Production and Testing of Ethyl and Methyl Esters

ABSTRACT

Test quantities of ethyl and methyl esters of four renewable fuels were processed, characterized and performance tested. Canola, rapeseed, soybean oils, and beef tallow were the feedstocks for the methyl and ethyl esters. Previous results have shown methyl esters to be a suitable replacement for diesel fuel; however, much less has been known about the ethyl esters. A complete set of fuel properties and a comparison of each fuel in engine performance tests are reported. The study examines short term engine tests with both methyl and ethyl ester fuels compared to number 2 diesel fuel (D2). Three engine performance tests were conducted including an engine mapping procedure, an injector coking screening test, and an engine power study.

The gross heat contents of the biodiesel fuels, on a mass basis, 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 those of the methyl esters. Ethyl and methyl esters have almost the same heat content. The viscosities of the ethyl esters is slightly higher and the cloud and pour points are slightly lower than those of the methyl esters. Engine tests demonstrated that methyl esters produced slightly higher power and torque than ethyl esters. Fuel consumption when using the methyl and ethyl esters are nearly identical. Some desirable attributes of the ethyl esters over methyl esters were: significantly lower smoke opacity, lower exhaust temperatures, and lower pour point. The ethyl esters tended to have more injector coking than the methyl esters and the ethyl esters had a higher glycerol content than the methyl esters.

INTRODUCTION

Vegetable oil as an alternative fuel has been under study at the University of Idaho since 1979 (Peterson et al., 1990). Since then researchers at Idaho have pioneered the use of rapeseed oil as a diesel fuel substitute. Although short term tests using neat vegetable oil showed promising results, longer tests led 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 ways and procedures to convert vegetable oil into a diesel-like fuel, the transesterification process was found to be the most viable oil modification process for Idaho researchers.

Transesterification is the process of using an alcohol (e.g., methanol or ethanol) in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to chemically break the molecule of the raw renewable oil into methyl or ethyl esters of the renewable oil with glycerol as a by-product. The University of Idaho Department of Agricultural Engineering operates an oil extraction plant of 19 liters per hour capacity and a batch esterification reactor of 750 liters capacity. Recipes have been developed for producing both ethyl and methyl esters of renewable oils. Fuel tests currently performed by the Department of Agricultural Engineering are heat of combustion, viscosity, flash point, pour point, cloud point, density, specific gravity, API gravity, residual catalyst, and alcohol content. Also available are facilities to do fuel performance evaluation in engines, Engine Manufacturer's Association (EMA) engine durability tests, injector coking tests, and vehicle performance tests. Transesterified, renewable oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel.

LITERATURE REVIEW

The emergence of transesterification can be dated back to as early as 1846 when Rochieder described glycerol preparation through ethanolysis of castor oil (Fcrmo, 1954). Since that time alcoholysis has been studied in many parts of the world. Other researchers 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 (Chancellor and Rauback, 1985; Clark et al., 1984; DuPlessis and DeVilliers, 1985; Feuge and Gros, 1949; Freedman and Pryde, 1982; Freedman et al., 1984; *Harrington* and D'Arcy-Evans, 1985; Kusy, 1982; Lago et al., 1985; Nye and Scuthwell, 1983; Peterson and Scarrah, 1984; Romano, 1982; Schwab et al., 1987; Stern et al., 1985; Stern et al., 1986). They also prepared methyl and ethyl esters from palm and sunflower oils using NAOH as the catalyst and using 100% excess alcohol and applied heat in the reaction. Lago et al. (1985) proposed the use of ethanol for both the oil extraction and the esterificaticn process. Clark et al. (1984) transesterified soybean oils into ethyl and methyl esters, and compared the performances of the fuels with diesel. DuPlessis and

DeVilliers (1985) have produced both methyl and ethyl esters of degummed sunflower oil using NAOH catalyst. Stem et al. (1986) worked on a process with at least two esterifications. The first esterification was catalyzed by an acidic chemical and the second by an alkali. Almost all the investigators 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. The application of heat during the reaction is not economically sound because of the additional cost and reduced energy efficiency.

