soyates compared to the reference fuel. The fuel-air ratio for the methyl and ethyl esters is about 13% greater than the reference fuel at 2200 rpm and about 17% higher for the butyl ester. This again is primarily due to the soyate fuel engine tests

exhibiting higher fuel flow rates than the baseline diesel fuel test.

Brake thermal efficiency is defined as the ratio of useful or brake mechanical energy output to the chemical energy available in the fuel, which is determined from the lower heating value of the fuel on a mass basis. There is very little difference between the fuels, as shown in Figure 9, which point to the soyates ability to achieve the same degree or completeness of combustion as #2 diesel fuel. The relatively high efficiencies achieved is not unusual for turbocharged engines, since more air is inducted, which helps drive the combustion of the fuel to a greater degree of completion.

The exhaust gas temperature at full rack (Figure 10) shows the ethyl ester to be about 20°C less than the diesel fuel. The methyl ester was similar to the diesel fuel's exhaust gas temperature and the butyl ester was 50 to 60°C higher than the diesel fuel.

In general, the soyates displayed engine performance characteristics very similar to diesel fuel. The small differences were mainly a result of the lower heating value of the soyates, their higher viscosity, and their greater density. The engine performed smoothly in all the tests and exhibited no starting problems. There was no audible knock, as indicated by the high cetane numbers for the esters.

Fuel filter plugging occurred roughly every 50 hours during the ethyl soyate tests. Peak torque could not be maintained and the engine rpm fluctuated as much as 100 rpm. The filters were replaced whenever this occurred, restoring normal engine performance. Inspection of the filters revealed a gummy substance on the "dirty" side of the filter. An analysis performed on the filter paper contaminants by the Biochemistry Dept. concluded that the

filter plugging was not due to a gummy substance but rather to an abundance of cracked soybean hulls, meal particles, and other foreign contaminants. Fuel filter plugging also occurred during the methyl soyate tests. The methyl soyate filter plugging, however, was due to a gummy substance, similar to very soft jello, in the bottom of the fuel drums. This may have been caused by the cold weather in which this fuel was exposed to prior to the tests conducted in the spring. Initially hypothesizing that this gummy material could be glycerol left from the transesterification process, which had solidified and settled out during the cold weather, an analysis was performed on it. These tests proved negative, therefore, oxidation could have taken place which caused the gummy substance or the heavier fatty acids had reached their melting points and solidified, thus settling to the bottom of the barrel. The other two soyate fuels did not have a gummy layer in the bottom of their barrels. Prefiltering into a new barrel was done which eliminated the engine fuel filter plugging during the methyl soyate tests. This obviously did not solve the problem since the prefilters plugged regularly. The butyl soyate fuel exhibited no fuel filter plugging problems.

The injection pump also displayed stickiness characteristics at idle speeds for the methyl and butyl ester engine tests which did not always allow the engine to reach the correct low idle speed. This occurred during their 50 hour break-in cycles on commercial diesel fuel as well as the 200-hour test cycle on the fuels. This is probably due to gum and varnish buildup from the previous tests with the reference fuel and the ethyl soyate. However, the injector and injection pump delivery tests performed by Electro-Magneto Corporation in Kansas City, Missouri were not affected (Table 11). When questioned about this problem, Electro-Magneto claimed that the Roosa Master model

DM injection pump was particularly sensitive to this type of problem even with straight diesel fuel.

Emissions Analysis

The specific emissions for the four fuels are shown in Figures 11 through 20. Only eight of the thirteen modes are presented in the graphs due to the extremely high numbers at the low power levels.

Figure 11 shows the carbon dioxide levels for the soyates to be slightly higher than the reference diesel fuel at 1500 rpm. In Figure 12 the difference between the fuels is less pronounced at 2200 rpm. For all fuels the carbon dioxide level was higher at 2200 rpm than at 1500 rpm, especially at the low power levels. This is due to the turbocharger increasing the air flow and resulting in a lower fuel-air ratio at the higher speed. Thus, the increased air volume tended to drive combustion more towards completion at the higher speed producing more CO₂.

Figures 13 and 14 show the oxygen emissions at 1500 and 2200 rpm respectively. There is little difference between the fuels at both speeds, but as expected the oxygen emissions were greater at 2200 rpm than at 1500 rpm for all the fuels. This is again a direct result of the turbocharger forcing more air, thus an abundance of oxygen, into the cylinder at the higher speed.

Carbon monoxide emissions, shown in Figures 15 and 16, were extremely low. This is typical of diesel engines due to the excess air available for combustion, especially at partial loads. There are no major differences between CO levels of the esters and the reference fuel. Although the curves show some trends, it may not be meaningful to draw any conclusions from this

data since the instrument was operating at less than 5% of full scale.

Hydrocarbon emissions for the four fuels are shown in Figure 17 and Figure 18. At 1500 rpm, the methyl and ethyl soyates have the lowest levels with the diesel slightly higher and the butyl soyate slightly higher yet. At 2200 rpm, all the soyates are significantly lower than the diesel up to the highest power level. The soyates are all similar with the methyl having the lowest levels, then the ethyl, followed by the butyl soyate.

Nitrous oxides, shown in Figure 19 for 1500 rpm and Figure 20 for 2200 rpm, reveal major differences between the soyates and the diesel fuel. The soyates' NO_x emissions, ranged from two to five times that measured for the diesel fuel. The methyl soyate produced the highest levels, and the butyl soyate the next highest, with the ethyl soyate producing the lowest levels of NO_x emissions for the soyate fuels at both engine speed settings. The exhaust gas temperatures followed the same order as the level of NO_x emissions among the fuels. However, the real effect of higher combustion temperatures yielding higher NO_x emissions can be supplied as a partial reason for the differences in the NO_x levels only if the exhaust gas temperature differentials between the fuels correspond to much higher combustion temperature differences between the fuels. In other words, the exhaust gas temperature differences between the fuels of 20 to 70°C cannot explain the large differences between the fuels' NO_x emissions unless they imply a correspondingly higher combustion temperature difference in the range of 100 to 200°C. All of the fuels gave lower values at 2200 rpm than at 1500 rpm which was expected due to the reduced residence time of the fuel in the combustion chamber at the higher speed setting. Higher combustion temperatures at 2200 rpm did not seem to occur as revealed by the exhaust gas temperatures at the two speeds (Figures

21 and 22) and the reduction in NO_x levels at 2200 rpm. This is most likely due to the added cooling from the increased amount of air forced into the cylinders by the turbocharger at the higher speed as evidenced by the lower fuel-air ratios (Figures 23 and 24).

Smoke readings were attempted with a Bosch spot smoke detector, but no actual data was accumulated due to exhaust gas water vapor causing unreliable results. Visible smoke, however, was less for the methyl and ethyl soyate fuels at full rack compared to diesel fuel. The butyl soyate, on the other hand, emitted more visible smoke than diesel fuel at full rack, especially below 1800 rpm. The butyl soyate also did not exhibit the smell of deep fat frying during the engine tests like the methyl soyate did.

CONCLUSIONS

1. Ethyl, methyl, and butyl soyates with commercial diesel fuel additives have fuel properties that compare very well with diesel fuel. The high gum content developed under ASTM D2274 test conditions, however, is undesirable from the standpoint of the soyate fuels' shelf life and fuel filter plugging problems.
2. The pour point improver provided a drop in the methyl and ethyl esters' pour points, but had no effect for the butyl ester. This suggests that experimentation with different treatment rates may improve the pour points for the soyate fuels which would benefit cold weather engine operation with these fuels.
3. The high flash points for the soyate fuels make them safer to handle than diesel fuel. These high flash points can only be achieved though if all the excess alcohol is removed following the transesterification process.
4. The transesterification process raises the cetane number for the vegetable oil to levels comparable to or better than diesel fuel. All the soyates also benefited from the cetane improver additive. This eliminates engine knock and ensures smooth engine operation.
5. The ASTM fuel tests for distillate fuels provide significant insight into the potential of a candidate compression ignition fuel. Following the general standards set for diesel fuel, suitable screening of prospective fuels may be provided.
6. The interrelation between fuel properties and engine performance makes good quality control in the ester fuel preparation mandatory. In the on-farm situation, suitable procedures and quality standards would have to be prescribed.
7. Engine performance for soybean oil esters does not differ to a great extent to that of diesel fuel performance. A slight power loss, combined with an increase in fuel consumption was experienced with all three soyate fuels. This is mainly attributed to the lower heating values of these fuels compared to diesel fuel since there was no perceptible difference in the thermal efficiencies between any of the fuels tested.
8. Volume displacement by the injection pump was greater for all the soyate fuels at the full rack setting, indicating that the slightly more viscous soyate fuels reduced the amount of internal pump leakage.
9. Engine wear for all the test fuels were found to be normal after each of the 200-hour tests. Deposits were comparable with respect to amount, but slightly different in color and texture between the ethyl soyate and diesel fuel. The methyl and butyl esters showed greater amounts of deposits on the pistons, especially in the top ring groove than the diesel fuel test.
10. Injection equipment tests showed no differences between any of the fuels, however, the injection pump displayed stickiness characteristics at idle

speeds during the 50 hour break-in on diesel fuel as well as during the actual engine test cycle for the methyl and butyl soyates which did not always allow the engine to reach the correct low idle speed. This is probably due to gum and varnish buildup from the previous tests ran with the reference diesel fuel and the ethyl soyate. Electro-Magneto Corporation of Kansas City, Missouri informed us that the Roosa Master model DM injection pump is particularly sensitive to this type of problem since they have had many similar experiences with them.

11. All emission levels except NO_x for the soyate fuels were similar to diesel fuel, with carbon monoxide too low to provide reliable data. Nitrous oxides on the other hand were significantly greater for all the soyate fuels, with the butyl soyate giving the highest readings followed by the methyl soyate. Smoke was definitely less visible under full rack conditions for the methyl and ethyl soyates compared to diesel fuel, but the butyl soyate was greater. These differences in emissions are likely due to the different combustion characteristics of the soyate fuels.
12. Any of the soyates could be used as an alternative fuel on a short term basis, provided certain fuel quality standards are met. On the basis of the deposit ratings from this research the ethyl soyate looks the most promising, followed by the methyl soyate. However, cost of the alcohol used in the transesterification reaction will probably become the deciding factor determining which ester, if any, will become a viable alternative fuel.
13. The 200-hour test cycle, as recommended by the EMA is adequate for the screening of alternative fuels. The long term effects can in no way be established during this cycle. For this reason, failures reported during this test must be regarded as highly significant, while success only justifies the pursuit of longer term tests.

SUMMARY

The results of this investigation show that a direct injection, turbo-charged diesel engine will perform satisfactorily when fueled with 100 percent soybean oil esters. Lubricating oil viscosity dropped significantly lower between oil changes for all the ester fuels compared with diesel fuel. Engine fuel filter plugging was a problem with the ethyl and methyl esters, however, the butyl ester exhibited no such problem. Engine piston deposits were greater for the methyl and butyl esters compared to the reference diesel fuel test, while the ethyl ester engine deposits were similar to the diesel fuel's.

These results can only be projected for the short term use of soybean oil esters, such as a diesel fuel substitute during fuel shortages. Long term tests must be conducted to verify that the variations found between the soyates, specifically the engine piston deposits, can be extrapolated beyond the 200-hour test. If so, this would conclude that the ethyl soyate is the best choice for extended use as a diesel fuel substitute with regards to expected engine life with the soyate fuels tested and that the butyl soyate is the worst.

SUGGESTIONS FOR FURTHER RESEARCH

Methyl, ethyl, and butyl soybean oil esters have been shown, through these tests, to fuel a compression ignition engine satisfactorily without major problems. However, only technical aspects concerning these fuels' suitability as a substitute for diesel fuel were considered. In-depth economic analysis must be conducted to fully determine the effects such as costs that would occur if soybean oil was to enter the fuel supply at any level on a commercial basis. Questions such as the fuel versus food problem would also need to be analyzed to determine the effects on food supply if part of our agricultural land would become devoted to producing fuel.

Few problems were encountered during the engine tests for the ester fuels. The high susceptibility of gum formation under the ASTM test conditions for all the ester fuels needs to be addressed more fully. New additives, as well as those now available, that can improve the oxidative stability of these fuels need to be evaluated. Possibly processes can be found that would reduce the number of unsaturated fatty acids in the esters, or that the unsaturated fatty acid content of the soybean oil could be genetically reduced through selective plant breeding. Research also needs to be conducted to define the problems associated with cold weather use and the benefits of different treatment rates of suitable additives.

Long term engine tests definitely must be performed to verify the results achieved from the 200-hour screening tests. If these tests proved favorable, actual tests conducted in the field could determine the effects of different climates, engine loads, operators, and maintenance procedures have on the durability of an engine operating on soybean oil esters.

Study of the combustion kinetics of the soyate fuels will provide a better understanding of emission levels and combustion chamber deposits. The nature of intermediate products of combustion could be revealed through gas chromatography analysis of the exhaust gases. Time-pressure diagrams of the combustion process would also aid in determining the intermediate products and the rates of combustion of the different esters. Such work could benefit attempts to optimize the engine performance characteristics for the ester fuels and reduce emission levels.

SUGGESTIONS FOR FURTHER RESEARCH

Methyl, ethyl, and butyl soybean oil esters have been shown, through these tests, to fuel a combustion ignition engine satisfactorily without major problems. However, only technical aspects concerning these fuels' suitability as a substitute for diesel fuel were considered. In-depth economic analysis must be conducted to fully determine the effects such as costs that would occur if soybean oil was to enter the fuel supply at any level on a commercial basis. Questions such as the fuel versus food problem would also need to be analyzed to determine the effects on food supply if part of our agricultural land would become devoted to producing fuel.

