

A COMPARISON OF ETHYL AND METHYL ESTERS OF VEGETABLE OIL AS DIESEL FUEL SUBSTITUTES

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ABSTRACT

Rapeseed oil and ethanol are renewable, agriculturally produced products which give the ethyl ester of rapeseed oil a significant appeal as a diesel fuel. The methyl ester has been shown to be a suitable replacement for diesel fuel; however, much less has been known about the ethyl ester. This study examines processes which might be used to develop a simple ethyl ester process similar to that used with methyl ester and reports on both short and long term engine tests with both fuels compared to No. 2 diesel fuel (D2). Ethyl esters form emulsions when washed with water at room temperature and thus both acid washing and unwashed fuels were evaluated. The gross heat contents of biodiesel were 9 to 13 percent lower than D2. The viscosities of biodiesel were twice that of diesel. The cloud and pour points of D2 were significantly lower than the biodiesel fuels. The biodiesel fuels produced slightly lower power and torque and higher fuel consumption than D2.

In general, the physical and chemical properties and the performance of ethyl esters, were comparable to that of the methyl esters. Ethyl and methyl esters have almost the same heat content. The viscosity of ethyl esters were slightly higher and the cloud and pour points were slightly lower than methyl esters. Methyl esters had significantly higher values of wear and friction force than ethyl esters on the four ball wear test. Engine tests demonstrated that methyl esters produced slightly higher power output and torque than ethyl esters. Fuel consumption when using the two different esters was nearly identical, and the metal concentration in the engine oil using ethyl esters was higher than methyl esters, although wear was considered normal. Some desirable attributes of the ethyl esters over methyl esters were significantly lower smoke opacity, lower exhaust temperatures, and lower injector coking.

INTRODUCTION

Vegetable oil as an alternative fuel has been under study at Idaho since 1979 (Peterson et al., 1990). Since then researchers at Idaho have pioneered the use of rapeseed as a diesel fuel substitute. Although short term tests using neat vegetable oil showed promising results, longer tests lead to injector coking, more engine deposits, ring sticking, and thickening of the engine lubricant. This experience led to the use of modified vegetable oil as a fuel. Although there are many procedures or ways to transform vegetable oil into a diesel-like fuel, the transesterification process was found to be the most viable modification process for Idaho researchers.

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Transesterification of triglycerides with different types of alcohol to produce esters has been the topic of alternative fuel researchers. In Idaho alone, a considerable number of graduate students investigated optimization of the reaction variables of temperature, agitation time, catalyst amount, and ratio of alcohol to rapeseed oil (Jo, 1984; Madsen, 1985; Melville, 1987; Mosgrove, 1987; Bam, 1991; Feldman, 1991; and Perkins et al., 1991). Other researchers (like Feuge and Gros, 1949; Freedman and Pryde, 1982; Kusy, 1982; Romano, 1982; Nye and Southwell, 1983; Clark et al., 1984; Freedman et al., 1984; Peterson and Scarrah, 1984; Chancellor and Reubach, 1985; Du Plessis and De Villiers, 1985; Harrington and D'Arcy-Evans, 1985; Lago et al., 1985; Stern et al., 1985; Stern et al., 1986; and Schwab et al., 1987) have also investigated the important reaction conditions and parameters on the alcoholysis of triglycerides such as fish oils, soybean, rapeseed, cottonseed, sunflower, safflower, peanut and linseed oils to produce ethyl and methyl esters .

Working on peanut oil, Feuge and Gros (1949) achieved 90 percent yield using NaOH catalyst and heated the mixture at 50°C. They reported that alcoholysis was affected by catalyst concentration, amount of alcohol, and the time of agitation. Other researchers prepared methyl and ethyl esters from palm and sunflower oils using NaOH catalyst (Chancellor and Reubach, 1985). They used 100 percent excess alcohol and applied heat in the reaction.