Nye and Southwell (1983) were the only workers to report a successful process for the transesterification of rapeseed oil at room temperature by systematically optimizing the other variables. In Idaho, a considerable number of graduate students have investigated the optimization of the reaction variables temperature, agitation time, catalyst amount, ratio of alcohol to rapeseed oil and degree of lipid conversion (Bam, 1991; Feldman, 1991; Jo, 1984; Madsen, 1985; Melville, 1987; Mosgrove, 1987; Perkins et al., 1991). They have confirmed the works of Nye and Southwelf. Based on their bench-scale results, workers at the UI Agricultural Engineering Department developed a small pilot plant system for rapeseed methyl and ethyl ester production (Peterson et al., 1991). The reactor is also utilized as a washing tank for the ester. A separate alcohol-catalyst mixer, made of a 208 liter plastic barrel, serves as an accessory to the reactor. The reactor and the oil press constitute the farm-scale rapeseed oil and Biodiesel processing plant.

Ethanol will produce a more environmentally benign fuel. The Dangerous Properties of Industrial Materials (Sax, 1975) reports,

> The systemic effect of ethyl alcohol differs from that of methyl alcohol. Ethyl alcohol is rapidly oxidized in the body to carbon dioxide and water, and in contrast to methyl alcohol no cumulative effect occurs. Methyl alcohol ... once absorbed is only very slowly eliminated. ...in the body the products formed by its oxidation are formaldehyde and formic acid, both of which are toxic. Because of the slowness with which it is eliminated, methyl alcohol should be regarded as a cumulative poison.

Ethanol is also a preferred alcohol in this process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment. Success of rapeseed ethyl ester (REE) production would mean that Biodiesel's two main raw materials would be agriculturally produced, renewable and environmentally friendly.

Engine Performance Tests: In a summary of 22 short term engine tests conducted at 12 locations worldwide (Peterson, 1986) in which vegetable oil was compared to diesel as a fuel, peak engine power on the vegetable oil fuels ranged from 91 to 109 percent of that produced when the same engine was operated with diesel fuel. In these tests, 16 of the 22 reported peak power equal to or exceeding that when the engines were operated on diesel.

Fuel consumption was generally slightly higher, reflecting the reduced energy content of the vegetable oil. Thermal efficiencies are also generally reported to be slightly higher than for diesel fuel.

Peterson et al. (1987) ran a series of short term engine tests to evaluate the effects of transesterification of winter rapeseed oil on injector coking. The results showed the transesterification treatment to decrease the injector coking to a level significantly lower than that observed with No. 2 diesel.

Einfait and Goering (1985) evaluated the methyl ester of soybean oil, Wagner et al. (1984) investigated three soybean oil esters (methyl,ethyl and butyl), Kaufman and Ziejewski (1984) evaluated methyl ester of sunflower oil, and Zhang et al. (1988) evaluated methyl esters of winter rape oil in 200 hour EMA test cycles. They concluded that the performance of the esters of vegetable oil did not differ greatly from diesel. The brake power was nearly the same as with diesel fuel, while the specific fuel consumption was higher than diesel. Based on crankcase oil analysis, engine wear rates were low but some oil dilution did occur. Carbon deposits inside the engine were normal with the exception of intake valve deposits.

Although most researchers agree that vegetable oil ester fuels are suitable for use in compression ignition engines, a few contrary results have also been obtained. Vinyard et al. (1982) reported an extensive coking problem while using degummed sunflower ethyl ester. The ester produced unacceptable coking levels after only 50 hours of operation under part load, even when diluted with up to 30% diesel fuel.

The results of these studies point out that most vegetable oil methyl esters are suitable as diesel substitutes but that more long term studies are necessary for commercial utilization to become practical.