Few problems were encountered during the engine tests for the ester fuels. The high susceptibility of gum formation under the ASTM test conditions for all the ester fuels needs to be addressed more fully. New additives, as well as those now available, that can improve the oxidative stability of these fuels need to be evaluated. Possibly processes can be found that would reduce the number of unsaturated fatty acids in the esters, or that the unsaturated fatty acid content of the soybean oil could be genetically reduced through selective plant breeding. Research also needs to be conducted to define the problems associated with cold weather use and the benefits of different treatment rates of suitable additives.

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APPENDIX

GRAPHICAL PRESENTATION OF ENGINE TEST RESULTS

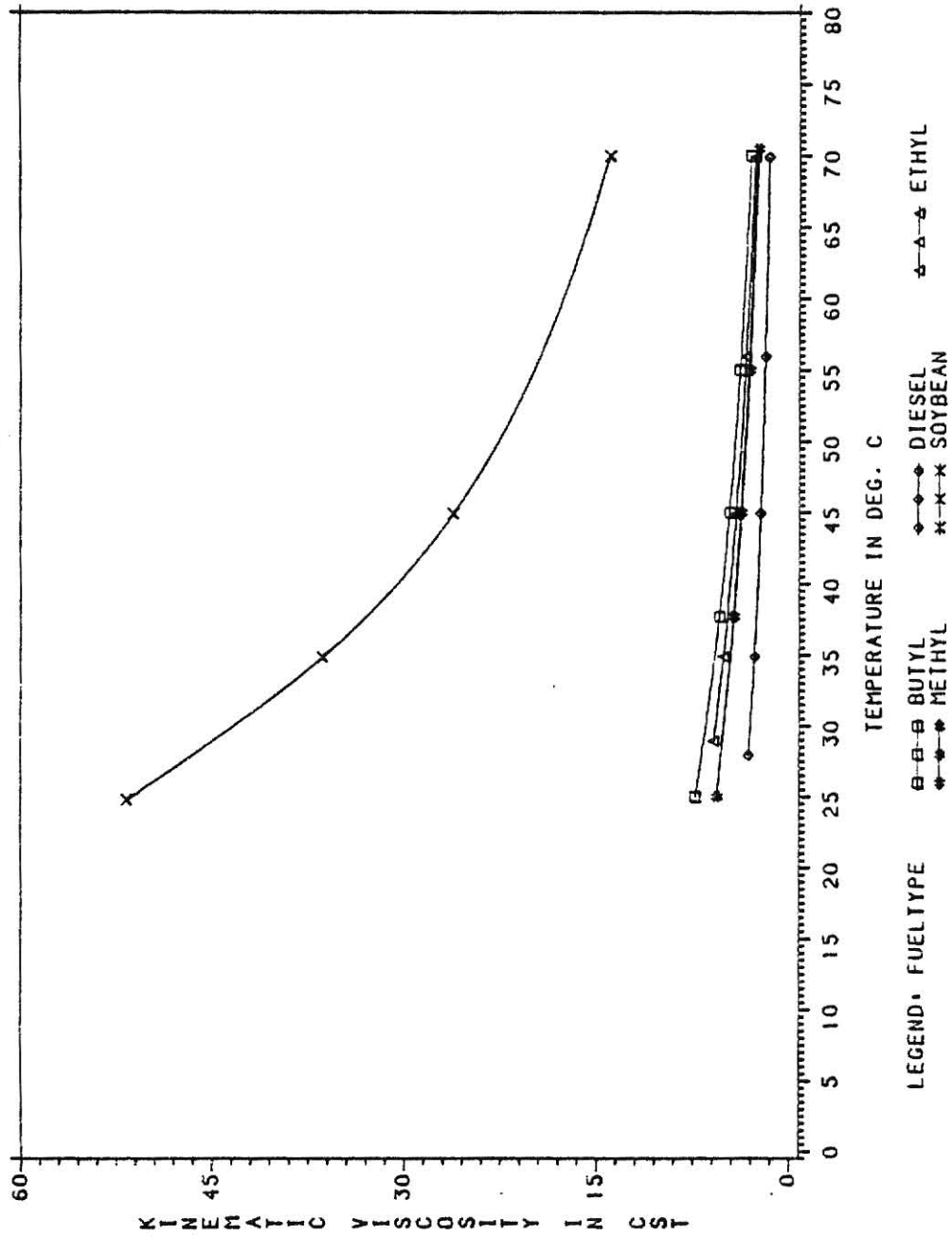


Figure 1. Viscosity of Soybean Oil, #2 Diesel Fuel, and Soybean Oil Esters vs. Temperature

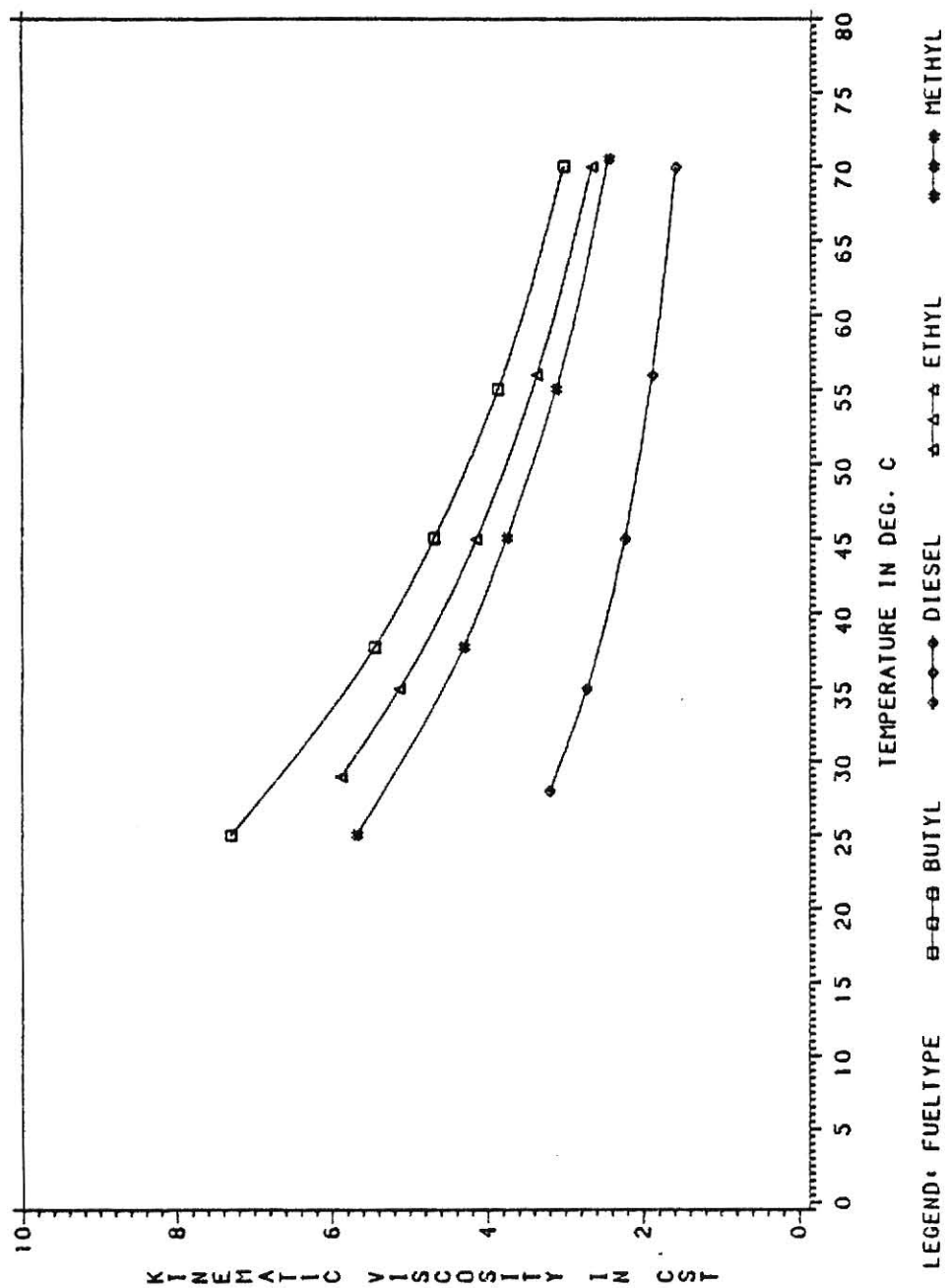


Figure 2. Viscosity of #2 Diesel Fuel and Soybean Oil Esters vs. Temperature

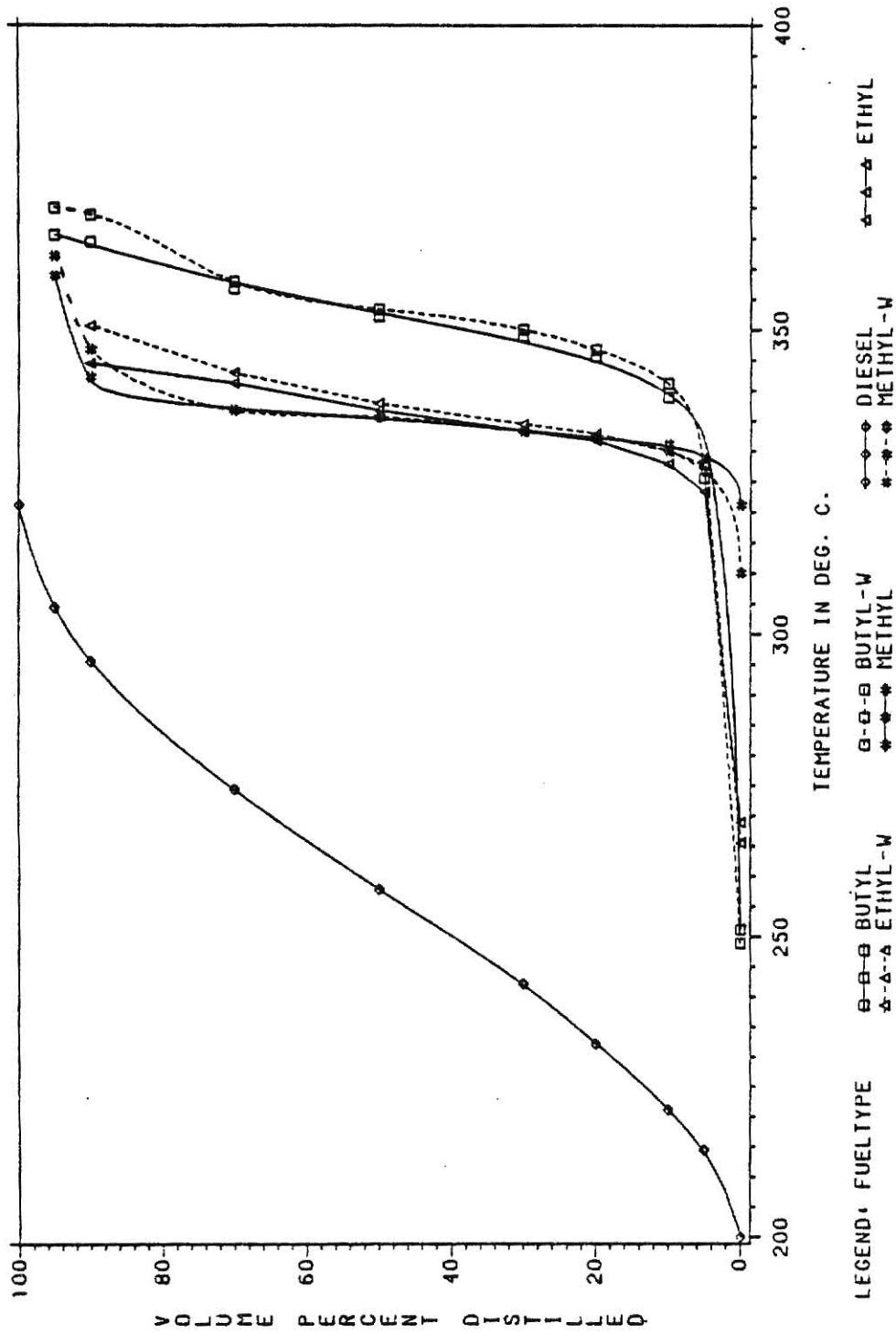


Figure 3. Distillation Curves of #2 Diesel Fuel and Soybean Oil Esters with & without Fuel Additives