Kusy (1982) followed the transesterification method patented by Bradshaw and Meuly in 1948, and proposed a continuous transesterification of ethyl ester. Lago et al. (1985) proposed the use of ethanol for both the oil extraction and the esterification process. Clark et al. (1984) transesterified soybean oils into ethyl and methyl esters, and compared the performances of the fuels with diesel. Du Plessis et al. (1985) produced both methyl and ethyl esters of degummed sunflower oil using NaOH catalyst, and molar ratios of 4.8:1 and 6:1 for methanol and ethanol were respectively required for satisfactory yields. Stern et al. (1986) worked on a process with at least two esterifications. The first esterification is catalyzed by an acidic chemical and the second by an alkali. A third esterification is sometimes done depending on the resulting ester. Almost all of them indicated that for a successful transesterification, preheating and/or heating the mixture of oil, alcohol and catalyst during the reaction was necessary to get satisfactory results. It would be more desirable to eliminate the heat used during the reaction because of the additional cost and reduced energy efficiency.

Peterson and Scarrah (1984) had investigated the use of 28 different heterogeneous catalysts. They reported a long reaction time (24 hours) for a reasonable ester conversion, they also had problem dissolving the catalysts and experienced the formation of unwanted fatty acids. Homogeneous catalysts, which are either basic or acidic showed more promise. Harrington and D'Arcy-Evans (1985) used 100:1 molar ratio of methyl alcohol to oil, and 30 percent (by weight) sulfuric acid catalyst. They reported 95 percent ester conversion from sunflower oil for 5 hours reaction time. Schwab, et al (1987) reported that high yields of butyl, ethyl and methyl esters can be attained using a molar ratio of 6:1 of alcohol to oil.

Nye and Southwell (1983) report a successful process on the transesterification of rapeseed oil at room temperature reaction by systematically optimizing the other variables. The works of graduate students at Idaho (Jo, 1984; Madsen, 1985; Melville, 1987; and Mosgrove, 1987) have built upon the work of Nye and Southwell. Based on their bench-scale results, workers at the UI Agricultural Engineering Department developed a small pilot plant system for rapeseed methyl ester production (Peterson et al., 1990).

1. Short term engine tests in the form of performance tests and opacity were conducted. Two formulas for ethyl ester, a methyl ester and D2 were used as fuels in the first test. The second test compared blends of ethyl ester and D2 from 0 to 100 percent in 20 percent increments. The order of testing was selected randomly with each test being replicated three times. The short term tests were performed with a John Deere 4239T diesel engine using a General Electric cradled dynamometer, a Telonic/Berkley opacity meter (Model 200), and a Hewlett-Packard Data Acquisition Unit (Model 87/3497). Torque, power, opacity, fuel consumption, and temperatures of different locations on the engine and exhaust were monitored and recorded in the tests. After each test run, the injectors were removed and photographed to measure the amount of coking following the procedure described by Korus et al.(1985).
2. Three 300-hour tests were conducted in two small Yanmar TS70C, 376 cc diesel engines (single cylinder, water cooled, precombustion chamber) with 3-kw generators, and connected to resistance banks to vary the engine loads. The tests were conducted as described by Peterson et al. (1983). The engines were rebuilt prior to the start of each test. Engine wear was monitored through crankcase oil analysis. Crankcase oil samples were sent to Oil Analysis Lab, Inc. in Spokane, WA and to Western States Caterpillar in Boise, ID for metal concentration analyses. Deposits on the pistons and valves were analyzed by the UI Analytical Services Lab to determine the components of the deposits. Samples of each fuel were sent to Oil Analysis Lab, Inc., and to UI Analytical Service for chemical and physical characterization.

Test 1: Two formulas for ethyl ester were compared. One utilized a sodium based catalyst and the second a potassium based catalysts. Neither fuel being used was washed.

Test 2: Methyl ester of rapeseed oil was compared with an ethyl ester of rapeseed oil both produced using a potassium catalyst. The methyl ester was produced using the method reported by Peterson et al. (1992). The ethyl ester was prepared with denatured ethanol and potassium hydroxide and was not washed.

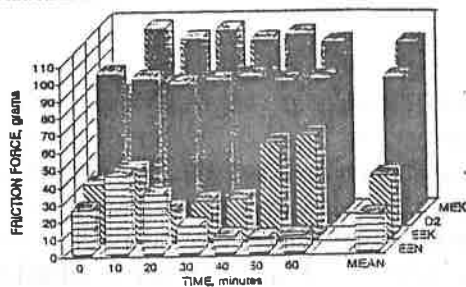
Test 3: Two types of ethyl esters were compared. One engine fueled with ethyl ester neutralized with hydrochloric acid, the other fueled with a washed ethyl ester.