University of Idaho 1000 Hour Tests: Tests at the University of Idaho (Perkins et al., 1991) have shown that use of the RME is equivalent to diesel fuel in direct injection diesel engines. Three engines, one fueled with 100% methyl ester of winter rapeseed oil (100 RME), one with a 50% Number 2 diesel - 50% methyl ester (50RME-5OD2 of winter rapeseed oil blend, and one with a reference fuel of 100% number 2 diesel (100 D2), were investigated in both 200 hour Engine Manufacturer's Association (EMA) test cycles (Zhang et al., 1988) and in 1000 hour test cycles by extending the EMA test procedure for alternate fuels (EMA, 1982). It was found that methyl ester of winter rapeseed oil was equivalent to number 2 diesel when compared on the basis of long term performance and engine wear. The primary factors which were evaluated included engine brake power and torque, injector tip coking, and engine component wear (based on oil analysis). The only noticeable adverse effect of the ester fuel was a slight decrease in engine oil viscosity.

OBJECTIVES

1.   Produce test quantities of ethyl and methyl esters of rapeseed oil, soybean oil, canola,   and tallow using the two procedures currently developed.

2.   Determine the complete set of fuel specifications on each of the fuels according to the requirements set forth in the proposed ASAE Engineering Practice, ASAE EP X552.

3.   Compare the performance of each of these fuels in short term engine performance tests.

MATERIALS AND METHODS

Seventy gallons of each of the esters were produced using the process developed by University of Idaho researchers. The feedstocks for these fuels were as follows: rapeseed from Dwarf Essex variety seed; canola from Stonewall variety seed; beef tallow purchased from Iowa Beef Products in Kennewick, Washington; and soybean oil purchased from Foodservices Brokerage Co. in Spokane Washington. In addition to these eight fuels, seventy five gallons of methyl soyate were purchased from Interchem, Inc., Overland Park, Kansas (Midwest Biofuels). The rapeseed and canola oils were expelled at the University of ldaho's Agricultural Engineering farm scale process facility. Each fuel, excluding the methyl soyate, was processed at this facility. Phillips 66 Company low sulfur diesel reference fuel was used as the baseline fuel.

The nomenclature for these fuels is as follows: R - rapeseed, C - canola, T- tallow, S soybean, with the following letters ME for methyl ester and EE for ethyl ester. MWF represents Midwest Biofuels methyl soyate, and D2 - Phillips low sulfur diesel reference fuel.

Fuel Characterization
The fuels were characterized by evaluating the parameters required in ASAE EP X552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Agricultural Engineering, University of Idaho. The boiling point, water and sediment, carbon residue, ash, sulfur, cetane number, copper corrosion, Karl Fischer water, particulate matter, iodine number, and the elemental analysis were performed at Phoenix Chemical Labs, Chicago Illinois. The HPLC and titraticn analysis for total and free glycerol, percent of oil esterified, free fatty acids, and mono-, di-, and trigylicerides were performed by Diversified Labs Inc., Chantilly, Virginia.

Engine Performance Tests
All engine performance tests were conducted in the engine performance lab at the University of Idaho. The equipment used and tests conducted are described below. The short term tests were performed with an in-line four cylinder John Deere 4239T

turbocharged, direct injected diesel engine. It has a displacement of 3.9 liters 239 cubic inches), a high RPM of 2650, 61 kw (82 hp) at 2500 RPM, and 290 Nm (214 ft lbf torque at 1500 RPM. It is attached to a General Electric 119 kw (159 hp) cradle dynamometer. The engine was not modified in any way for use with the renewable fuels.

A Hewlett Packard data acquisition unit (model 3497-A) and a personal computer were used to collect data every thirty seconds for each of the tests. Torque, power, opacity, fuel consumption, and temperatures of various engine parameters were monitored throughout the testing and saved into a data file.