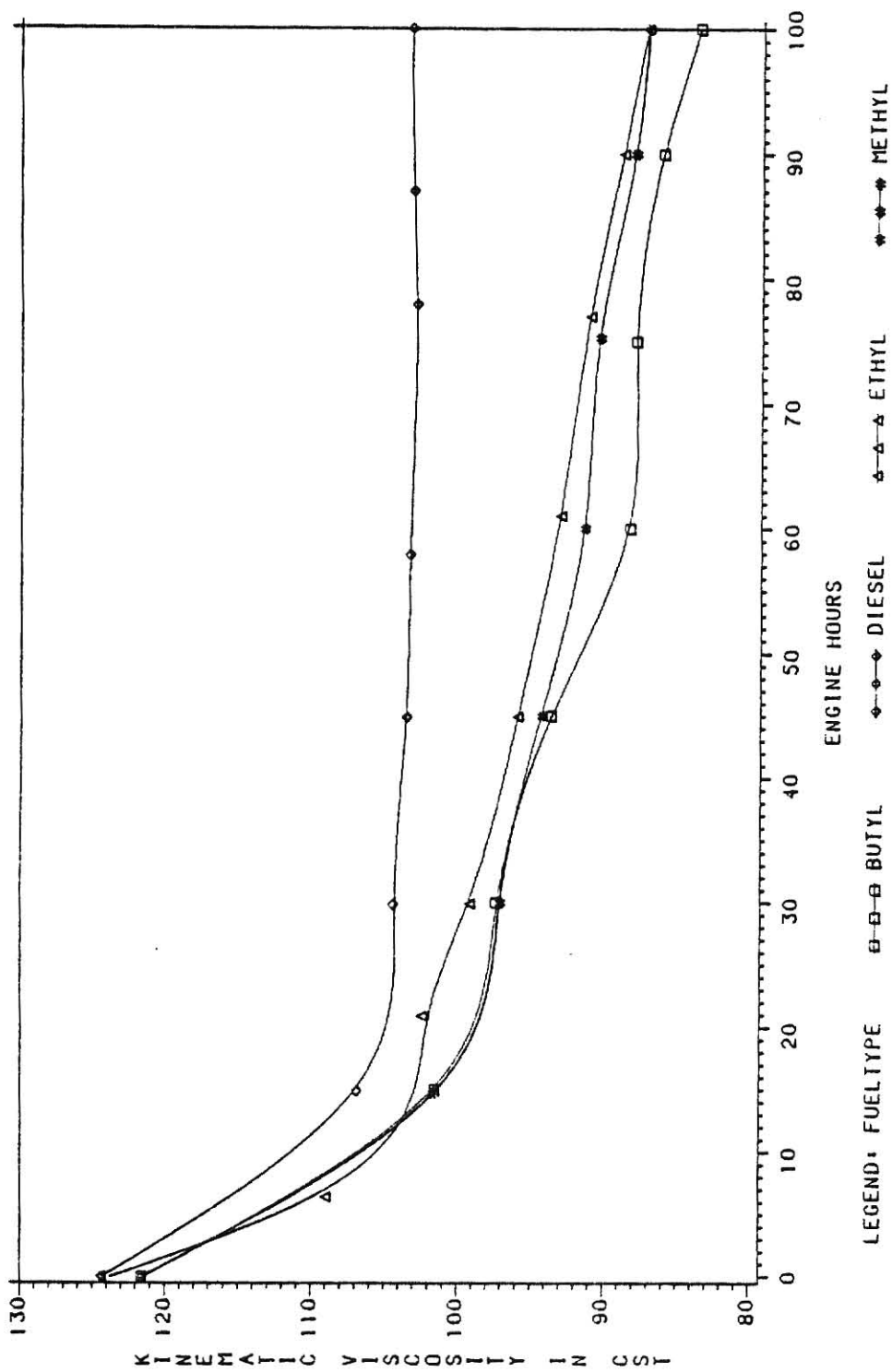


Figure 4. Crankcase Lubricating Oil Viscosity vs. Engine Hours for #2 Diesel Fuel and Soybean Oil Esters

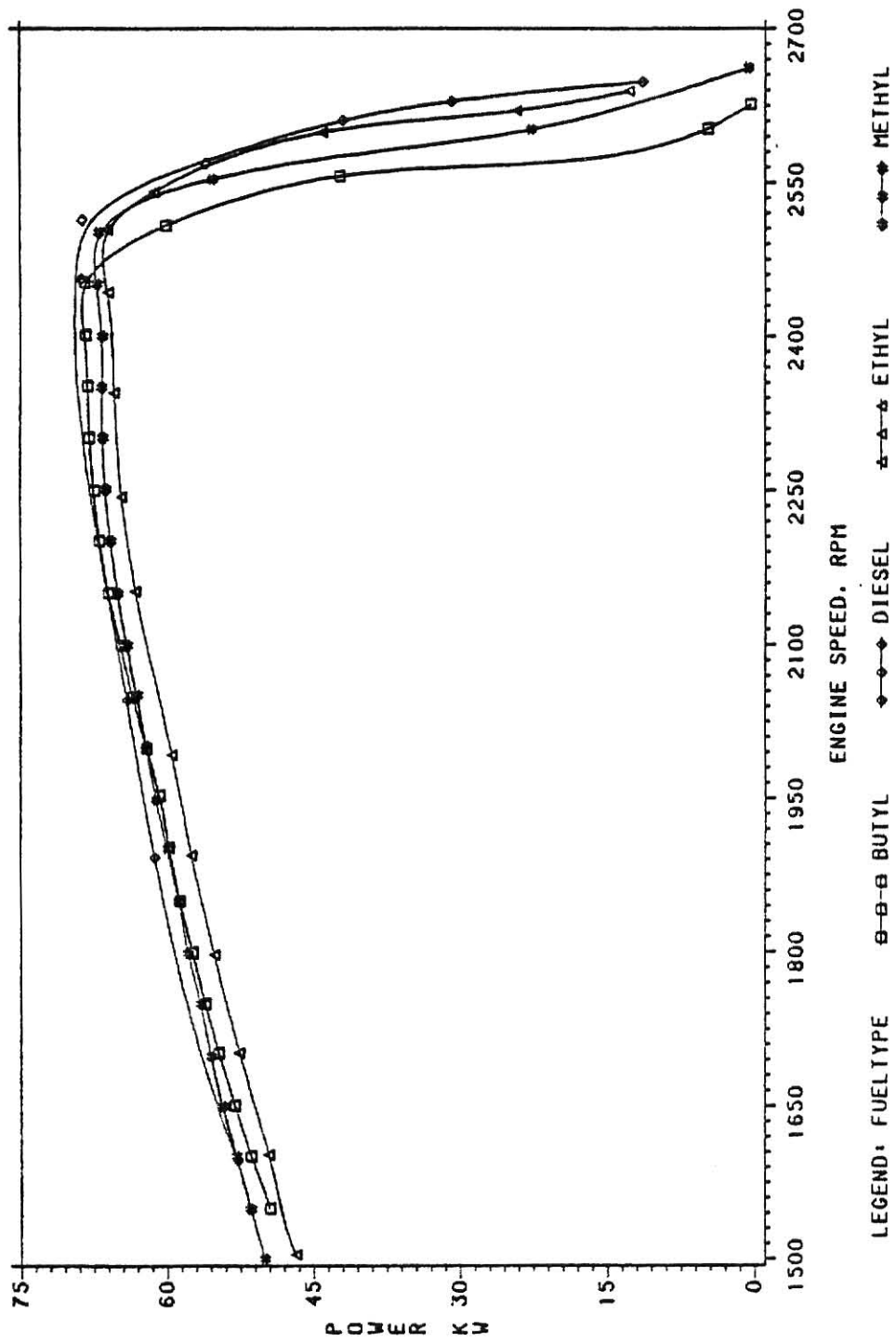


Figure 5. Brake Power Output at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

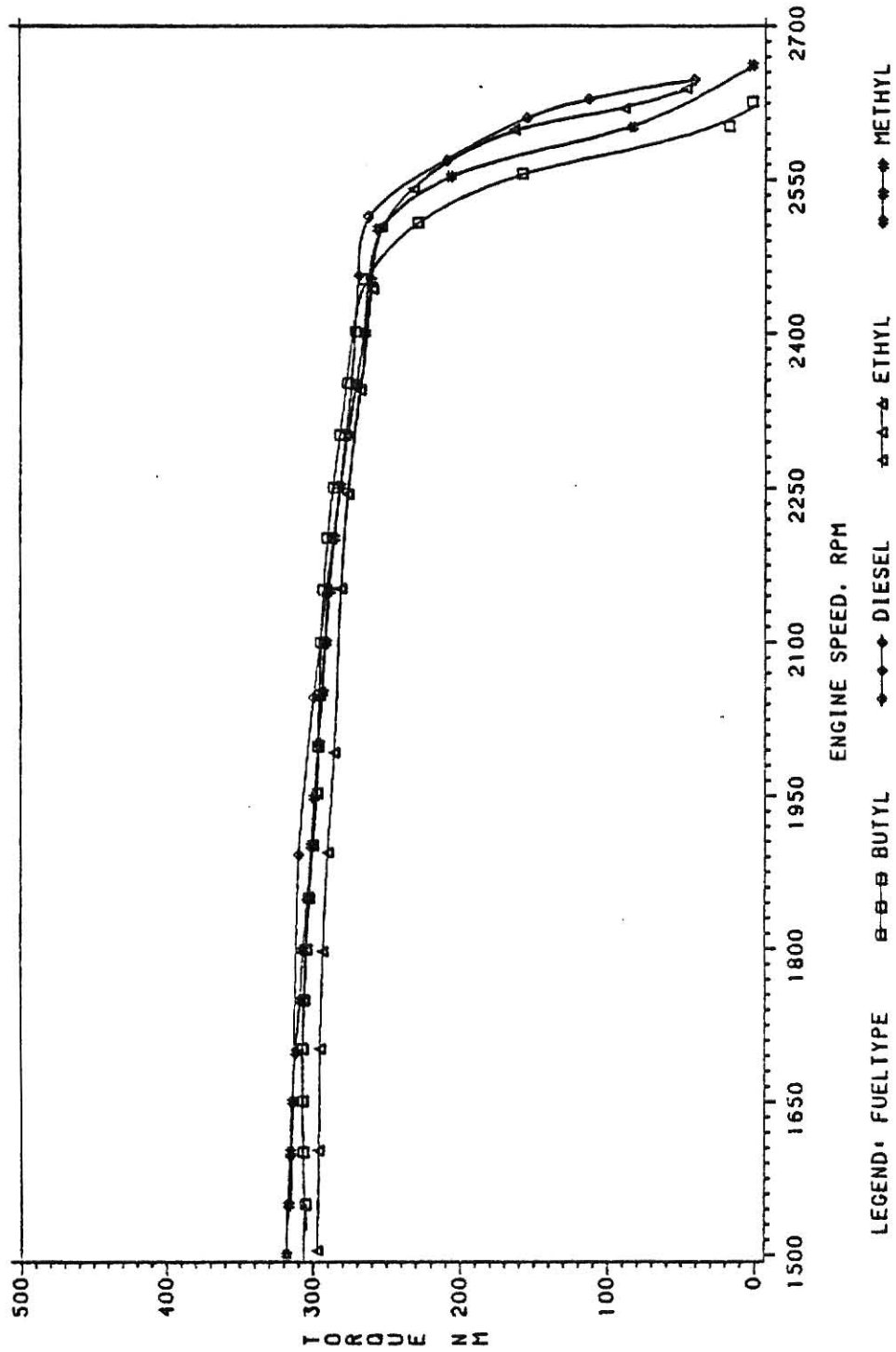


Figure 6. Torque Output at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

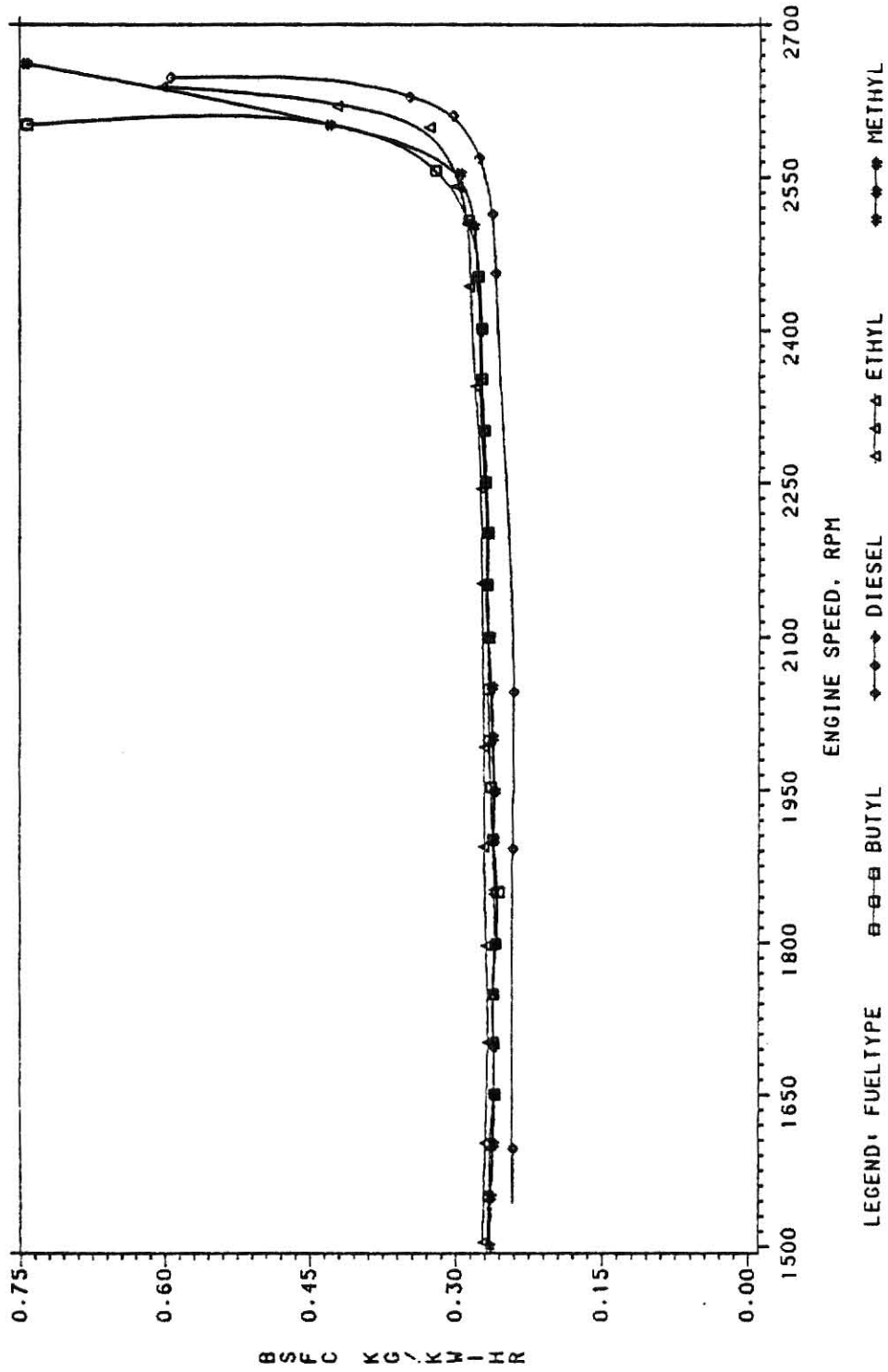


Figure 7. Brake Specific Fuel Consumption at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