RESULTS AND DISCUSSIONS

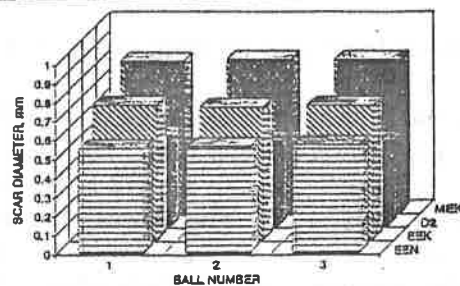
Fuel Preparation Tests

The major problems associated with ethyl ester production are (1) degree of esterification, (2) formation of emulsions when using water for washing, and (3) continual production or residual glycerol in the unwashed formulations.

The transesterification material balance tests were carried out on bench scale and larger scale. The criteria for a successful process was at least 95 percent ester conversion by volume and a very good phase separation. The chromatographic analyses revealed that the most successful transesterification processes produced 89-93 percent esters and 7-11 percent glycerol by weight. The ester phases usually contained 84.5 percent esters, 15.0 percent ethanol, and 0.5 percent glycerol. The crude glycerol layer usually contained about 50 percent ethanol and 50 percent glycerol. Material balance calculation and ion concentration determination of both esters and glycerol revealed that only 3.3 percent of the total amount of sodium methoxide used went into the ester phase. The remaining amount of the catalyst, which was more than 96 percent, went into the glycerol phase.



a. Friction Forces



b. Scar Diameters

Figure 2. Four-ball wear test results using four fuels: EEN, EEK, MEK, and D2.

Table 1. Fuel properties of D2, ethyl esters and methyl esters.

PROPERTIES	FUELS ¹			
	MEK	EEK	EEN	D2
Heat Content, MJ/kg (gross)	40.12b ²	41.41b	0.18b	45.71a
Kinematic Viscosity, cs (@ 40°C)	6.10c	6.75a	6.51b	3.51d
Cloud Point, °C	-3.3a	-4.7a	-7.3b	-14.3c
Pour Point, °C	-14.7a	-18.7b	-20.3b	-27.7c
Four-Ball Wear Test				
Friction force, grams	97.9a	36.4b	21.4c	85.6a
Scar diameter, mm	0.81a	0.71b	0.56c	0.46d

- 1 - MEK = Methyl ester; washed; potassium-based catalyst
 EEK = Ethyl ester; unwashed; potassium-based catalyst
 EEN = Ethyl ester; unwashed; sodium-based catalyst
 D2 = Diesel No.2
- 2 - Numbers followed by the same letters in a row are not significantly different using DMRT at 5 percent probability level.

Table 2. Chemical and physical properties of the fuel¹.

PROPERTIES	ACIDIFIED		WASHED	
	Batch 1	Batch 2	Batch 1	Batch 2
Heat content, MJ/kg (gross)	39.89	39.93	39.46	39.94
Viscosity, cs (@ 40°C)	6.65	6.93	6.59	6.48
Sp. Density, kg/l (@ 22°C)	0.877	0.858	0.871	0.871
Flash Point, °C ²	171	23	170	165
Ethanol Content, %	0.22	4.13	0.21	0.67
Cloud Point, °C	2.2	2.2	-1.1	-1.1
Freeze Point, °C	-26	-26	-26	-26
Element Screen, % weight				
Sulfur	0.007	0.0014	0.0041	0.0005
Potassium	0.014	0.0252	0.0061	0.0001

¹ Based on analyses of samples done at UI Analytical Services Lab, and AgE Analytical Lab, Univ. of Idaho, Moscow, ID; and at The Oil Analysis Lab Inc, Spokane, WA.

² Flash Point Procedure used was not the recommended ASTM Method for such fuel. Flash occurs for alcohol present.

Is this summary?

Table 3. Summary of the fuel tests using D2, ethyl esters and methyl esters.

