combustion chamber. As previsously mentioned, Van der Walt and Hugo (7) found that cooler injection tips are less likely to foul.

REFERENCES

1. Barenescu, R.A. and J.J. Lusco, in Vegetable Oil Fuels–Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982, American Society of Agricultural Engineers Publication 4-82, ASAE, St. Joseph, MI, 1982, p. 312.
2. Goering, C.E., A.W. Schwab, R.M. Campion and E.H. Pryde, Ibid., p. 279.
3. Peterson, C.L., G.L. Wagner and D.L. Auld, Paper No. 81-3578 presented at the 1981 Winter Meeting of the American Society of Agricultural Engineers, Chicago, IL, ASAE, St. Joseph, MI, 1981.
4. Varde, K.S., in Vegetable Oil Fuels—Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982, American Society of Agricultural Engineers Publication 4-82, ASAE, St. Joseph, MI, 1982, p. 312.
5. Northern Agricultural Energy Center Notes for September, 1982, NAEC/NRRC, USDA, Peoria, IL, 1982.
6. Niejewski, M., and K.R. Kaufman, in Vegetable Oil Fuels—Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982, American Society of Agricultural Engineers Publication 4-82, ASAE, St. Joseph, MI, 1982, p. 354.
7. Van der Walt, A.N. and F.J.C. Hugo, Ibid. p. 230.
8. Goering, C.E., A.W. Schwab, M.J. Daugherty, E.H. Pryde and A.J. Heakin, ASAE Trans, 25:1472-1477, 1483 (1982).
9. Faletti, J.J., S.C. Sorenson and C.E. Goering, Paper No. 82-1548 presented at the 1982 Winter meeting of the American Society of Agricultural Engineers, Chicago, IL, ASAE, St. Joseph, MI, 1982.
10. Quick, G.R., B.T. Wilson and P.G. Woodmore, in Vegetable Oil Fuels–Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, Fargo, ND, 1982, American Society of Agricultural Engineers Publication 4-82, ASAE, St. Joseph, MI, 1982, p. 239.
11. Ziejewski, M.Z., K.R. Kaufman, and G.L. Pratt, in Vegetable Oil as Diesel Fuel—Seminar III, Peoria, IL, 1983, Proceedings ARM-NC-28, the Northern Agricultural Energy Center, NRRC/ARS, USDA, Peoria, IL 1983, p. 106.

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Methyl and Ethyl Soybean Esters as Renewable Fuels for Diesel Engines[1]

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ABSTRACT

The primary problems associated with using straight soybean oil as a fuel in a compression ignition internal combustion engine are caused by high fuel viscosity. Transesterification of soybean oil with an alcohol provides a significant reduction in viscosity, thereby enhancing the physical properties of the renewable fuel to improve engine performance. The ethyl and methyl esters of soybean oil with commercial diesel fuel additives revealed fuel properties that compared very well with diesel fuel, with the exception of gum formation, which manifested itself in problems with the plugging of fuel filters. Engine performance using soybean ester fuels differed little from engine performance with diesel fuel. A slight power loss combined with an increase in fuel consumption were experienced with the esters, primarily because of the lower heating value of the esters than for diesel fuel. Emissions for the 2 fuels were similar, with nitrous oxide emissions higher for the esters. Measurements of engine wear and fuel-injection system tests showed no abnormal characteristics for any of the fuels after the 200-hr tests. Engine deposits were comparable in amount, but slightly different in color and texture, with the methyl ester engine experiencing greater carbon and varnish deposits on the pistons.

INTRODUCTION

Modern, mechanized food production systems are particularly sensitive to energy shortages, as was demonstated in the early 1970's. Petroleum prices rose dramatically, increasing the farmer's cost of production because of diesel fuel and through nitrogen fertilizer and pesticides derived from fossil fuel. Stringent conservation practices eased the burden somewhat, but the fact remains that petroleum is not a renewable resource and recent predictions (1) are that world oil production could start to decline in the 1990's.

Research and engine testing on the use of vegetable oils date back to the 1930's. Most of the data reflects the findings that these oils are practical for use in diesel engines. Problems were encountered because of excessive carbon deposits and thickening of lubricating oil. The high viscosity of the vegetable oils was largely responsible for these problems. The availability of low cost petroleum meant that little was done to solve these difficulties.

Recently, renewed interest in vegetable oils led to the testing of sunflower-oil esters by Bruwer (2) as a fuel for diesel engines. The ester form of sunflower oil has fuel properties that compare far better with diesel fuel than does neat sunflower oil. The engine test results were very encouraging. Dynamometer tests revealed that after 100 hr of operation at 80% of maximum power, the ester fuels actually caused less injector tip fouling than diesel fuel and yielded higher brake thermal efficiencies and lower smoke values.