Fuel Flow Equipment
The fuel delivery and return lines were adapted with quick couplers for fast and clean changing of the different fuels. Individual 19 liter (5 gallon) metal fuel tanks were modified with a fuel filter and flexible fuel lines which could be connected to the engine quick couplers. Fuel flow rate was determined by direct weighing. The fuel containers were placed on an electric 45.4 kg (100 lb) scale accurate to 23 grams (0.05 lb) with RS232 capability.

Opacity Meter
A Telonic Berkley model 200 portable opacity meter was connected to the data acquisition unit. The opacity meter consists of a light source positioned on one side of the exhaust stream and a photo resistor mounted on the opposite side. The meter provides an output voltage ranging from 0 to 1.00 volts. One hundred percent opacity (1.0 volt) corresponds to no light transmission whereas 0 percent opacity corresponds to complete light transmission. The uncertainty of this reading is +/- 1 percent opacity.

Smoke density is a function of smoke particles per unit gas volume, the size distribution of the smoke particles, and the light absorption and the scattering of the particles. Opacity is converted to smoke density with the use of the Beer-Lambert Law relationships between transmittance and the effective optical length. Smoke density has units of meters-[1] and should be reported at a standard temperature of 100 degrees C for comparative purposes (Proposed SAE J1667).

Injector Coking
Three sets of fuel injectors were used for the purpose of running three injector coking tests each day. The injector coking tests were performed using the procedure described in "A Rapid Engine Test to Measure Injector Fouling in Diesel Engines Using Vegetable Oil Fuels" (Korus et al, 1985). The engine was operated for ten minutes at each interval for data collection.

Torque Tests

The torque tests were performed with the engine operating at 2600 RPM to 1300 RPM in 100 RPM increments with the same data collection procedure as previously described. The engine was operated for 2 1/2 minutes at each interval for data collection.

Mapping Engine Performance

The engine mapping tests were performed using the procedure described in "Procedure for Mapping Engine Performance-Spark Ignition and Compression Ignition Engines" (SAE J1312, 1990). The mapping tests were performed at 2500, 2250, and 2000 RPM with loadings of 100, 75, 50, 25, and 0 percent of maximum power. The engine was operated for 5 minutes at each data collection interval.

Experimental Design

The engine performance data was collected using a randomized complete block experimental design. Each fuel was tested once in each block in random order for each of the three blocks. This resulted in a total of 30 injector coking tests, 30 torque tests, and 30 fuel mapping studies.

PROCEDURES

Fuel Preparation

The eight Biodiesel fuels were processed in a batch type reactor. The methyl ester process utilizes 1 00 percent molar excess alcohol (preferably absolute or 100 percent pure), or a molar ratio of 6:1 alcohol to oil ratio. Based on the amount of input oil by weight, 1.1 percent of potassium hydroxide (KOH) is used, The following equations were used for the quantities processed:

$$MeOH = 0.225 \text{ x Oil} \qquad KOH = Oil/100$$

where;   Oil = desired amount of oil, in liters
MeOH = amount of methanol needed, in liters
KOH = amount of potassium hydroxide required, in kg

The ethyl ester process utilizes 70 percent stoichiometric excess ethanol (absolute, 100 percent pure), or a molar ratio of 5.1:1 ethanol to oil ratio. Based an the amount of input oil by weight, 1.3 percent of KOH is used. The following equations were used for the quantities processed:

$$EtOH = 0.2738 \text{ x Oil} \qquad KOH = Oil/85$$

where;   Oil = desired amount of oil, in liters
         EtOH   amount of ethanol needed, in liters