PARAMETERS/ RPM	FUELS ¹		
	MEK	EK	D2
a) Power, hp			
1500	60.89b ²	58.84c	62.87a
1700	68.73b	66.46c	71.97a
1900	74.82b	72.34c	79.07a
2100	77.62b	75.02c	82.61a
2300	81.19b	77.45c	86.50a
2500	4.14a	4.03a	3.97a
b) Torque, ft-lbs			
1500	213.15b	205.98c	220.11a
1700	212.32b	205.29c	222.34a
1900	206.80b	199.95c	218.52a
2100	194.09b	187.58c	206.56a
2300	185.37b	176.83c	197.48a
2500	8.69a	8.44a	8.31a
c) Smoke opacity, percent			
1500	12.47b	7.58c	20.54a
1700	5.84b	3.90b	11.71a
1900	2.85b	2.41b	3.23b
2100	1.44b	1.65b	1.85b
2300	1.18b	1.42b	1.30b
2500	0.51a	0.38a	0.40a
d) Exhaust temperature, K			
1500	1192.86b	1130.69c	1237.74a
1700	1173.98b	1130.37c	1224.25a
1900	1153.56b	1113.58c	1210.00a
2100	1131.53b	1101.17c	1192.06a
2300	1101.40ab	999.92b	1158.34a
2500	575.29a	586.91a	581.67a
e) Fuel consumption, lb/min			
1500	0.4664a	0.4620a	0.4453b
1700	0.5184a	0.5125b	0.4945c
1900	0.5660a	0.5670b	0.5385c
2100	0.5922a	0.5905b	0.5720c
2300	0.6468a	0.6310a	0.6075b
2500	0.2228a	0.2235a	0.1990a
f) Injector coking, relative number			
	9.96a	6.15b	5.97b

1 - MEK = Methyl ester; washed; potassium-based catalyst
 EK = Ethyl ester; unwashed; potassium-based catalyst
 EEN = Ethyl ester; unwashed; sodium-based catalyst
 D2 = Diesel No.2
 2 - Numbers followed by the same letters in a row are not significantly different using DMRT at 5 percent probability level.

Table 4. Summary of the fuel tests using D2, ethyl esters and D2-ethyl ester blends.

PARAMETERS/ RPM	FUELS ¹					
	OEE	20EE	40EE	60EE	80EE	100EE
A. Power, HP						
1500	61.52a ²	61.14ab	61.20ab	60.65ab	60.12b	58.22c
1700	70.92a	70.24ab	69.92ab	68.94bc	67.92c	65.88d
1900	77.42a	76.52ab	75.67bc	74.81cd	73.63d	71.17e
2100	80.38a	79.39ab	78.59bc	77.60cd	76.22d	73.44e
2300	83.87a	82.93ab	81.73bc	80.61c	78.85d	76.88e
2500	4.50a	4.58a	4.56a	4.53a	4.57a	4.62a
B. Torque, ft-lbs						
1500	215.38a	214.06ab	214.24ab	212.34ab	210.47b	203.52c
1700	219.06a	216.96ab	215.98ab	212.97bc	209.96c	203.49d
1900	213.97a	211.48ab	209.12bc	206.77cd	203.52d	196.71e
2100	200.99a	198.51ab	196.52bc	194.05cd	190.58d	183.65e
2300	191.46a	189.34ab	186.59bc	184.05c	180.02d	175.52e
2500	9.41a	9.57a	9.54a	9.49a	9.56a	9.66a
C. Smoke opacity, percent						
1500	21.52a	20.02ab	16.78bc	14.50c	13.14cd	8.86d
1700	11.89a	11.47ab	9.97abc	8.85bc	7.56c	4.72d
1900	6.97a	6.66a	5.76ab	5.15bc	4.05cd	2.98d
2100	3.95a	3.94a	3.00b	2.98b	2.32cd	1.70c
2300	2.70ab	2.84a	2.25c	2.20bc	1.55d	1.04e
2500	0.25b	0.45a	0.29b	0.36ab	0.21b	0.21b
D. Exhaust temperature, K						
1500	1137.34a	1197.57a	1146.85a	1121.49a	1132.21a	1113.97a
1700	1200.31a	1188.50a	1142.05bc	1131.06c	1134.49c	1100.61c
1900	1151.68a	1121.64ab	1118.39a	1091.21c	1076.07a	1066.65a
2100	1174.38a	1163.13b	1142.59c	1122.26d	1109.19e	1103.58e
2300	1142.09a	1131.30a	1110.75b	1094.44c	1086.74c	1071.01d
2500	593.29a	586.30a	594.07a	583.44a	595.40a	588.13a
E. Fuel consumption, lbs/min						
1500	0.4328e	0.4350e	0.4425d	0.4500c	0.4540b	0.4590a
1700	0.4910d	0.4915d	0.4990c	0.5065ab	0.5080ab	0.5125a
1900	0.5315d	0.5340d	0.5390c	0.5485b	0.5515b	0.5565a
2100	0.5685bc	0.5625c	0.5700bc	0.5795a	0.5830a	0.5870a
2300	0.6085c	0.6095c	0.6150c	0.6235b	0.6260b	0.6345a
2500	0.1975d	0.2020cd	0.2060c	0.2150b	0.2175b	0.2240a
G. Injector coking, relative number						
	8.51a	10.31a	10.18a	9.71a	7.66a	7.57a