In light of the promising results obtained with sunflower-oil esters, a suitable basis existed for comprehensive tests involving soybean-oil esters. Soybean oil was chosen because it is a renewable resource with well established crop production practices. The oil extraction process itself yields a valuable, high-protein oilcake as the major product. Soybean plants also supply most of their own nitrogen through nitrogen fixation, reducing fertilizer energy inputs and contributing to a positive energy balance in producing soybean oil (3). Soybean oil esters exhibit fuel properties similar to diesel fuel.

The objectives of this investigation were (a) to determine how the physical properties of ethyl and methyl esters of soybean oil compare with a standard diesel fuel and (b) to perform prescribed medium-term tests on a direct injection, turbocharged diesel engine to determine how engine wear, oil deterioration, exhaust emissions and engine performance for a soybean oil ester-fueled engine compare with a standard diesel fueled engine.

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[1] Presented at the American Oil Chemists' Society meeting, Chicago, May 1983.

EXPERIMENTAL PROCEDURES

Fuel Properties

Transesterification is the process of producing a reaction in a triglyceride and an alcohol in the presence of a catalyst to produce glycerol and fatty acid esters. The molecular weight of a typical ester molecule is roughly 1/3 that of typical soybean-oil molecule and therefore has a much lower viscosity.

Because the viscosity of the fuel was of prime concern from its effect on injector nozzle spray patterns, extensive viscosity tests were done to determine how much the transesterification process affected viscosity. Using a temperature-controlled water bath and Ubbelohde-type viscometers, viscosity tests were performed that complied with ASTM D445, on #2 diesel fuel, soybean oil and the ethyl and methyl soybean-oil esters. The results are shown in Figure 1. A significant reduction in viscosity occurred. The viscosities of the esters are very close to diesel fuel.

The test fuels, #2 reference diesel fuel and soybean ethyl and methyl esters (trade names ethyl soyate and methyl soyate) were purchased from Phillips Petroleum and Emery Industries. Table I shows the fatty acid composition of degummed soybean oil and the ethyl and methyl esters of soybean oil. These values are typical for soybean oil but are known to be influenced by many conditions, e.g., climate, variety, soil type, etc. Other properties related to the esters are shown in Table II. These values are important to the long-term storage properties of the fuel and in how they affect engine performance (3).

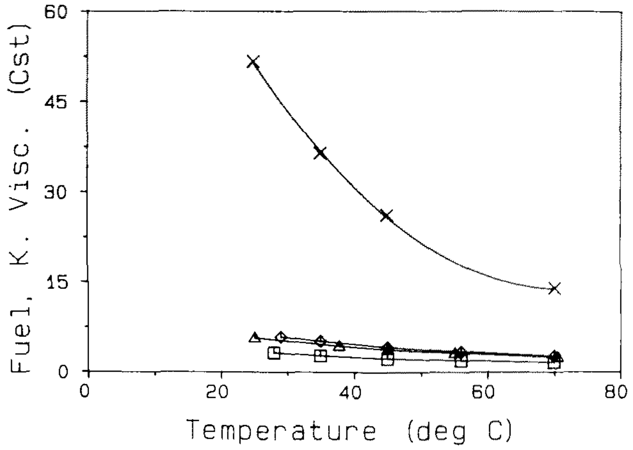

FIG. 1. Viscosity of soybean oil, soybean oil esters and diesel fuel in centistokes as a function of temperature, C. ⊞—⊞ Diesel, ◈—◈ ethyl, ▲—▲ methyl, ×—× soybean oil.

TABLE I

Fatty Acid Composition (molar %) of Raw Material and Ester Fuels

	Degummed Oil*	Ethyl	Methyl
C15	0.1	0.4	0.05
C16	10.76	10.0	9.6
C16:1	0.23	0.8	0.1
C17	0.17	–	–
ISO-C18	0.1	0.6	–
C18	4.13	5.7	4.5
C18:1	23.03	22.2	22.35
C18:2	52.67	51.2	54.35
C18:3	7.6	6.5	8.35
C20	0.33	–	0.3
C20:1	0.7	–	0.2
C22	0.07	0.2	–

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

TABLE II

Other Physical Properties of Ethyl and Methyl Soyate

Property	Value Ethyl	Value Methyl
Acid value (mg KOH/g)	<0.1	0.9
Moisture content (%)	0.073%	0.2
Appearance	clear	clear
Iodine number (cg I_2/g)	123.0	135.1
Saponification value (mg KOH/g)	182.8	190.8

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 Distillate 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 emulsification agent. The DII-3 provides a gain in diesel cetane number of ca. 5 for diesel fuels. The CFI-42 acts to depress the pour point. The following treatment rates were used: EDA-2: 0.02% by weight; DII-3: 0.1% by volume; CFI-42: 0.1% by weight. All these additives are currently being used in commercial diesel fuel.