KOH   amount of potassium hydroxide required, in kg

The following transesterification procedure is for the methyl and ethyl ester production. The catalyst is dissolved into the alcohol by vigorous stirring in a small reactor. Pure methanol is very flammable and its flame is colorless when ignited. The oil is transferred into the Biodiesel reactor and then the catalyst/alcohol mixture is pumped into the oil and the final mixture stirred vigorously for two hours. A successful reaction produces two liquid phases: ester and crude glycerol. Crude glycerol, the heavier liquid will collect at the bottom after several hours of settling. Phase separation can be observed within 10 minutes and can be complete within two hours after stirring has stopped. Complete settling can take as long as 20 hours. After settling is complete, water is added at the rate of 5.5 percent by volume of the oil and then stirred for 5 minutes and the glycerol allowed to settle again. After settling is complete the glycerol is drained and the ester layer remains. Washing the ester is a two step process which is carried out with extreme care. A water wash solution at the rate of 28 percent by volume of oil and 1 gram of tannic acid per liter of water is added to the ester and gently agitated. Air is carefully introduced into the aqueous layer while simultaneously stirring very gently. This process is continued until the ester layer becomes clear. After settling, the aqueous solution is drained and water alone is added at 28 percent by volume of oil for the final washing.

Engine warm-up and cool-down
Each test started with a warm-up and ended with a cool-down period. The warm-up period consisted of a two minute interval on D2 at low idle. Then there was an eight minute interval with the fuel to be tested. During this eight minute period there is a gradual increase in load and RPM to the rated horsepower and load. The cool-down period consisted of 10 minutes on D2 at low idle. For both the warm-up and cool-down periods the return fuel line was placed into a separate container.

RESULTS

A total of over 150 hours were logged on the John Deere diesel engine and 2,250 liters of fuel were consumed during the performance testing.

Fuel Characterization
Comments on each parameter would be excessively lengthy; however, some deserve attention.

Viscosity -The Biodiesel fuels had viscosity from 1.3 to 2.1 times that of D2. SME and MWF had the lowest viscosities of the biodiesels and RME and REE the highest viscosities.

Cloud and Pour Point - All the biodiesels have higher cloud and pour points than D2. RME and REE had the lowest pour points only 1 and 5 degrees respectively higher than D2 while the tallow esters were 28 and 32 degrees higher than D2. The soy esters were 13 to 19 degrees higher than D2.

Sulfur - All of the Biodiesel fuels contain considerably less sulfur than even the low sulfur diesel fuel used for comparison. The Biodiesel fuels were 0.55 to 0.22 that of D2.

Heat of Combustion - All of the Biodiesel fuels are lower in heat content than D2 by an average of 11.8 percent on a mass basis. Since the Biodiesel fuels have a 4.1 percent higher specific weight, the energies average 8.2 percent lower on a volume basis.

Percent Esterified - The methyl esters were 97.5 percent esterified while the ethyl esters were only 94.3 percent esterified. SME and RME had the highest esterified values of the methyl ester and TEE the highest of the ethyl esters. CEE was the lowest level.

Total Glycerol - Glycerol levels were consistently higher than the 0.25 percent allowed in the proposed ASTM standard based on the analysis provided. SEE was highest at 1.88 percent and TME lowest at 0.6 percent. The average total glycerol was 0.87 percent for the methyl esters and 1.4 percent for the ethyl esters. Note that the commercial Biodiesel had a total glycerol content of 1.25 percent.

Alcohol and Catalyst - All of the Biodiesel fuels had less than one percent alcohol. Residual catalyst varied form I 1 to 36 parts per million (ppm).

The fatty acid compositions and the theoretical formulas were determined using a weighted average of the fatty acid composition.

Injector Coking
A visual inspection of the injector tips would indicate no difference between the Biodiesel fuels compared to when tested on diesel fuel. The data is an average of three runs, four injectors for the four cylinder engine, and two orientations for a total of 24 samples averaged for each fuel. The overall injector coking is low, especially when compared with older tests that included runs with raw vegetable oil. A typical worst case injector coking photograph with Biodiesel is a level of 3.0 shown.

Linear regression was used to compare injector coking, viscosity, percent oil esterified, total glycerol, and heat of combustion data with the others. It was hypothesized that the total glycerol

would be responsible for an increase in injector coking, however the r-squared value was less than 0.01 between these parameters. The most significant values in this comparison for the Biodiesel fuels was, heat of combustion and viscosity with an r-squared value of 0.9, and the molecular weight and heat of combustion with an r-squared value of 0.78. The r-squared values for injector coking versus molecular weight and viscosity were 0.61 and 0.68 respectively.