1 - Numbers represent the percentage of ethyl ester in the fuel.
 2 - Data followed by the same letters in a row are not significantly different using DMRT at 5 percent probability level.

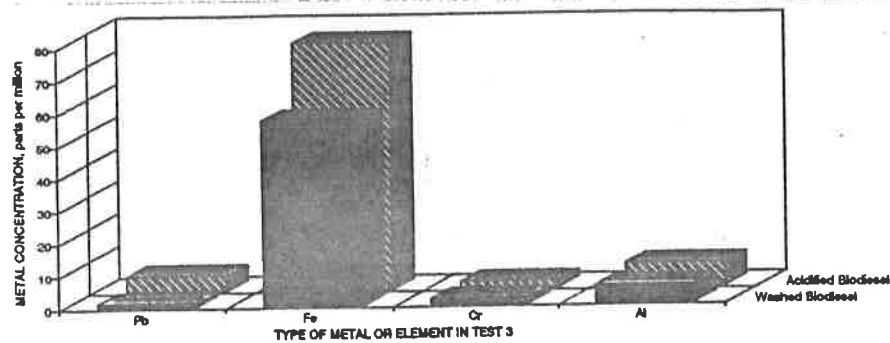


Figure 6. Aluminum, iron, chromium and lead concentration in the crank case oil using acidified and washed ethyl esters.

CONCLUSIONS

In general, the ethyl ester fuels, while more difficult to produce than the methyl esters, had comparable properties and engine performance. Power and fuel consumption, compared to diesel, were in proportion to their heat contents which are 9 to 13 percent less on a mass basis. Ethyl esters form emulsions when washed with water at room temperature and thus both acid washing and unwashed fuels were evaluated.

Some specific comparisons of ethyl and methyl esters are:

1. Ethyl and methyl esters have almost the same heat content.
2. The viscosity of the ethyl esters were slightly higher than methyl esters while the cloud and pour points of ethyl esters were slightly lower than methyl esters.
3. Wear and friction force produced on the four ball test by the methyl esters were significantly higher values than that of the ethyl esters.
4. Engine tests demonstrated that methyl esters produced slightly higher power output and torque than ethyl esters. The fuel consumption of the ester fuels were nearly identical but higher than diesel.
5. Metal concentration in the engine oil using ethyl esters were higher than methyl esters, although wear was considered normal.
6. Some desirable attributes of the ethyl esters over methyl esters were: significantly lower smoke opacity, lower exhaust temperatures, lower injector coking, and fewer elements in the combustion chamber deposits.

When comparing the overall performance of the biodiesel fuels (ethyl and methyl esters of rapeseed oil) in comparison to D2 fuel the following conclusions were noted:

1. The gross heat contents of biodiesel were 9 to 13 percent lower than D2.
2. The viscosities of biodiesel were twice that of D2 while the cloud and pour points of D2 were significantly lower than the biodiesel fuels.
3. The biodiesel fuels produced slightly lower power and torque and higher fuel consumption than D2 similar to the gross heat contents.
4. Injector coking was similar for all the fuels except for methyl ester, which showed a slightly higher coking index.
5. Smoke opacities of biodiesel were one-third that of D2 and exhaust temperature produced by biodiesel were at least 50°C lower than D2.