Table III summarizes the results of complete ASTM fuel tests on #2 reference fuel oil, ethyl soyate, ethyl soyate with additives, methyl soyate and methyl soyate without additives. These tests were performed by the Petroleum Research Division of Farmland Industries, Kansas City, MO, with the exception of cetane number, which was done by Dresser Industries' Waukesha Engine Division in Waukesha, WI.

Both soyates had cetane numbers (ASTM D613) higher than that of the #2 diesel fuel with the esters containing additives significantly improved over the soyates without additives. ASTM D976 is an indirect measure of cetane number using the fuel's API gravity and midpoint distillation temperature. This indirect method of obtaining a cetane index gave values that were off-scale, indicating that this method is not a valid fuel test for the soybean-oil esters. This result was expected because 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, taking into account the different composition and properties of the soyates. The CFI-42 additive did lower the pour point for both soyates. A major cause for concern is the ASTM D2274 16-hr gum test. This test indicates that the soyates are much more susceptible to gum formation problems than diesel fuel, although the values presented here are far beyond the upper limits of the test.

Engine Test Equipment and Procedures

A John Deere 4239TF direct-injection, turbocharged diesel engine was used as the test engine. It is a 4-cylinder unit with a bore of 106 mm, a stroke of 110 mm, a displacement of 3.917 L and a compression ratio of 16.2:1. The engine was equipped with a Roosa Master model DM distributor-type pump and Roosa Master 9.5 mm (22044-AR88241) injection nozzles.

Before any startup, the engine was "blueprinted" by Farmland Industries' Petroleum Research Division at Kansas City, Missouri. Engine measurements were taken at critical wear points on the crankshaft journals, pistons, piston pins, valve guides and valve stems. Maximum cam-

TABLE III

ASTM Fuel Tests on #2 Fuel Oil, Ethyl Soyate, Ethyl Soyate with Additives, Methyl Soyate and Methyl Soyate with Additives

Test property	ASTM no.	# 2 Ref. diesel fuel	Ethyl soyate	Ethyl soyate with additives	Methyl soyate	Methyl soyate with additives
Viscosity @ 40 C (cSt)	D-445	2.39	4.41	4.40	4.08	4.14
Specific gravity @ 15.6 C	–	0.847	0.881	0.882	0.884	0.887
Higher heating value (MJ/kg)	D-240	45.2	40.0	40.0	39.8	39.9
Cetane no.[a]	D-613	45.8	48.2	49.0	46.2	48.7
Cetane index	D-976	46.0	—[b]	—[b]	—[b]	—[b]
Distillation 90% °C	D-86	296	344	351	342	347
Pour point (°C)	D-97	-23	-4	-7	-1	-4
Cloud point (°C)	D-2500	-19	1	-2	2	1
Flash point (°C)	D-93	78	160	157	141	135
H_2O and sediment (% vol)	D-1796	trace	trace	trace	trace	trace
Sulfur (% mass)	D-129	0.25	0.01	0.01	0.01	0.01
Corrosion	D-130	1-a	1-a	1-a	1-a	1-a
Ash (% mass)	D-482	0.025	0.01	0.01	<0.01	0.01
Gum no. (cg/1)	D-2274	6.0	19,200	18,400	16,400	15,500
Color ASTM color code	D-2274	L3.0	L1.0	L1.5	L.15	L1.5
Color ASTM color code	D-1500	L2.0	L2.0	L2.0	L2.0	L2.0

[a] Cetane no. ran by Waukesha, all others by Farmland Industries.
[b] Off scale.

shaft lobe height was measured as well as piston ring end gap in a standard liner. Rod bearing weights were also recorded. The fuel system injection pump was calibrated and injectors tested for leakage and chatter. The spray patterns were observed and the cracking pressure recorded.

The engine was reassembled using new gaskets, valve clearances were set and the injector pump statically timed. A 50-hr break-in period followed, using commercial diesel fuel with the engine running at various part-load conditions. The fuel screening engine tests consisted of 200 hr of operation on the particular test fuel according to the following Engine Manufacturers' Association recommended cycle (4): (a) 30 min at low idle; (b) 60 min at rated power; (c) 60 min at peak torque; (d) 30 min at 80% speed and 25% load. Five of the above cycles were run, then the engine was shut down until the following morning.

A 130 kW Midwest eddy current dynamometer equipped with constant speed or constant load modes of automatic control was used throughout the tests. Copper-constantan thermocouples measured oil, water, fuel (at the injector pump) and intake air temperatures, whereas the exhaust gas temperature was measured by an iron-constantan thermocouple. Air flow was measured by an ASME nozzle-plenum chamber configuration; the nozzle drop, turbocharger inlet, turbocharger boost and ambient pressures were measured by capacitance-type pressure transducers. Fuel consumption was measured by a load cell and engine speed by a gear tooth pulse counter.

