step. However, longer tests of 40 hr (11) indicated that much more rapid fouling of the lubricating oil occurs with these fuels and their use is not recommended at this time. Crude sunflower and cottonseed oils are definitely undesirable as alternative diesel fuels.

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☆ Efficiencies of Various Esters of Fatty Acids as Diesel Fuels

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ABSTRACT

Methyl esters of commercial grades of lauric, myristic, palmitic, stearic, linoleic and linolenic acids, as well as ethyl and butyl esters of oleic acid, were burned in a diesel engine to determine their efficiencies as fuels. Triolein and some common vegetable oils were burned as comparison fuels and No. 2 diesel fuel was used as a control. The fuels were tested in a single-cylinder direct-injection engine running at rated speed and load in short-term, performance engine tests. Specific fuel consumption and thermal efficiencies of the engine burning these fuels were then determined. Among the methyl esters of the saturated acids, thermal efficiency was inversely related to chain length of the fatty acid. Introduction of a double bond resulted in increased efficiency. Further increases in unsaturation had negligible effects on thermal efficiencies. Ethyl oleate had the highest thermal efficiency and butyl oleate had the lowest thermal efficiency of any of the ester fuels tested. Most of the ester fuels produced higher thermal efficiencies than did No. 2 diesel fuel. Triolein produced the lowest specific fuel consumption of the triglyceride fuels and peanut oil produced the lowest specific fuel consumption of the vegetable oils. The data suggest that ethyl esters of monounsaturated or short-chain fatty acids should make good alternative fuels and that they should be further evaluated in long-term engine tests.

INTRODUCTION

With the gradual depletion of the world petroleum supplies, provisions must be made for the continuation of energy sources for mechanized agriculture, most of which is powered by diesel engines. Vegetable oils are attracting considerable attention as diesel fuel extenders or substitutes either in the form of the triglycerides or transesterified with various monohydric alcohols. Most vegetable oils contain a common set of fatty acids (saturated fatty acids, 12-18 carbons), along with oleic, linoleic and sometimes linolenic acids, although the proportions of the individual acids may vary considerably from one oil to the next. Some oils contain characteristically high concentrations of less common fatty acids, for example, erucic acid in rapeseed oil and ricinoleic acid in castor oil. We undertook our study to determine whether the esters of any of these common fatty acids are especially desirable as diesel fuels.

PROCEDURE

Practical grades of saturated fatty acids from 12 to 18

carbons plus linoleic and linolenic acids were purchased from Eastman Kodak (Rochester, NY). Oleic acid was purchased from Fisher Scientific (Fairtown, NJ). Salad grade vegetable oils were purchased from local groceries. Linseed oil (raw) was obtained from a local lumber yard and cottonseed and castor oil were purchased from Eastman Kodak.

Esters of the fatty acids were prepared by refluxing overnight with a 4-fold molar excess of the alcohol containing 2% H_2SO_4 as catalyst. Esters were recovered by extraction with petroleum ether and water. The ether extracts were extensively washed with water and 5% $NaHCO_3$, dried over anhydrous Na_2SO_4 and the ether removed under vacuum on a rotary evaporator in a 50 C water bath. Fatty acid composition was determined by gas liquid chromatography on a Hewlett-Packard 5880A with columns packed with 10% DEGS on 100-120 mesh Chromosorb W.

The test engine was a Fairbanks-Morse model 45B-81 single-cylinder, direct-injection diesel rated at 5.25 hp at 1800 rpm, driving an electric dynamometer and running at rate load. Volumetric fuel consumptions were measured for each fuel by measuring the time required to burn 100 mL of fuel. At least four replicate readings were taken for each fuel. Volumetric fuel consumptions were converted to weight fuel consumptions using the densities, taken from literature data (1) or determined in the laboratory, of the individual esters at the test temperatures. Specific fuel consumptions in terms of grams per horsepower-hour (g/hp hr) were then calculated. Heats of combustion of the fatty acid esters were determined by bomb calorimetry using an Emerson calorimeter. Thermal efficiencies for the ester fuels in the engine were calculated by dividing the heat equivalent of the work produced by the engine by the heat of combustion of the fuel required to perform that work.

RESULTS AND DISCUSSION

The fatty acid compositions of all of the fuels used are listed in Table I. The saturated fatty acids ranged in purity from over 99% for 12:0 to less then 93% for 18:0. The unsaturated acids were less pure, ranging from 75% for 18:1 to less than 50% for 18:3. The fatty acid compositions determined for the vegetable oils were consistent with published compositions (2).

