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,

gentle reflux temperature, 40 hr; and for basic catalysis: 0.4% potassium hydroxide, 50 C, 24 hrs.

PROCEDURES

Materials

The crude cafeteria oil was filtered through glass wool while hot to remove pieces of food. It was then allowed to settle in 45-gallon drums at 25 C for several weeks. The test sample was taken from the semisolid bottom sediment. It was melted and refiltered through Whatman no. 4 filter paper. The fatty acid ratios were determined to be 14:0 (1.6%), 16:0 (25.9%), 16:1 (8.0%), 18:0 (8.7%), 18:1 (48.9%), 18:2 (6.7%). From this analysis the average molecular weight of the oil was calculated to be 860. The free fatty acid content was determined by titration to be 1.5%, assuming a fatty acid molecular weight of 274.

Preparation of Fuel

The reactions were carried out in Erlenmeyer flasks with calcium chloride drying tubes attached, and stirring and heating were achieved using a combination magnetic stirrer/hot plate. Details of concentrations, temperature and time are given in Table I. In the work-up, hexane (3× volume) was added to the reaction to produce two phases. The bottom glycerol layer was separated and weighed. The top layer was washed three times with dilute hydrochloric acid or saturated sodium bicarbonate followed by water (three times) and then dried over anhydrous sodium sulfate. After evaporation of the hexane, the crude fuel was allowed to stand at 25 C for 48 hrs followed by removal of solid by gravity filtration. The filtrate was then left at 5 C for 7 days and refiltered. The weights of all fractions were measured.

Determination of Composition of Fuel

Each reaction was followed by obtaining proton magnetic resonance spectra on both layers. The appearance of peaks for protons alpha to the alcohol oxygen was particularly informative and indicated yields compatible with those determined by chromatography.

Gas chromatography with a 20% diethyleneglycol succinate on Chromosorb W column at 190 C was the method applied to quantify the yields of esters. Paradinitrobenzene, as internal standard, was added to the fuel prior to injection. The standard previously had been tested satisfactorily for stability in fuel solutions. Preliminary studies of various esters of various carboxylic acids showed that the response factors for the thermal conductivity detector were more dependent on carboxylic acid chain structure than alcohol structure, and that the variation with alcohol structure was

not very significant relative to experimental error. In this work, response factors were determined for ethyl and methyl esters and assumed to be similar for the other esters. The response factors were determined by running chromatograms on solutions of mixtures of weighed amounts of the pure ester and paradinitrobenzene, then measuring the areas of the peaks by cutting and weighing.

Iodine numbers were determined by the usual method.

Determination of Properties of Fuel

Viscosities were measured using a Brookfield Synchro-lectric Viscometer with a UL adapter thermostatted at 25 C.

The methyl ethyl and butyl esters were tested as fuels in two laboratory diesel engines, namely, an MWM Murphy model D990 direct-injection high-speed single-cylinder engine rated at 11 hp at 3600 rpm, and a Perkins model P6 direct-injection slow-speed six-cylinder engine rated at 65 hp at 2000 rpm.

RESULTS

Yields

The yields by weight of liquid fuel after crystallization at 25 C for two days and at 5 C for seven days are recorded in Table II.

The results under acid conditions show that 1-propanol produces the most liquid fuel and 2-ethoxyethanol the least. All alcohols except the latter formed liquid fuel in yields greater than 50%. Yields would have been considerably higher if centrifugation rather than gravity filtration had been used. Centrifuge equipment was overruled as not readily accessible to the do-it-yourself enthusiast. Under basic conditions, the only ester fuel which was not solid at 5 C was the methyl ester, and this one, in fact, exhibited the highest yield (84%) of all twelve reactions.

The yields of glycerol recorded in Table II do not quantitatively correlate with the yields of liquid fuel or composition of the fuels (Table III). However, the five reactions which yielded no glycerol were also the runs which gave no liquid at 5 C. Thin layer chromatography showed these fuels contained appreciable amounts of monoglycerides and diglycerides.

Composition

Table III shows the percentage by weight of ester in liquid fuel obtained at 25 C and 5 C as determined by gas chromatography. It can be seen that, as expected, the 5 C fuel is generally richer in ester than the 25 C fuel (by ca. 3%), except for the 1-butyl ester formed by acid catalysis.

The fuels with the highest ester composition were 1-

TABLE I

Reaction Conditions for Fuel Preparation

Alcohol	Volume percent	Molar ratio	Temperature (C)	Time (hr)	Catalyst
Methanol	15.0	3.6:1	~ 65	40	0.1% H_2SO_4
	15.0	3.6:1	50	24	0.4% KOH
Ethanol	21.6	3.6:1	~ 73	40	0.1% H_2SO_4
	21.6	3.6:1	50	24	0.4% KOH
1-Propanol	28.1	3.5:1	~ 90	40	0.1% H_2SO_4
	28.1	3.5:1	50	24	0.4% KOH
2-Propanol	28.1	3.5:1	~ 80	40	0.1% H_2SO_4
	28.1	3.5:1	50	24	0.4% KOH
1-Butanol	34.7	3.6:1	~105	40	0.1% H_2SO_4
	34.7	3.6:1	50	24	0.4% KOH
2-Ethoxyethanol	42.2	4.2:1	~125	40	0.1% H_2SO_4
	42.2	4.2:1	50	24	0.4% KOH

TABLE II

Yields of Liquid Fuels (Weight Percent)