An ADAC 1000 Series computer-based data acquistion system incorporating a DEC LSI 11/23 computer and DEC VT100 terminal was used to collect, process and store data online. A 12-bit resolution ADAC 1023AD analog-to-digital card collected analog voltages from the fuel scales, dynamometer and pressure transducers. Twelve-bit resolution ADAC 1113AD and 1113EX low-level analog-to-digital cards were also used to collect all the thermocouple voltages.

Lubricating oil viscosity was checked daily (Fig. 2) and samples were sent to Farmland Industries at 45 hr, 90 hr, 142 hr and 200 hr to monitor wear metal levels and oil deterioration. The sampling frequency was increased to every 15 hr for the ethyl and methyl soyates in order to have early warning of any malfunction. Exhaust gas emissions measurements including hydrocarbons, carbon monoxide, carbon dioxide, oxides of nitrogen and oxygen were made according to SAE J1003. At each mode, the emissions were recorded every 2 min for 10 min. The emissions could be analyzed as a composite for all 4 cylinders, or for each individual cylinder. This was done to facilitate the early detection of an injector malfunction. The instruments used for these measurements included: (a) Beckman 865 infrared CO analyzer; (b) Beckman 864 infrared CO2 analyzer; (c) Beckman 402 flame ionization HC analyzer, (d) Beckman 955 chemiluminescence NO_X analyzer; (e) Beckman OM-11 polarographic O_2 analyzer.

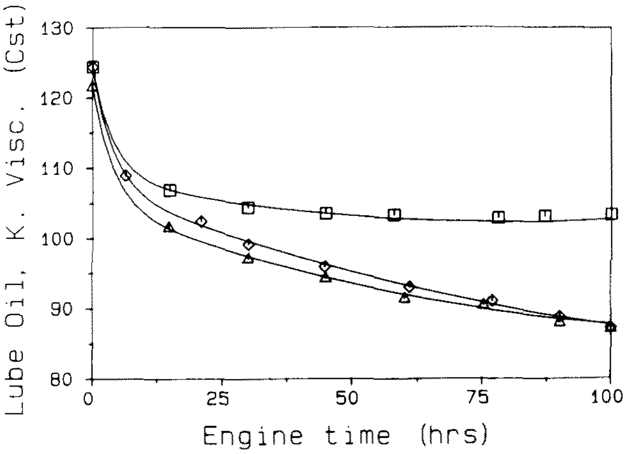

FIG. 2. Crankcase lubricating oil viscosity in centistokes as a function of accumulated engine time for soybean oil esters and diesel fuel. ⊞—⊞ Diesel, ◇—◇ ethyl, △—△ methyl.

Maximum power runs were done at the beginning, middle and end of each 200-hr cycle. After completion of the 200-hr baseline test with the reference fuel and each soyate, the engine was disassembled and evaluated for wear, carbon deposits, sludges and varnishes. To provide a comparison between the fuels, the engine was blueprinted using new sleeves, pistons, and bearings before beginning each subsequent test.

RESULTS

Engine Performance

The brake power output at full rack is shown in Figure 3. The maximum power for both fuels occurred at ca. 2500 rpm with the reference fuel producing a maximum power of 68.6 kW, compared with 65.8 kW for the ethyl soyate and 67.0 kW for the methyl. This represents a difference of 4.0% and 2.5% for the soyates. The difference in heating values between the soyates and the reference fuel is ca. 11% on a mass basis. Because the injection pump meters fuel on a volumetric basis, the denser soyates exhibited increased specific fuel consumption. This accounts for most of the discrepancy between heating value and power differences.

Figure 4 shows the torque output at full rack. At 1600 rpm, the reference fuel and the methyl soyate yielded torques of 315 Nm, whereas the ethyl soyate yielded 296 Nm at the same speed, a difference of ca. 6%. Brake specific fuel consumption, shown in Figure 5, was ca. 12% higher for the ethyl soyate and 10% higher for the methyl soyate over the 1500-2500 rpm range. The higher brake-specific fuel consumptions for the soyates are caused mainly by the lower heating values of these fuels compared with the diesel fuel thus more fuel is needed for the same amount of energy. This increased fuel flow for the soyates consequently provided higher fuel-air ratio values than the diesel fuel.

Little difference was found in thermal efficiency among the fuels. Not much difference occurred in exhaust gas temperature between the ethyl soyate and the reference fuel, but the methyl ester had a higher exhaust gas temperature than the diesel fuel.

In general, the soyate displayed engine performance characteristics that were very similar to diesel fuel. The small differences were mainly a result of the difference in heating values. The engine performed smoothly and exhibited no starting problems. No audible knock occurred, as predicted by the high cetane numbers reported for both soyates.

During the ethyl ester engine tests, fuel filter plugging occurred roughly every 50 hr. 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. We first suspected that gum formation took place after the fuel drum was opened to be used. After experiencing the same problem in the methyl ester tests, the fuel was filtered as it was removed from the barrel using a cannister filter. This procedure eliminated the plugging problem in the engine filter.