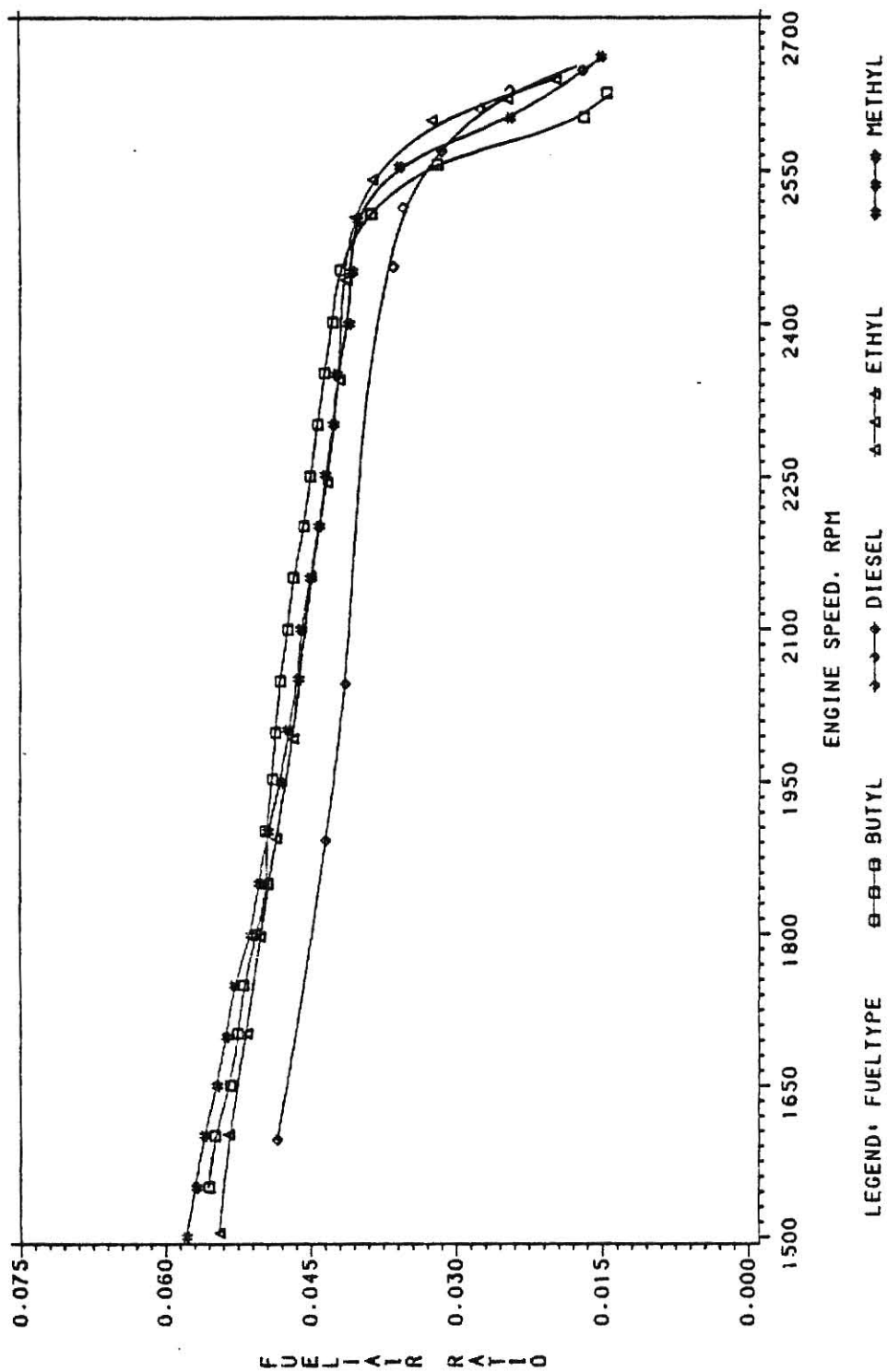


Figure 8. Fuel-Air Ratio at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

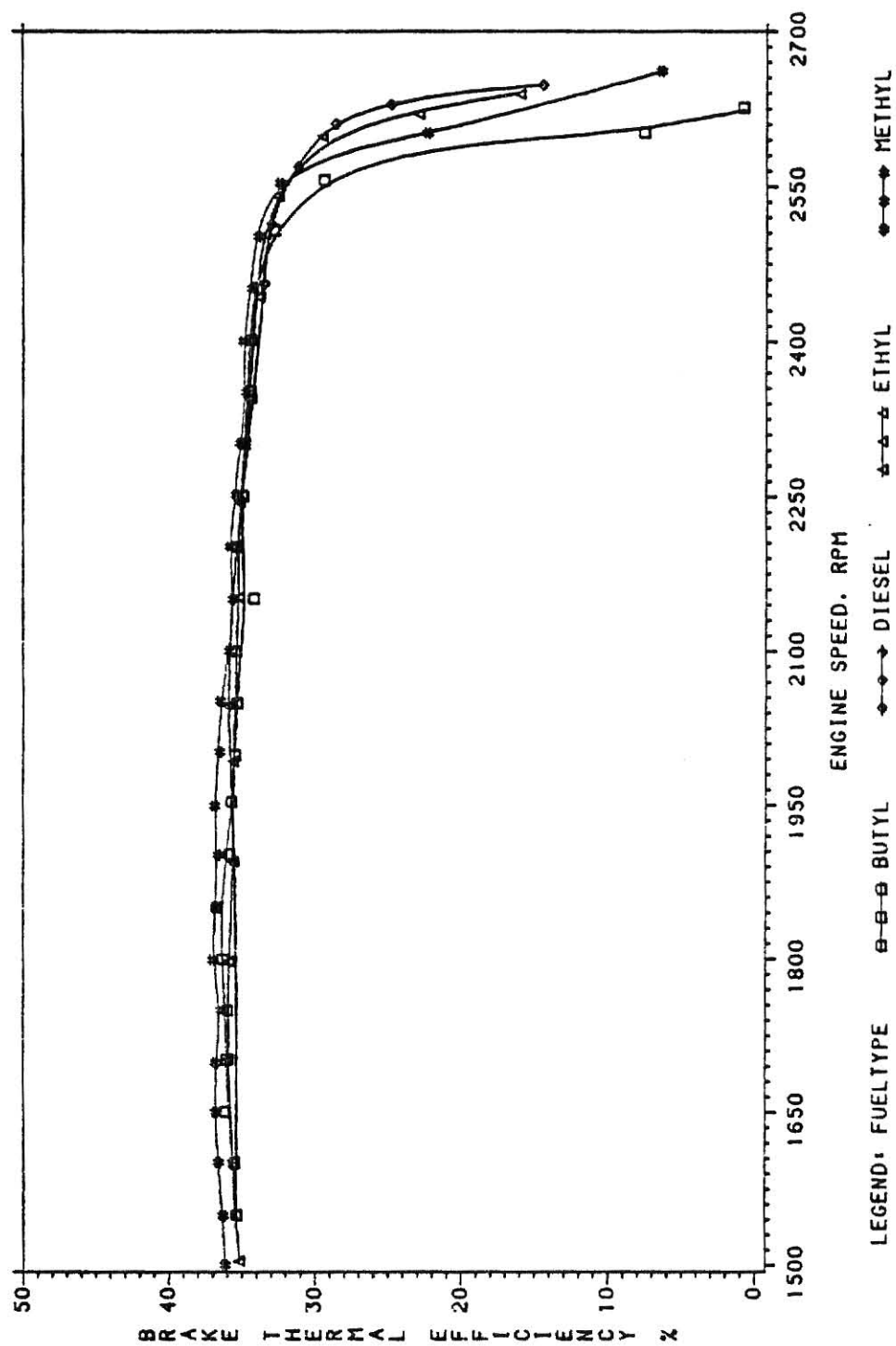


Figure 9. Brake Thermal Efficiency at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

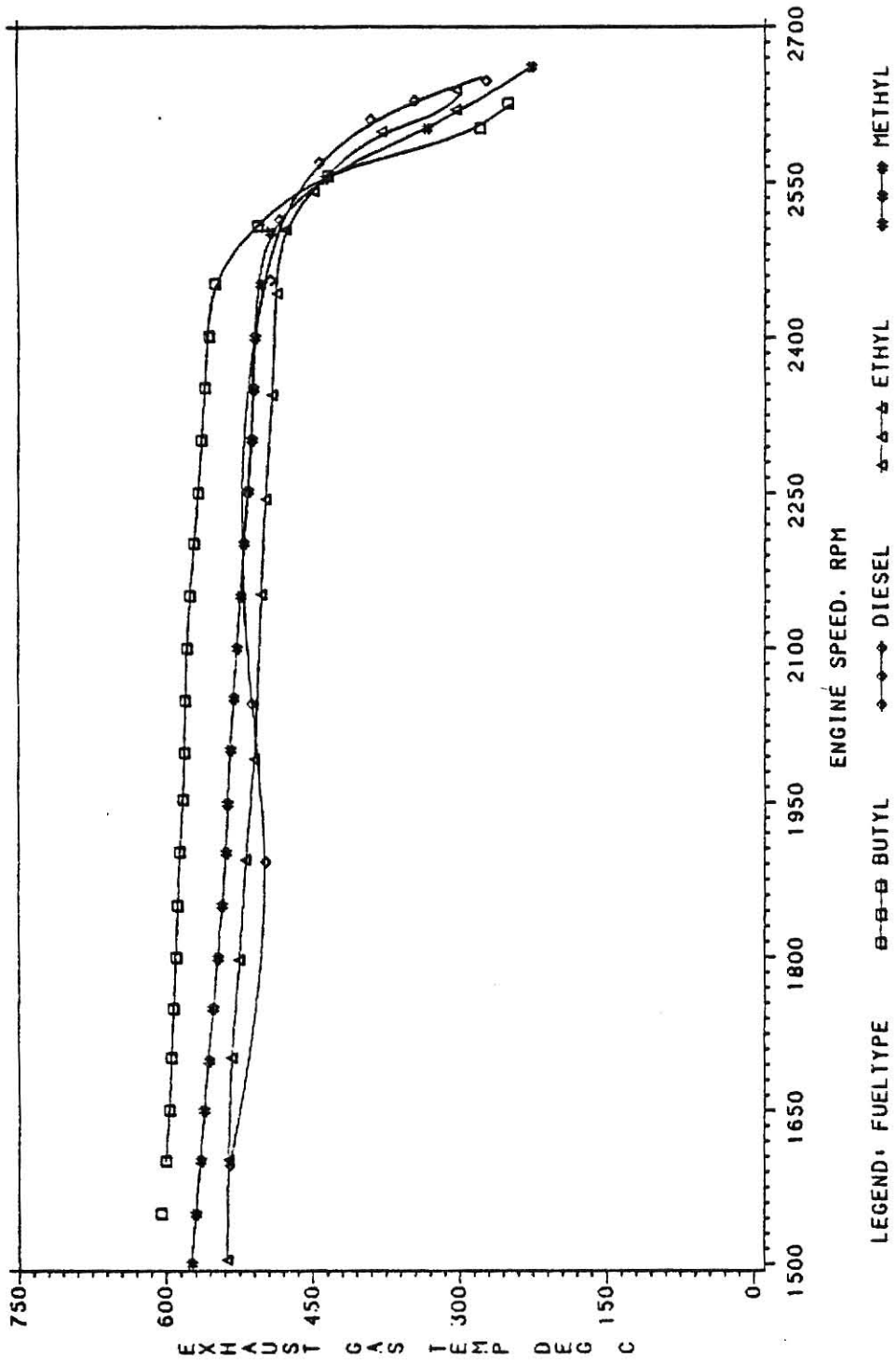


Figure 10. Exhaust Gas Temperature at Full Rack for #2 Diesel Fuel and Soybean Oil Esters

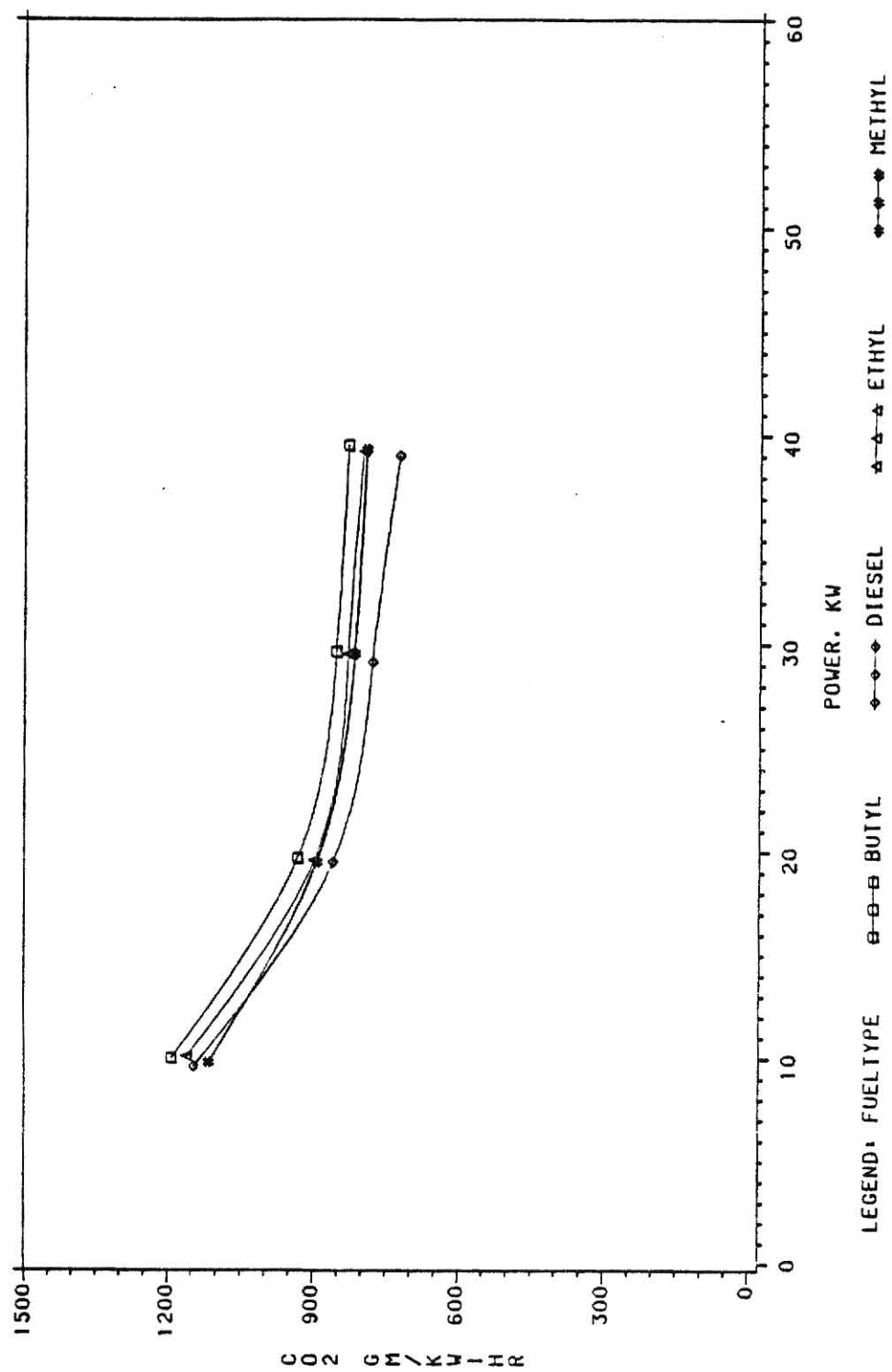


Figure 11. Carbon Dioxide Emissions at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