Torque Tests
Testing included the power and torque of the ethyl esters and diesel fuel and methyl esters versus diesel fuel. The Biodiesel fuels on the average decrease power by 4.9 percent compared to that of diesel at rated load.

Peak torque is less for the ester fuels than for diesel but occurs at lower engine speed and generally the torque curves are flatter. At 1700 RPM the torque is reduced 5 percent while at 1300 RPM it is reduced only 3 percent.

Smoke density was calculated using the data collected during the torque test for each fuel. Smoke density decreased by an average of 75 percent for the Biodiesel fuels compared to D2. TME and SME produced the least smoke.

Mapping Engine Performance
Table 4 presents the engine mapping data for all the fuels at 3 engine RPM's in a accordance with SAE J1312. This table shows the power (kw) and the actual fuel consumption (gis). A visual example of the results at each RPM is shown for CEE in Figure 7.

CONCLUSIONS

A complete set of fuel characteristics for a variety of Biodiesel fuels and D2 are presented. Performance tests demonstrated that these fuels are similar to diesel fuel. In general, the testing performed has shown that torque and power are similar to D2 and as the molecular weight of the Biodiesel decreases so does the torque and power. Injector coking is greater for the ethyl esters which are also higher in total glycerol, even though with linear regression there is no correlation based on glycerol content alone. As the heat of combustion for the Biodiesel fuels increases so does the viscosity and molecular weight.

In general, the physical and chemical properties and the performance of ethyl esters are comparable to those of the methyl esters. Ethyl and methyl esters have almost the same heat content. The viscosity of ethyl esters are slightly higher and the cloud and pour points are slightly lower than methyl esters. Engine tests demonstrate that methyl esters produced slightly higher power output and torque than ethyl esters. Fuel consumption when using the two different esters is nearly identical. Some desirable attributes of the ethyl esters over methyl esters are significantly lower smoke opacity, lower exhaust temperatures, and lower pour point.

Specific conclusions of this study are:
1.   Fuel characterization data show some similarities and differences between biodiesel fuels and diesel. a) Specific weight is higher for Biodiesel, heat of combustion is lower,

viscosities are 1.3 to 2.1 times that of D2. b) Pour points for Biodiesel fuels vary from 1 to 25 degrees Celsius higher for Biodiesel fuels depending on the feedstock. c) Sulfur content for Biodiesel is 20 to 50 percent that of D2.

2.   The percent oil esterified as determined by an outside lab was lower than expected. Methyl esters averaged 97.5 percent and ethyl esters 94.3 percent esterified.

3.   Total glycerol was higher than expected averaging 1. I percent. Methyl esters averaged   0.87 percen

4.   The esters all have higher levels of injector coking than diesel fuel. Ethyl esters had higher levels than did the methyl esters. Injector coking was more related to apparent molecular weight and viscosity than to total glycerol. Visually all injector coking was low especially compared with older tests that included raw vegetable oils.

5.   Smoke density, as determined by an opacity meter, decreased an average of 75 percent for the Biodiesel fuels compared to D2. CEE and CME produced the most smoke of the Biodiesel fuels and TME and SME the least smoke.

6.   At rated load, engine power produced by the Biodiesel fuels decreased an average of 4.9 percent compared to D2.

7.   Peak torque for Biodiesel at 1700 RPM was reduced 5 percent on the average compared to D2 while at 1300 RPM it was reduced only 3 percent, demonstrating the flatter torque curve characteristic of Biodiesel.

8.   The average Biodiesel fuel consumption (g/s) on a mass basis was 7 percent higher than that of D2. On a volume basis (Ils) the consumption would be 6.7 percent higher than that of D2.

9.   Average thermal efficiencies for Biodiesel fuel in the mapping test was insignificant by difference when compared to D2.