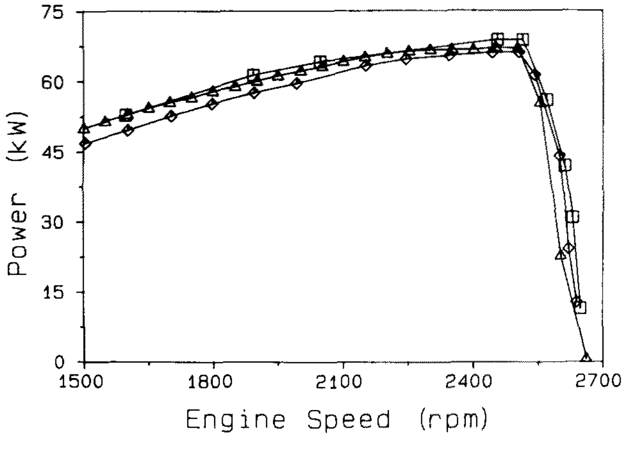

FIG. 3. Power, kW, vs speed for John Deere 4239TF engine at full rack for soybean oil esters and diesel fuel. □—□ Diesel, ◇—◇ ethyl, △—△ methyl.

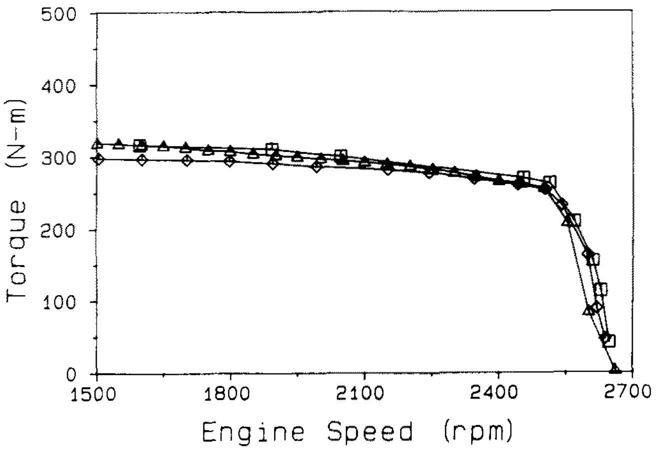

FIG. 4. Torque, N-m, vs speed for John Deere 4239TF engine at full rack for soybean esters and diesel fuel. □—□ Diesel, ◇—◇ ethyl, △—△ methyl.

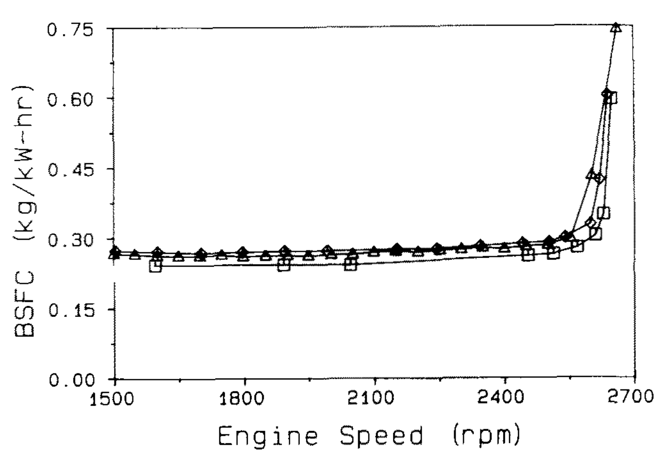

FIG. 5. Brake specific fuel consumption, kg/kW-hr, vs speed for John Deere 4239TF engine at full rack for soybean oil esters and diesel fuel. □—□ Diesel, ◇—◇ ethyl, △—△ methyl.

Emissions

Carbon monoxide emissions were extremely low. This is typical of diesel engines. No major difference was found between the CO values of the fuels. Although the curves produced show some trends, no conclusions can be drawn from the data because the instrument was operating at less than 5% of full scale. However, the CO levels for the soyates correspond to those found for cottonseed esters by Fort and Blumberg (5).

The soyates had slightly lower hydrocarbon levels than the reference fuel, with engine speed having little or no effect. The hydrocarbon emissions of the soyates at rated power again compared well with the findings of Fort and Blumberg (5). Because the intermediate products of combustion for the soyates are not known, some questions might be raised as to the applicability of the flame ionization method of hydrocarbon detection.