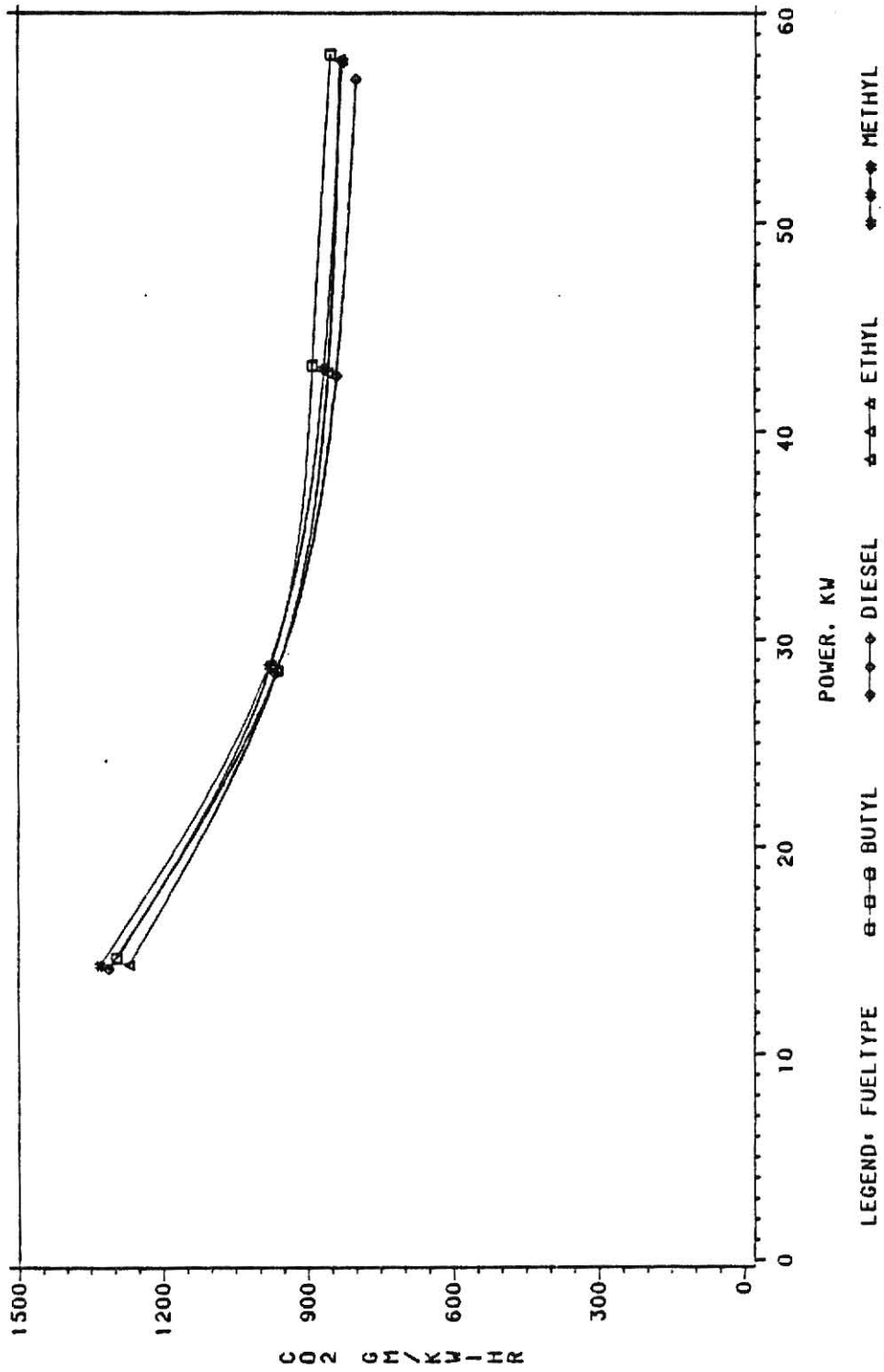


Figure 12. Carbon Dioxide Emissions at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

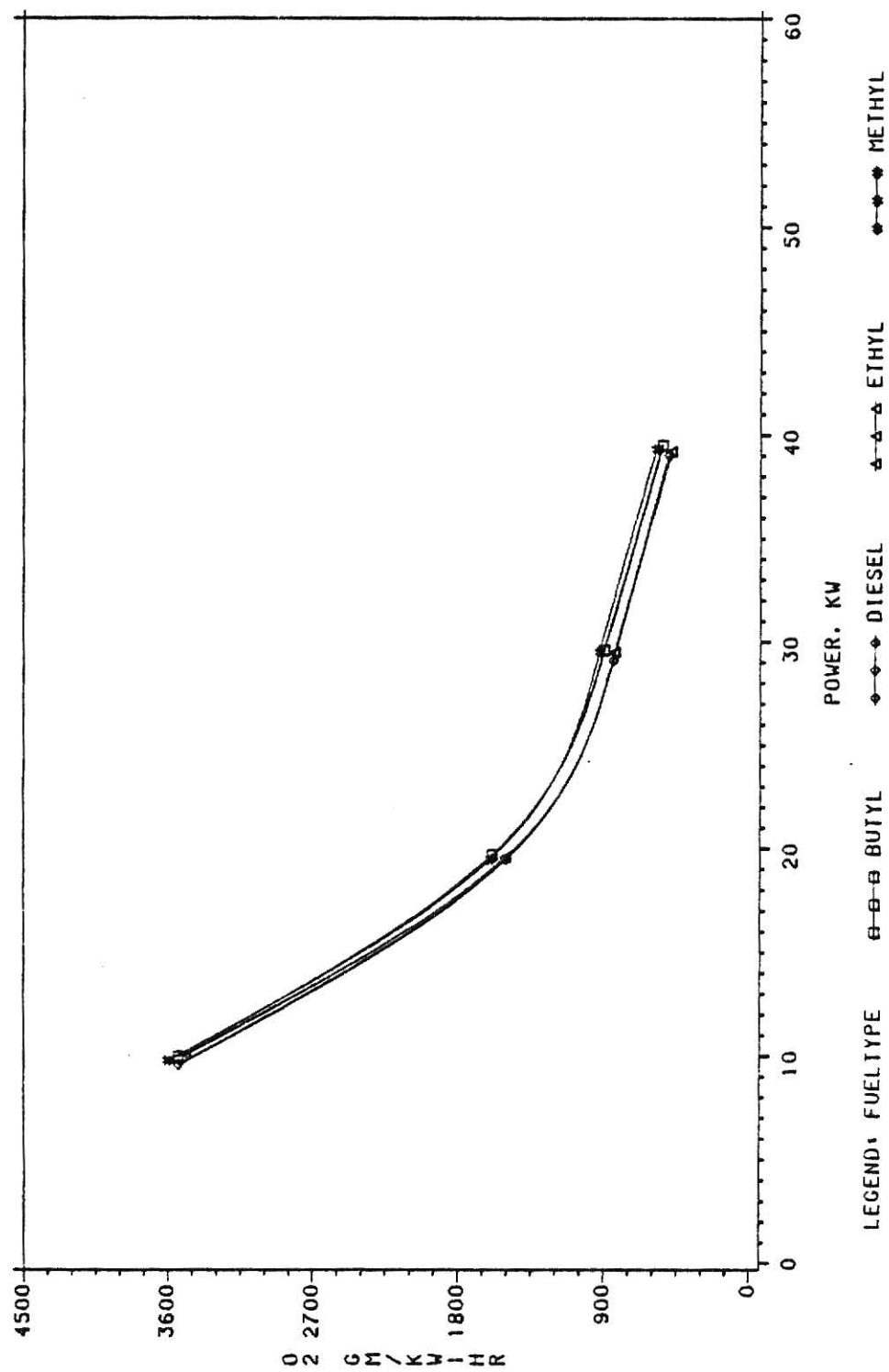


Figure 13. Oxygen Emissions at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

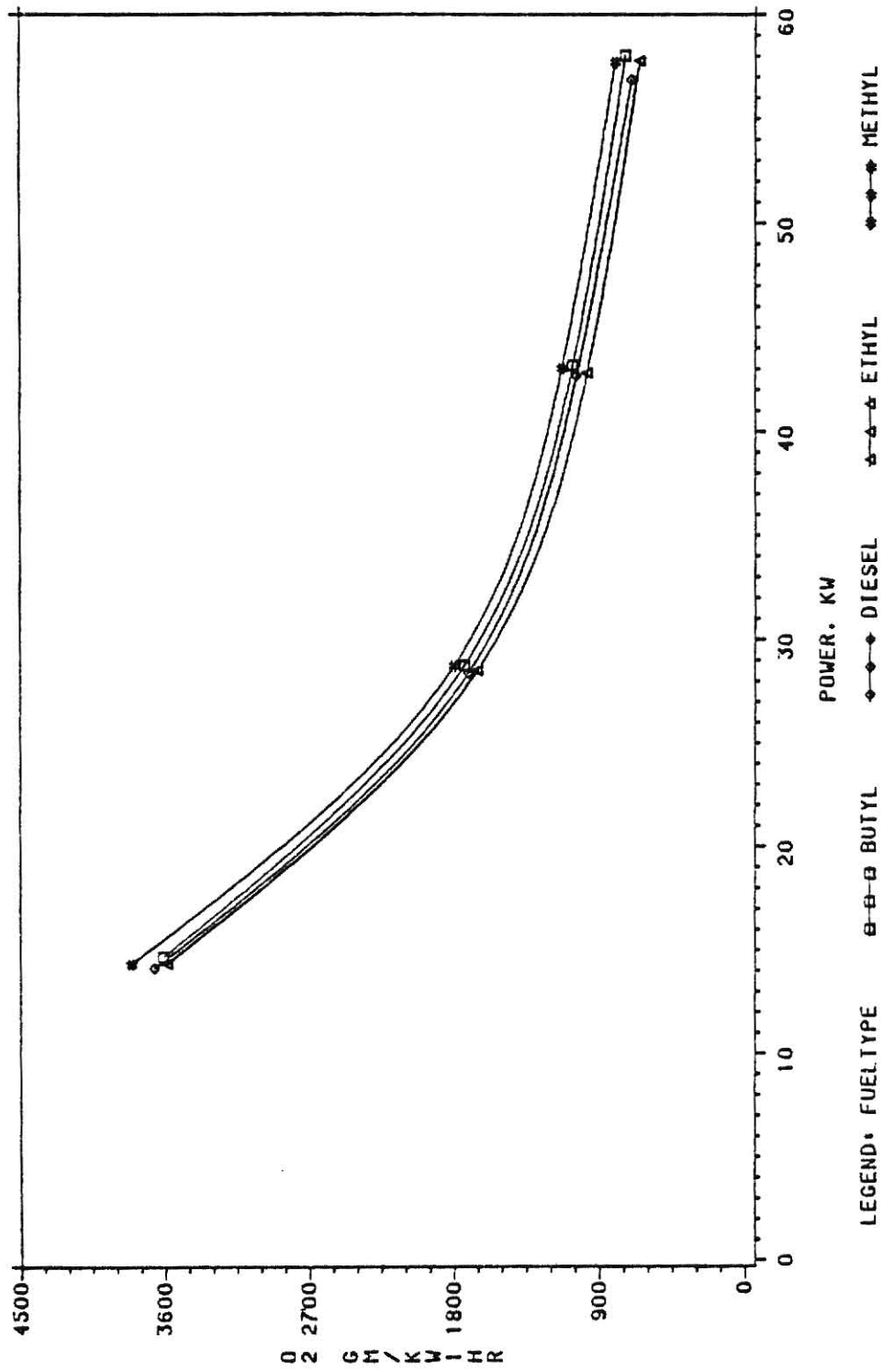


Figure 14. Oxygen Emissions at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