Alcohol	Acid catalysis			Base catalysis		
	Percent yield 2 days at 25 C	Percent yield 7 days at 5 C	Percent yield glycerol	Percent yield 2 days at 25 C	Percent yield 7 days at 5 C	Percent yield glycerol
Methanol	79.3	64.0	4.2	91.9	85.3	13.45
Ethanol	66.9	54.8	5.3	28.9	—	—
1-Propanol	92.2	76.2	3.3	42.7	—	—
2-Propanol	78.7	54.4	0.6	51.2	—	—
1-Butanol	78.1	61.9	3.8	59.5	<11.9	—
2-Ethoxyethanol	53.5	39.2	0.8	37.0	—	—

TABLE III

A. Percentage of Ester in Fuel (Weight/Weight Percent)
B. Percentage Yield of Ester in Fuel (5 C) Relative to Oil at Start (Weight/Weight Percent)

	Acid catalysis			Base catalysis		
	A 25 C	A 5 C	B 5 C	A 25 C	A 5 C	B 5 C
Methanol	52.7 (77.8)	55.5 (75.1)	35.5	73.8 (60.3)	75.7 (62.6)	64.6
Ethanol	72.0 (55.5)	73.5 (56.9)	40.3	46.1 —	—	—
1-Propanol	53.9 (84.3)	57.7 (90.2)	44.0	31.9 —	—	—
2-Propanol	48.3 (74.9)	54.6 (75.8)	29.7	2.2 —	—	—
1-Butanol	81.3 (49.4)	80.5 (52.4)	49.8	47.7 —	—	—
2-Ethoxyethanol	47.5 —	50.4 —	19.8	29.4 —	—	—

Iodine numbers are given in brackets. Crude oil iodine number is 61.6.

butyl ester (acid catalysis) 81%, methyl ester (base catalysis) 74%, and ethyl ester (acid catalysis) 72%. The results correlate approximately with the percentage yields (Table II) and viscosities (Table IV).

Combination of the data from Tables II and IIIA allows one to calculate (Table IIIB) a more meaningful value for percentage yield, namely, percentage yield of ester in the fuel relative to the weight of oil at the start. Methyl (base catalyzed), ethyl (acid catalyzed), 1-propyl (acid catalyzed) and 1-butyl (base catalyzed) are all formed in overall yields greater than 40%, with the methyl fuel (64.6%) the best. These figures could be boosted substantially if centrifugation were used rather than gravity filtration to remove the solids. Concerning base catalysis, it is remarkable that the methyl ester is formed in so much higher yield than the other five esters. This difference in rates may have been exaggerated by the fact that only a very slight excess (0.094%) of alkali over free fatty acid was used. Slight differences in the exact free fatty acid content and the amount of carbon dioxide absorbed from the atmosphere could have led to significant differences in the amount of excess alkali in the different experiments. Later tests showed that higher yields of the esters can be obtained if slightly higher concentrations of alkali are used. Therefore, interpretation of the relative rates of ester formation in this study should be done with caution.

Comparison of the iodine numbers of the fuels shows an increase of ca. 4% on cooling the fuel to 5 C accompanied by crystallization indicating, as expected, that more saturated material is crystallizing preferentially. The acid-catalyzed methanol experiment was an exception.

TABLE IV

Viscosity of Liquid Fuels (Cps at 25 C)

Alcohol	Acid catalysis		Base catalysis	
	25 C	5 C	25 C	5C
Methanol	8.98	9.22	5.9	5.8
Ethanol	7.60	7.44	14.8	—
1-Propanol	8.56	8.38	20.00	—
2-Propanol	10.80	11.76	41.30	—
1-Butanol	7.26	7.02	13.20	—
2-Ethoxyethanol	12.32	12.00	22.80	—

Viscosity

All of the acid-catalyzed fuels had low viscosities (less than 13 Cps), but all the base-catalyzed fuels had higher viscosities, except for the methyl fuel which was the least viscous of all 24 samples (Table IV). As expected, the plot of viscosity vs percentage of ester (Fig. 1) approximately follows a smooth curve.

Engine Tests

The three best fuels, methyl (base catalysis), ethyl (acid catalysis) and butyl (acid catalysis) were tested as fuel in half-hour runs in the MWM high-speed diesel engine, and no problems were observed with regard to starting (at 25 C), smoothness of running and smokiness of exhaust. The first two fuels were also tested and ran well in a Perkins P6 slow-speed diesel engine. Longer term tests including power
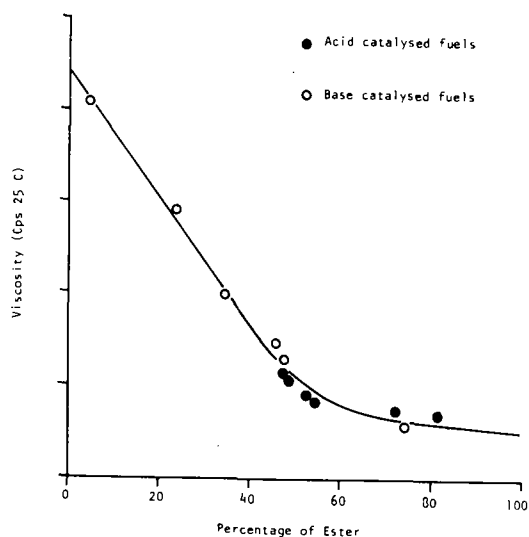
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FIG. 1. Graph of viscosity of fuels (25 C) vs percentage of ester present.

curves, fuel consumption and engine inspection are planned for these fuels in both the MWM engine and a Volkswagen diesel Rabbit on the road.

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