The nitrous oxides emissions for one engine speed are

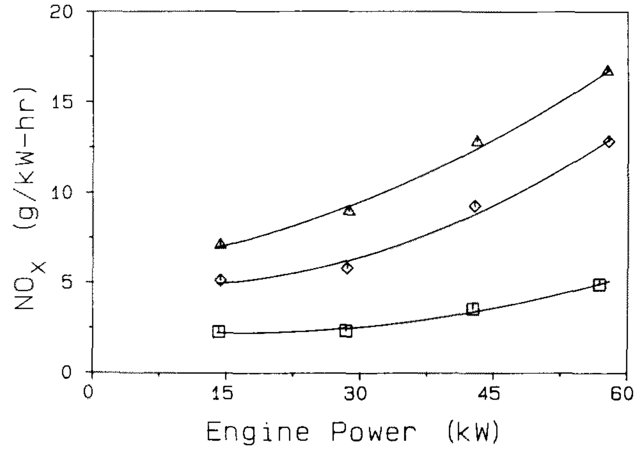

FIG. 6. Nitrous oxides emissions, g/kW-hr, vs power, kW, for John Deere 4239TF engine for soybean oil esters and diesel fuel at 2200 rpm. ⊞—⊞ Diesel, ◇—◇ ethyl, △—△ methyl.

shown in Figure 6. The methyl and ethyl soyates produced consistently higher levels of NO_x than the reference fuel. All fuels also had higher levels at a slower engine speed possibly caused by higher temperatures due to greater fuel-air ratios and longer residence times at the 1500 rpm setting. The reason for the difference in NO_x levels between the soyate fuels and the reference fuel is not apparent. The differences in exhaust gas temperature correspond with the differences in NO_x levels. However, exhaust gas temperature can be useful in explaining NO_x levels only if the 25-50 C temperature differences measured correspond to much higher combustion temperature differences. Combustion temperatures were not measured. The rated power NO_x level for the soyates was lower than the cottonseed ester value reported by Fort and Blumberg (5).

Engine Wear and Deposits

Engine wear was monitored by analyzing the lubricating oil for wear-metal levels. In Table IV the levels of the most important metals are shown for the test fuels. Wear-metal levels for the soyate fuels were considered to be normal throughout the 200-hr test. Initially high levels of lead were of some concern, suggesting that abnormally high wear was taking place on the bearings. Following the oil change at 100 hr however, the lead concentration returned to normal. A slightly different alloy may have been used on the surfaces of the replacement bearings, containing a higher percentage of lead.

The lubricating oil viscosity, monitored over the 100-hr oil-change interval, is shown in Figure 2. For all the fuels, the shearing forces acting on the oil caused an initial rapid drop in viscosity during the first 10-20 hours. In the case of the reference fuel, the viscosity then stabilized at ca. 103 cSt. For the ethyl and methyl soyates however, the viscosity continued to drop for the entire 100-hr, suggesting that more oil dilution was taking place. This could eventually lead to oil thickening as the antioxidant additives in the oil become depleted. However, this did not happen during the normal 100-hr oil service interval.

With the manufacturer's recommended oil change interval, no problems with oil polymerization should occur, at least not on a short-term basis. In the long run, deposits might increase to the point where combustion of the ester fuel will deteriorate, resulting in more unburned fuel in the cylinder. This will accelerate oil dilution, so that the oil change interval may need to be shortened. In a worn engine, more blow-by will occur, accelerating the oil dilution process.

Conclusive evidence of engine wear can only be established by physically measuring the various parts. The measurements and inspection show that no notable differences occurred among the fuels. No wear was measureable on the cylinder walls (liners) and pistons, and no rings were stuck. In all cases, the original honing marks in the liners were still clearly visible, as were the machining marks on the pistons. Gap increases on all rings (first, second and oil control) were satisfactory and wear on the wrist pin was nil. The rod and main bearings were weighed for loss of material and showed normal wear as did the camshaft lobes. Valve lifters, valve stem caps and valve seats were in good condition, and no wear was measured on the intake and exhaust valve stems. The valve stems had faint polishing marks on them, with the valve seat interference angle just starting to show. Bearing discolorization was only evident on the thrust side of the bearing.

CRC (6) engine deposit ratings for the test fuels are summarized in Table V. The CRC Weighted Total Demerits (WTD) deposit rating for pistons uses a comparison scale where the greater the score, the more severe the deposits. The CRC WTD for a piston is rated according to amount and type of deposits as well as the location of the deposits on the piston. The CRC sludge and varnish deposit rating and valve ratings use a scale of 0-10 with a score of 10 equal to a new part. Deposits for the ethyl soyate appeared to be the same as for diesel, with the exception of the color of the exhaust valve deposits. These deposits were light brown in the ethyl soyate, compared with black in the diesel tests. The ethyl ester carbon deposits were relatively dry and soft, except around the injector bodies, where gum-

TABLE IV

Engine Oil Wear Metal Analysis, ppm

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
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
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