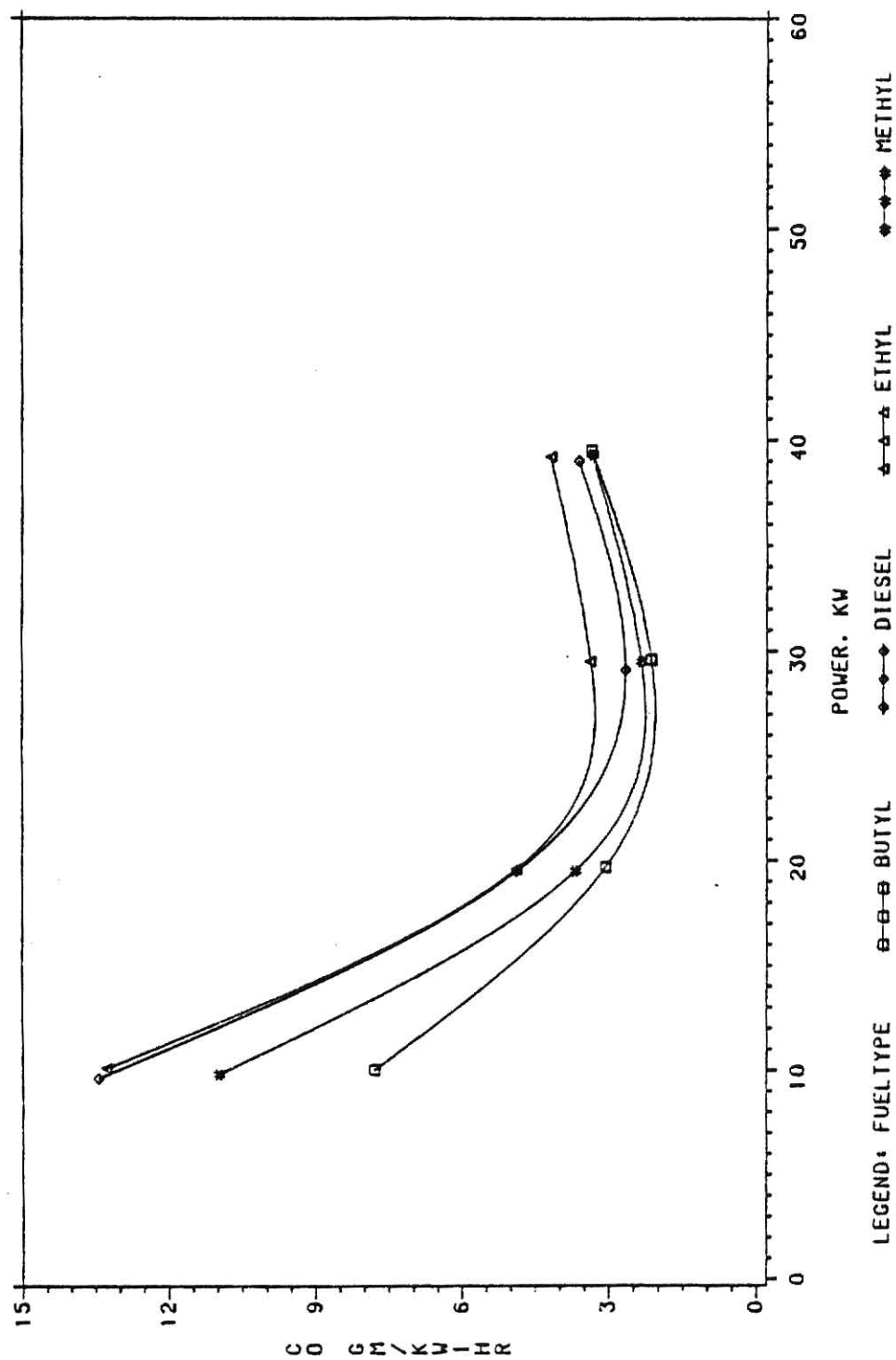


Figure 15. Carbon Monoxide Emissions at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

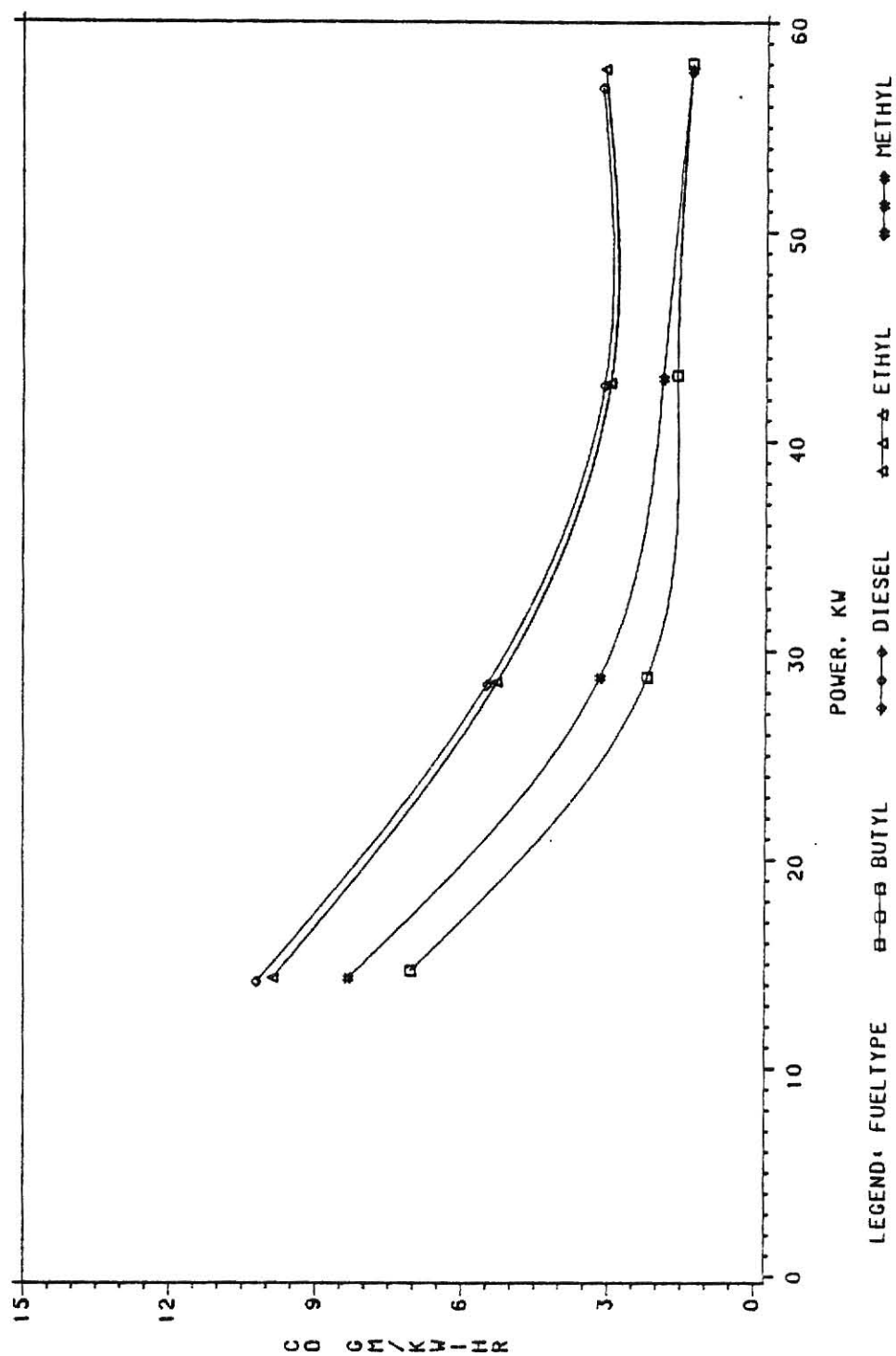


Figure 16. Carbon Monoxide Emissions at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

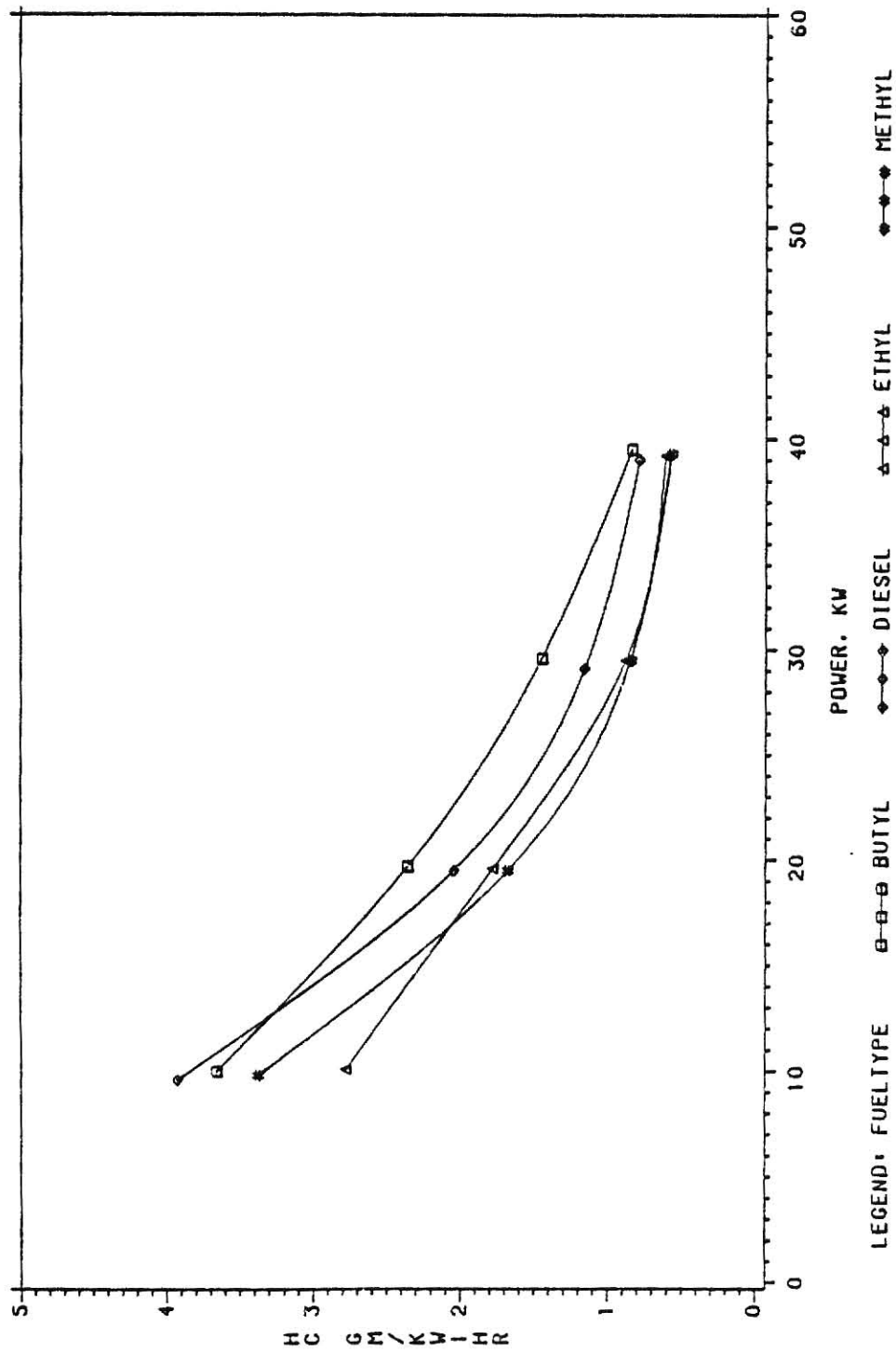


Figure 17. Hydrocarbon Emissions at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

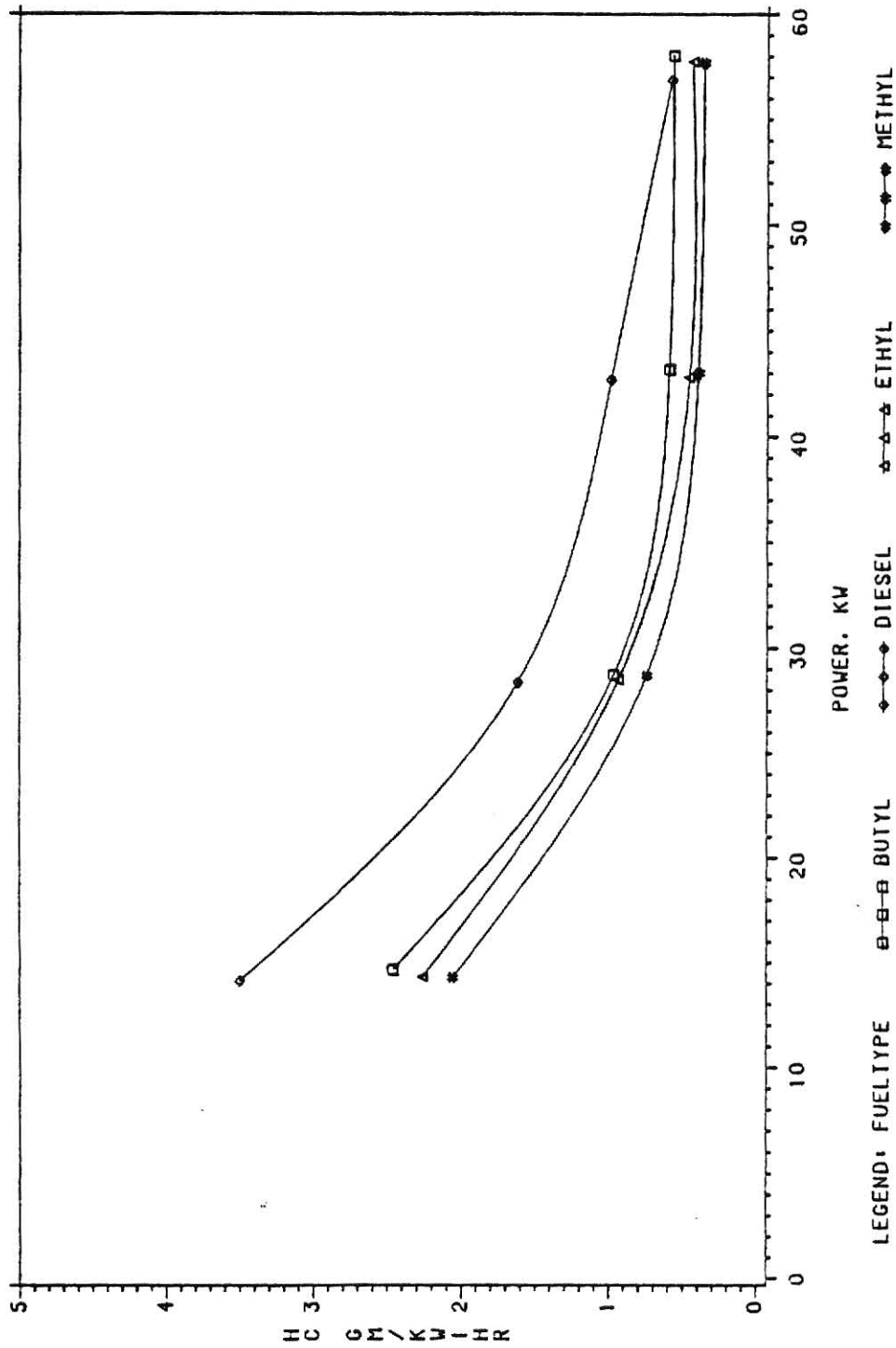


Figure 18. Hydrocarbon Emissions at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