The engine ran well on all of the fuels tested except for

TABLE I

Fatty Acid Composition of Fuels

Fuels	12:0	14:0	16:0	16:1	17:0	18:0	18:1	18:2	18:3	22:0
Methyl laurate	99.54	0.46	—	—	—	—	—	—	—	-
Methyl myristate	0.63	94.84	2.94	—	—	—	—	—	—	---
Methyl palmitate	—	0.59	94.60	—	—	1.71	5.33	—	—	-
Methyl stearate	—	0.06	3.65	—	1.46	92.83	0.55	—	—	1.42
Methyl oleate	—	2.00	2.71	6.80	—	0.55	75.33	7.87	1.51	—
Methyl linoleate	—	—	0.25	—	—	0.76	32.44	55.36	6.79	-
Methyl linolenate	—	—	6.16	—	—	6.07	20.88	17.88	49.15	-
Corn oil	—	—	11.15	—	—	1.20	24.66	61.74	1.24	-
Cottonseed	—	0.74	22.18	—	—	0.97	18.68	57.39	—	---
Linseed oil	—	—	2.57	—	—	1.29	17.68	19.78	58.68	--
Peanut oil	—	—	11.29	—	—	—	50.00	32.30	—	1.75
Safflower oil	—	—	6.51	—	—	1.08	10.06	82.29	—	-
Soybean oil	—	—	10.89	—	—	2.89	24.03	54.38	7.81	-
Sunflower oil	—	0.04	6.63	—	—	2.81	18.72	70.77	—	—
Triolein	0.72	0.39	6.34	—	—	1.93	75.11	14.36	—	—

castor oil, on which the engine quit. This was probably due to the extremely high viscosity of castor oil. Although cold starting tests were not made for all of the fuels, it was observed by chance that the engine would not start on linseed oil, although it ran well on this fuel after a warm-up on No. 2 diesel fuel. The tests were not of long enough duration for any observable effects on the injector or lubricating oil to develop.

The heats of combustion for the fatty acid esters and No. 2 diesel fuel are shown in Table II. Among the saturated series, the heat of combustion per gram increased with chain length, reflecting their higher proportion of reduced carbon. For the same reason, the esters of the unsaturated acids had somewhat lower heats of combustion than the corresponding saturate. The heats obtained agree well with the general value of 9 kcal/g for lipids (3). Diesel fuel has a higher heat content than the fatty acid esters. Our value was slightly lower than the values of 10.79-10.94 reported by others (4-7).

The fuel consumption data are shown in Table III for the fatty acid esters and in Table IV for the triglycerides. For the series of saturated esters, the volumetric fuel consumption is seen to increase with increasing chain length. This might be expected in view of the inverse relationship which exists between density and chain length for fatty acid esters at temperatures near room temperature (1). Similarly, the decreased volumetric consumptions observed for methyl oleate, linoleate are partially accounted for by increases in density with increased unsaturation. The specific fuel consumptions of the methyl esters of the unsaturated acids are nearly identical. However, the specific fuel consumptions for the esters of the saturated acids increase with chain length. The ethyl ester of oleic acid was consumed at

TABLE II

Heats of Combustion of Fatty Acid Esters

Ester	Heat of combustion (kcal/g)
Methyl laurate	8.842 ± 0.04
Methyl myristate	9.161 ± 0.03
Methyl palmitate	9.451 ± 0.002
Methyl stearate	9.615 ± 0.003
Methyl oleate	9.295 ± 0.0002
Ethyl oleate	9.216 ± 0.009
Butyl oleate	9.647 ± 0.0
Methyl linoleate	9.254 ± 0.090
Methyl linolenate	9.530 ± 0.013

TABLE III

Fuel Consumption and Thermal Efficiencies of Ester Fuels in a Diesel Engine

No. 2 Diesel	mL/hp hr	g/hp hr	Efficiency (%)
No. 2 Diesel	330	280	21.7
ME 12:0	345	298	24.4
ME 14:0	350	302	23.3
ME 16:0	382	321	21.1
ME 18:0	386	322	20.8
ME 18:1	343	297	23.3
ET 18:1	325	281	24.8
BU 18:1	378	328	20.3
ME 18:2	341	299	23.2
ME 18:3	336	298	22.7

TABLE IV

Fuel Consumption of Triglyceride Fuels in a Diesel Engine

Triglyceride fuels	mL/hp hr	g/hp hr
Corn oil	358	330
Cottonseed	366	335
Linseed	374	348
Peanut	347	317
Safflower	355	327
Soybean	374	341
Sunflower	368	336
Triolein	306	278

a lower rate than the methyl ester, whereas the butyl ester was consumed at a greater rate. We do not have comparable data for any other acid.

The fuel consumption data for the triglycerides (Table IV) show triolein to be consumed at the lowest rate, followed by peanut oil. Ryan (8) found that peanut oil mixed with diesel fuel was consumed at lower rates than similar mixtures of cottonseed oil and diesel fuel. It is interesting to note that, of the vegetable oils tested, peanut oil had the highest content of oleic acid (Table I). No particular pattern could be detected among the other oils.