TABLE V

Engine Inspection of John Deere 4239TF Engine for Carbon and Laquer Deposits

	Diesel	Ethyl	Methyl
Pistons deposit rating CRC-weighted total demerits (WTD)[a]			
% Top groove fill	0.0	0.0	17.5
2nd groove, % carbon fill	0.0	0.0	0.0
Oil groove & cover	100% clean	100% clean	33.8% clean 66.2% very light amber laquer
Top land % med. carbon	7.0	0.0	0.0
2nd land % carbon + black laq.	0.0	0.0	0.0
Wtd. total demerits (grooves)	42.4	45.3	56.6
Wtd. total demerits (lands)	4.8	5.2	7.8
Total piston WTD (avg.)	47.2	50.5	64.4
Sludge CRC Rating[a]			
Rocker arm cover	9.5	9.5	9.6
Valve deck	9.5	9.6	9.5
Oil pan	9.2	9.2	9.5
Timing gear cover	9.5	9.5	9.6
Rocker arms	9.5	9.5	9.6
Average sludge	9.44	9.44	9.58
Total sludge	47.2	47.2	47.9
Varnish CRC rating[a]	9.9		
Rocker arm cover	9.9	9.9	9.9
Rocker arm assy.	9.9	9.9	9.9
Piston skirt	10.0	10.0	10.0
Cylinder walls	9.9	9.9	9.9
Push rods	9.9	9.9	9.9
Lifter bodies	9.9	9.9	9.9
Oil pan	9.8	9.8	9.8
Average varnish	9.9	9.9	9.9
Total varnish	69.3	69.3	69.3
Valves CRC rating			
Exhaust valves	9.0	9.5	9.2
Intake valves	7.2	8.4	7.8

[a] Piston weighted demerits deposit rating increases with increased deposits whereas other CRC ratings decrease with increased deposits.

like deposits made removing the injectors more difficult. This was not the case for the methyl ester. However, piston deposits were significantly greater for the methyl ester.

The injector tips were as free of deposits as in the diesel test for both soyate fuels. No obstructed orifices were found and the spray patterns were unaffected. Cracking pressures declined by an average of ca. 600 kPa for the ethyl soyate opposed to ca. 1400 kPa for the reference fuel test and ca. 1000 pKa for the methyl soyate. The lower cracking pressure decrease was not an abnormal condition, as injectors tend to wear less rapidly as hours are accumulated (injectors were not replaced after the 200-hr diesel fuel baseline test). The injector pump calibration was checked before the diesel test and after the ethyl soyate test. The pump delivery did not change significantly, indicating that no abnormal wear had taken place.

DISCUSSION

The ASTM standard tests for diesel fuel provide significant insight into the potential of a candidate compression-ignition fuel and provide suitable screening of prospective fuels. The relationship between fuel properties and engine performance makes good quality control in the ester fuel preparation mandatory. In the on-farm situation, suitable procedure and quality standards would be necessary. The ASTM tests indicated high cetane numbers for the esters compared with those normally associated with diesel fuels, helping to eliminate engine knock and ensuring smooth engine operation. The pour point improver provided a significant drop in both of the esters' pour points, meriting further experimentation with different treatment rates for added improvement. The high flash points of the esters make them safer to handle than diesel fuel. The rate of gum formation under the conditions of the ASTM D2274 test, however, is undesirable from the standpoint of possible fuel filter clogging and long-term fuel storage.

Engine performance for the soybean esters does not differ greatly from that of diesel fuel. A slight power loss, combined with an increase in fuel consumption, was experienced with the esters. We attributed this mainly to the lower heating value of the esters. However, in times of fuel scarcity diesel fuel-ester blends could certainly be used.

Emissions for the 3 fuels were essentially similar, with carbon monoxide too low to provide reliable data. Hydrocarbons for the esters were slightly lower than for diesel whereas nitrous oxide emissions are significantly higher for the esters. Not enough is known about the combustion kinetics of esters to draw significant conclusions from these facts. Measurements of engine wear for the 3 fuels were found to be normal after the 200-hr tests with tests on injection equipment showing no differences between the 3 fuels. Deposits were comparable in amount, but slightly different in color and texture, with the methyl ester engine experiencing greater piston carbon deposits.

The ethyl and methyl esters could be used as alternative fuels on a short term basis, provided certain fuel quality standards are met, although the gum problem needs to be solved to eliminate the nuisance of fuel filter plugging and problems relating to storage.