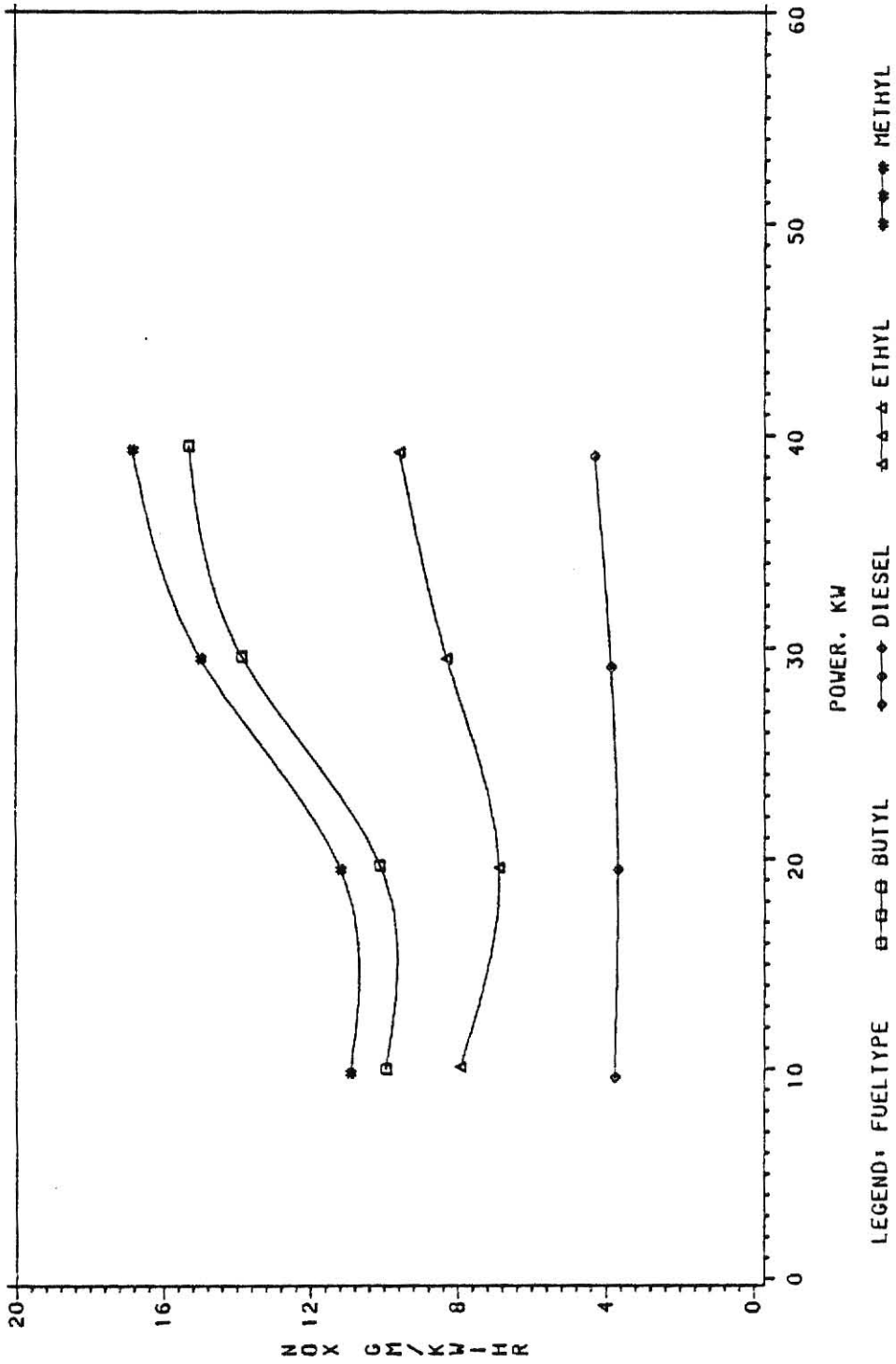


Figure 19. Nitrous Oxide Emissions at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

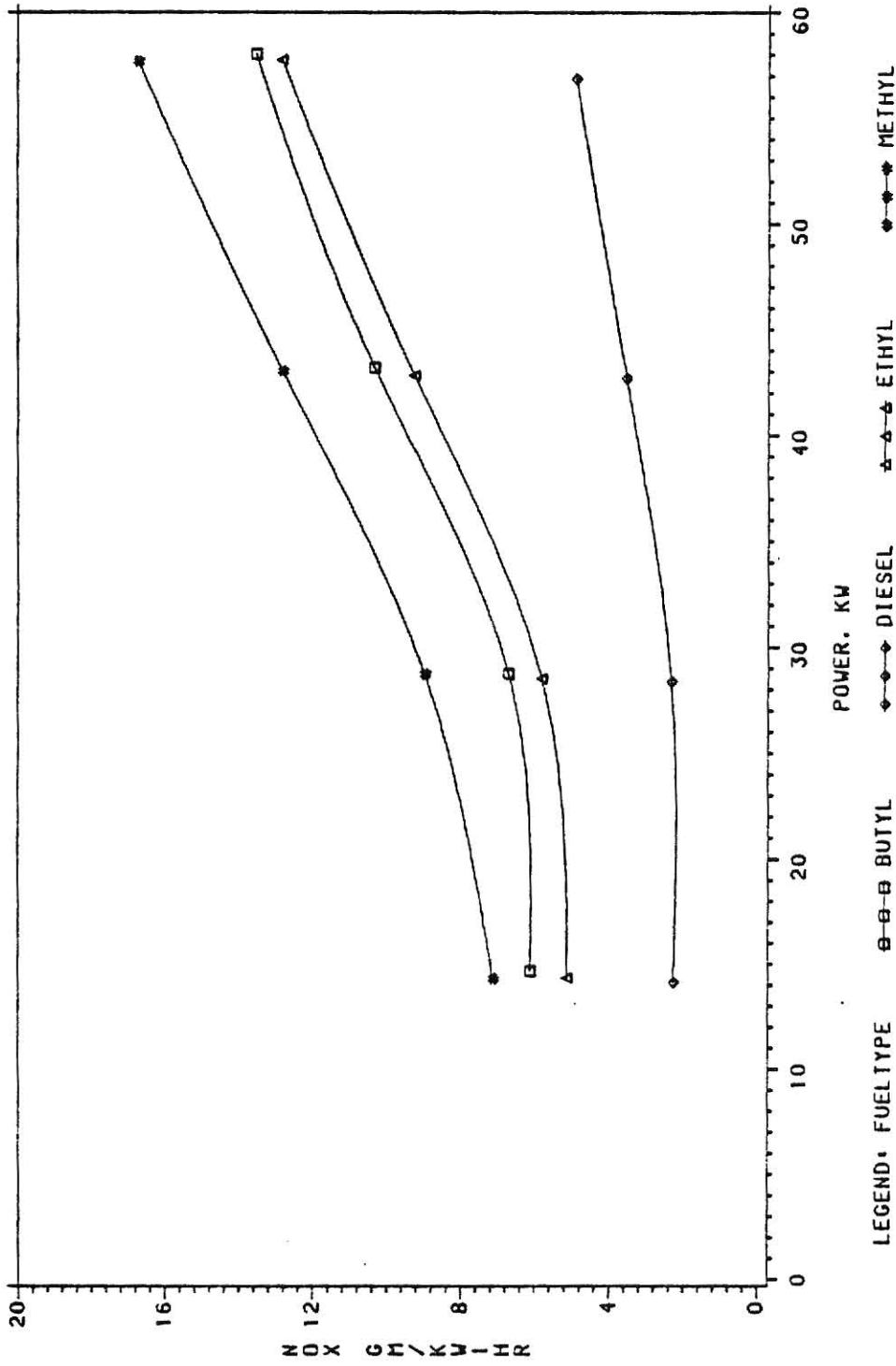


Figure 20. Nitrous Oxide Emissions at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

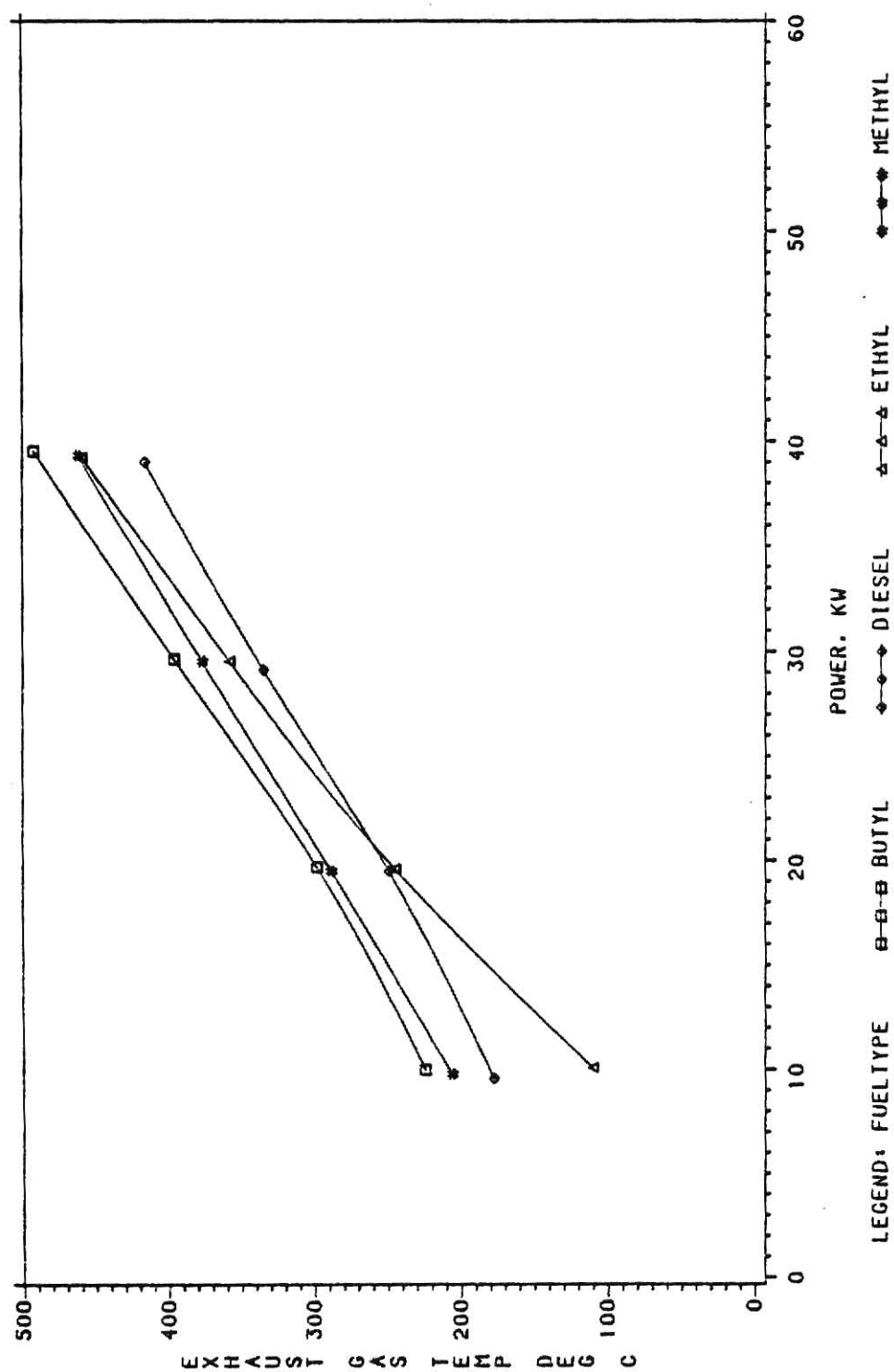


Figure 21. Exhaust Gas Temperature at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