The thermal efficiencies of the ester fuels are shown in Table III and Figure 1. Figure 1 shows the relationship between carbon chain length of the saturated fatty acids and thermal efficiency. Although the energy content of
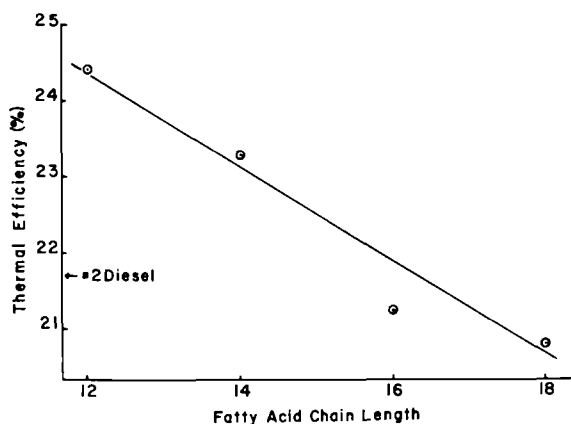
FIG. 1. Effect of fatty acid chain length of methyl esters on thermal efficiency as fuels for a diesel engine. Thermal efficiencies were calculated from fuel consumption data shown in Table III and heats of combustion shown in Table II and plotted against chain lengths of the methyl esters as a linear regression line. The line has a correlation coefficient of -0.97. Thermal efficiency of No. 2 diesel fuel is shown as an arrow for reference.

the esters increases with chain length, the increased specific fuel consumption with increasing chain length produces a marked linear decrease in thermal efficiency. The reasons for this are not known. The thermal efficiency does not vary greatly among the methyl esters of the 18-carbon unsaturated acids (Table III). Ethanol used to esterify fatty acid appears to provide marginally higher efficiency than when methanol is used and substantially higher efficiency than when butanol is used for esterification. All of the esters except methyl palmitate, methyl stearate and butyl oleate produced higher thermal efficiencies than did No. 2 diesel fuel.

These data suggest that a vegetable oil having a rather high content of oleic acid or short-chained saturated acids, transesterified to produce ethyl esters, should produce a good test material as an alternative diesel fuel.

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☘ Conversion of Used Frying Oil to Diesel Fuel by Transesterification: Preliminary Tests

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ABSTRACT

Used frying oil was transesterified by reaction with excess alcohol under both acidic and basic conditions. The alcohols used were: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-ethoxyethanol. Yields of the fuels determined by gas chromatography and their viscosities are reported. The best result was obtained using methanol with catalysis by potassium hydroxide. The methyl ethyl and 1-butyl esters all ran very well in short-term engine tests with a laboratory high-speed diesel engine.

INTRODUCTION

Two areas of concern to man are pollution control and the discovery of renewable energy sources. The conversion of used frying oil to diesel fuel combines both these items.

During times of acute energy shortage, such as during World War II in Europe and at present in Brazil, vegetable oils have been used as diesel fuel, either neat or in blends with diesel oil (1-4). However, the fuels give rise to excessive carbonaceous deposits in the cylinders and on injector nozzles and put extra strain on fuel filters and pumps (5). These problems largely arise from the high viscosity of the oils, and one way of tackling the problem is to reduce the viscosity of the fuel, which can be done either by adding viscosity depressants (6) or by chemical modification of the fuel. The latter is simply done by transesterification of the triglyceride. Interest in this process was rekindled in 1980 in South Africa when methyl ester fuel was produced from sunflower oil and shown to be an effective diesel fuel (4). Since then, a number of groups over the world have been studying ester fuel (7) with most attention being paid to methyl and ethyl esters.

The purpose of the present study was to find out which alcohol is best for the convenient transesterification of used frying oil from the several cafeterias at the University of Guelph. The two main types of oil used on campus are partially hydrogenated soybean oil (semiliquid) and margarine (solid). Consequently, the oil varies enormously in consistency when collected. However, all of it is combined in 45-gallon drums to yield a fairly uniform mixture of liquid and solid, which slowly settles at 25 C. For this study, a sample of fairly high consistency from the bottom of the drum was selected on the premise that, if esters of high fluidity can be made from this, then ester of even greater fluidity could be produced from liquid starting material. The alcohols studied were: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-ethoxyethanol. The main purpose was to compare the yields of fuel using the different alcohols and the two catalysts, acid or alkali. Therefore, one specific set of conditions was chosen for all reactions, and no attempt was made to optimize the conditions for the individual reactions. The molar ratio chosen was 3.5 moles of alcohol to one mole of average triglyceride. For the acid-catalyzed reactions, the conditions were: 0.1% concentrated sulfuric acid,