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REFERENCES

1. Energy Information Administration, Projection of Energy Supply and Demand and Their Impacts, Annual Report to Congress, Vol. II, Executive Summary, Department of Energy/EIA-0036/2, Washington, DC, 1977.
2. Bruwer, J.J., B.v.D. Boshoff, F.J.C. Hugo, J. Fuls, C. Hawkins, A.N.v.d. Walt, A. Engelbrecht and L.M. du Plessis, in Agricultural Energy, Vol. 2, Biomass Energy/Crop Production, ASAE Publication 4-81, American Society of Agricultural Engineers, St. Joseph, MI, 1981, pp. 385-390.
3. Kaufman, K.R., in Fuels and Chemicals from Oilseeds: Technology and Policy Options, edited by E.B. Shulz, Jr., and R.P. Morgan, Westview Press/AAAS Selected Symposium Series Volume, Boulder, CO, 1983, chapt. 8.
4. Alternate Fuel Council, Engine Manufacturers Association 200-Hour Screening Test for Alternate Fuels in Energy Notes for September 1, 1982, Northern Agricultural Energy Center/Northern Regional Research Center, ARS/USDA, Peoria, IL.
5. Fort E.F., and P.N. Blumberg, in Vegetable Oil Fuels, Proceedings of the International Conference on Plant and Vegetable Oils as Fuels, August, 1982, Fargo, ND, ASAE Publication 4-82, American Society of Agricultural Engineers, St. Joseph, MI, 1982, pp. 374-383.
6. Diesel Vehicle Fuel, Lubricant, and Equipment Research Committee, Diesel Engine Rating Manual, Coordinating Research Committee (CRC), Inc., New York, NY, 1959.

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Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils[1]

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ABSTRACT

Transesterification reaction variables that affect yield and purity of the product esters from cottonseed, peanut, soybean and sunflower oils include molar ratio of alcohol to vegetable oil, type of catalyst (alkaline vs acidic), temperature and degree of refinement of the vegetable oil. With alkaline catalysts (either sodium hydroxide or methoxide), temperatures of 60 C or higher, molar ratios of at least 6 to 1 and with fully refined oils, conversion to methyl, ethyl and butyl esters was essentially complete in 1 hr. At moderate temperatures (32 C), vegetable oils were 99% transesterified in ca. 4 hr with an alkaline catalyst. Transesterification by acid catalysis was much slower than by alkali catalysis. Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils.

INTRODUCTION

Fatty esters from vegetable oils have shown promise as alternative diesel fuels as a result of improved viscosity and volatility relative to the triglyceride (1-3) and this has stimulated interest in optimization of transesterification reaction conditions (4-7). Transesterification (also called alcoholysis) has been studied intensively by numerous investigators (8-12). Of the more than a dozen US patents on transesterification, the patent of Bradshaw and Meuly (13) is cited frequently.

Our objectives were to develop basic information concerning the transesterification reaction of crude and refined oils to resolve inconsistencies in the literature, such as molar ratios, and to delineate optimum reaction conditions for maximum conversion to fatty esters with both alkali- and acid-catalyzed reactions. The effects of such variables were evaluated quantitatively with an Iatroscan TLC/FID (thin layer chromatography/flame ionization detector) analyzer not available to earlier investigators.

EXPERIMENTAL PROCEDURES

Materials

All refined vegetable oils were edible grade. Refined soybean oil was obtained from Central Soya, Chattanooga, Tennessee; sunflower oil from PVO International Inc., Richmond, California; peanut oil from Hain Pure Food Co., Los Angeles, California. Crude vegetable oils were obtained from the following sources: soybean and safflower oil from Arrowhead Mills, Inc., Hereford, Texas; peanut oil from Birdsong Corp., Suffolk, Virginia; cottonseed oil from Texas A&M University; sunflower oil from North Dakota State University.

The crude oils were processed by mechanical pressing, were not further refined and contained sediment but no added preservatives. They were used as received; uniform samples were obtained by thorough mixing of oil and any solids present. The edible-grade oils were degummed, alkali-refined, bleached, filtered and deodorized.

Sodium methoxide, as an anhydrous powder, was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, sodium hydroxide (ACS grade) from J.T. Baker Co., Phillipsburg, New Jersey; concentrated sulfuric acid from Mallinckrodt, Inc., St. Louis, Missouri). Methanol and butanol were MCB Omnisolv (spectrograde) and were stored over molecular sieves 4A. Ethanol was distilled before use and stored over molecular sieves 4A.

Transesterification Reaction Procedures

A 100 mL 3-necked flask equipped with mechanical stirrer, thermometer and condenser (to which a drying tube was attached) was heated to expel moisture. On cooling, 60 g (0.0682 mol, assuming a molecular weight of 879.5 for sunflower oil) edible-grade sunflower oil was added to the flask, followed by 16.572 mL (13.115g, 0.4093 mol) methanol. The mixture was stirred and heated in a silicone oil bath to 60 C, at which point 0.3 g sodium methoxide (0.5%, by weight of oil) was added rapidly. The temperature rose to 63.3 C in 1 min, and the reaction mixture become less turbid. Heating continued for 1 hr at 60-63 C, at which point the reaction was 98% completed as determined by Iatroscan analysis. After the reaction mixture was allowed to cool to room temperature, the ester and glycerol layers were separated in a separatory funnel. Excess methanol in the ester layer was removed on a rotary evaporator at reduced pressure or by distillation at atmospheric pressure. The ester was purified further by dissolving in

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