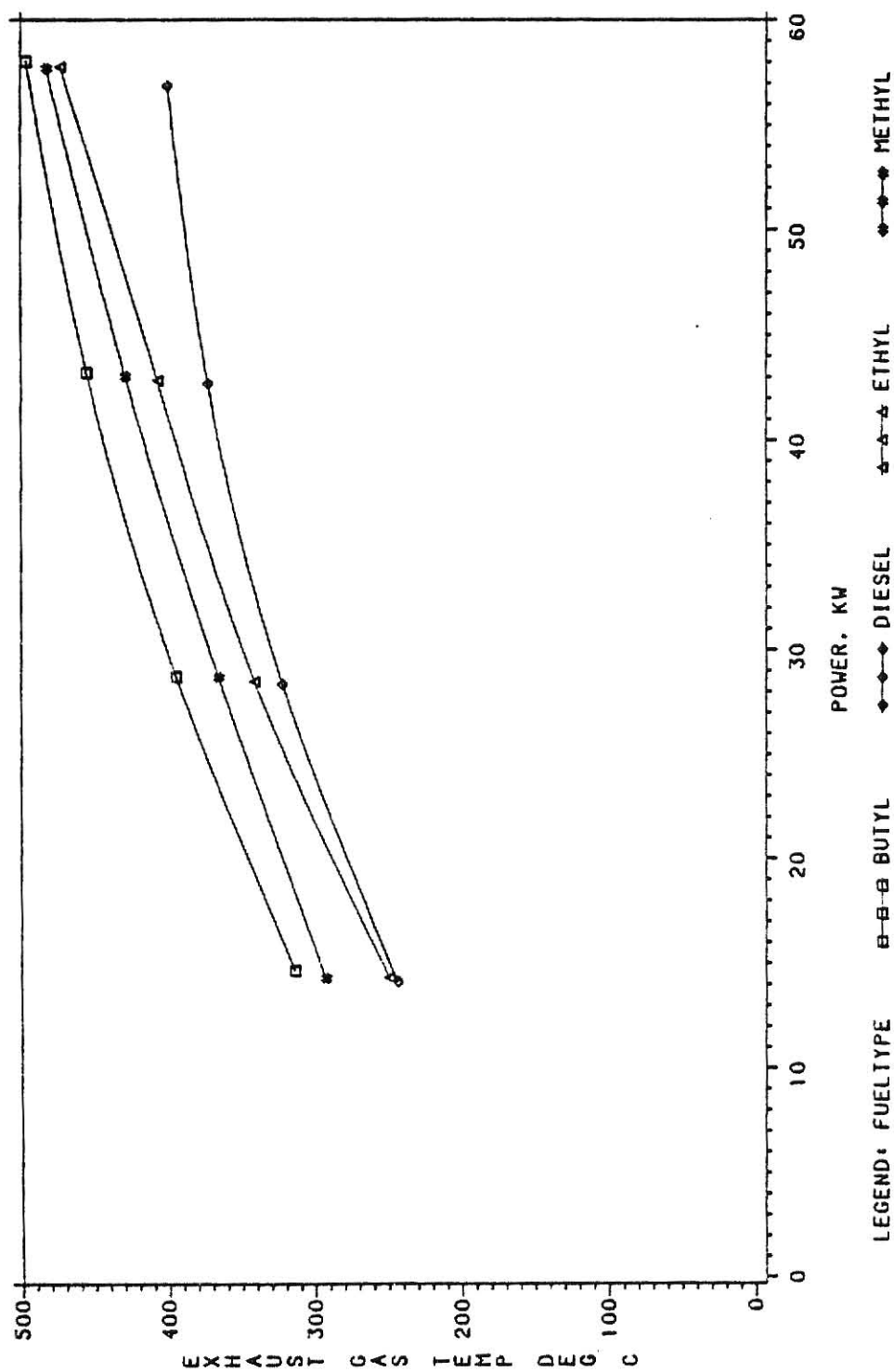


Figure 22. Exhaust Gas Temperature at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

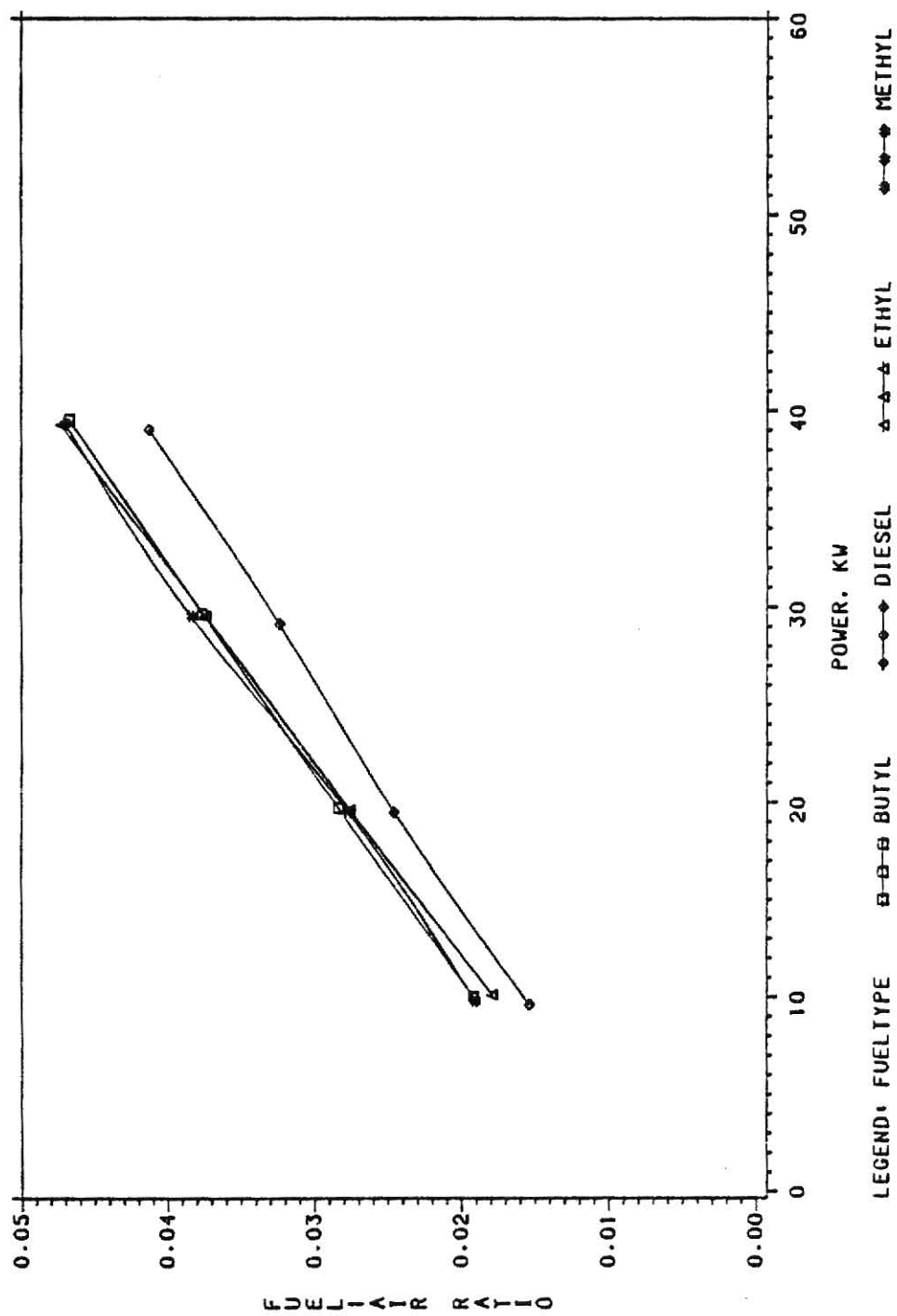


Figure 23. Fuel-Air Ratio at 1500 rpm for #2 Diesel Fuel and Soybean Oil Esters

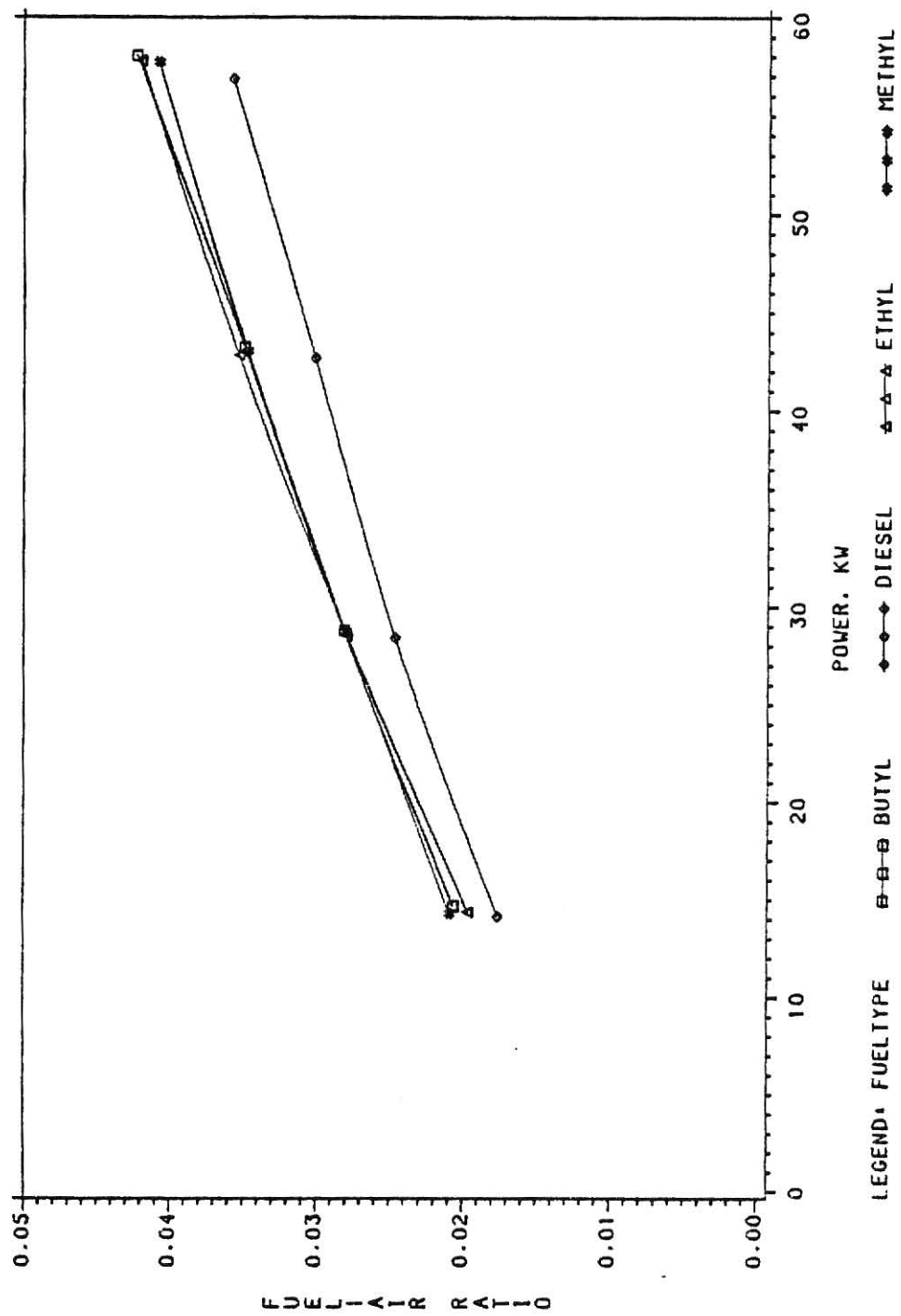


Figure 24. Fuel-Air Ratio at 2200 rpm for #2 Diesel Fuel and Soybean Oil Esters

METHYL, ETHYL, AND BUTYL SOYBEAN OIL ESTERS - ALTERNATIVE FUELS

FOR COMPRESSION IGNITION ENGINES

by

LARRY E. WAGNER

B.S., Kansas State University, 1982

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agricultural Engineering

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1983

Most farm equipment is powered by diesel fuel, making agriculture particularly vulnerable to petroleum fuel shortages. Fossil fuel shortages and rapidly rising prices in the last decade has sparked renewed interest in alternative fuels for internal combustion engines. Vegetable oils have primarily been the leading candidates for fuel extenders and/or replacements for diesel fueled compression ignition engines.

The primary problems involved with the use of vegetable oils, however, is their high viscosity. The process of transesterification of a vegetable oil with an alcohol significantly reduces the viscosity, which improves the fuel's suitability as a diesel fuel substitute without major engine modifications.

Complete ASTM fuel oil tests were conducted for #2 reference diesel fuel, and methyl, ethyl, and butyl esters of soybean oil to provide a comparison of the esters' physical properties to diesel fuel. A commercial diesel fuel additive package was used to improve some of the fuel properties of the esters. A gain in cetane number and a reduction in pour point temperature was achieved through the use of these additives. ASTM accelerated gum formation tests revealed very high values for all three ester fuels which indicate that the esters will have longterm storage problems. The gum formation is due to the oxidation of the unsaturated fatty acids.

Engine tests were performed on a direct injection, four cylinder, turbo-charged engine. The 200-hour test cycle was the alternative fuel screening test recommended by the Engine Manufacturers' Association. This test was ran for Phillips #2 reference diesel fuel and the ethyl, methyl, and butyl esters of soybean oil. Engine performance, exhaust emissions, lubricating oil deterioration, and engine wear and deposits were measured or monitored to com-

pare the ester fuels to diesel fuel as potential alternative compression ignition engine fuels.

A slight decrease in power and an increase in brake specific fuel consumption was observed for all the ester fuels. This was primarily due to the lower heating values of the ester fuels and increased fuel flow through the injection pump at the same rack setting. All three esters' exhaust emissions were similar to diesel fuel except the nitrous oxide emissions which were significantly higher for all the ester fuels.

The lubricating oil viscosity was monitored for all fuels at frequent intervals. The viscosity stabilized after 20 hours for the diesel fuel but continued to decline for each of the ester fuels, suggesting that more fuel dilution was taking place or that the fuel entering the crankcase was harsher on the lubricating oil. Wear metal levels from the oil analysis were normal for all four fuels indicating that no abnormal wear was occurring. This was confirmed when the engine was torn down and measured for wear following each test. Engine deposits were similar for the ethyl ester and diesel fuel except for differences in color. The methyl and butyl esters showed higher piston carbon deposits, especially in the first ring groove, than for the reference diesel fuel.

A problem encountered during the ester fuel tests was engine fuel filter plugging for the ethyl and methyl ester fuels. Filter plugging was not a problem with the butyl ester. Also inability to obtain a consistent low idle speed was experienced during the methyl and butyl ester engine tests.