TWO YEAR STORAGE TEST
with RME and REE

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ABSTRACT

Methyl and ethyl esters prepared from various vegetable oils by the process of transesterification have shown much promise as fuels for all types of diesel engines. As part of a larger study entitled "Development of Rapeseed Biodiesel for Use in High-speed Diesel Engines", this activity was designed to determine the extent of deterioration of Rape Methyl Ester (RME) and Rape Ethyl Ester (REE) in storage. The study involved triplicate samples of RME and REE stored in glass and steel containers at room temperature (inside) and at the local ambient outdoor temperatures (outside). The study was conducted for two years.

At the beginning of the study and at 3 month intervals, samples were taken for measurement of: Peroxide value, Acid value, Density, Viscosity, and Heat of Combustion. At the conclusion of the study, engine performance tests were conducted with the two year stored REE and RME, new REE and RME, and low sulfur diesel reference fuel.

On the average, the esters tended to increase over time in all of the previously mentioned properties with the exception of heat of combustion, which decreased. Regression models are presented to predict the deterioration with time. Engine power varied less than 1% for both Biodiesel fuels compared to the stored counterparts while smoke density decreased 32% for the stored RME.

INTRODUCTION

Biodiesel is gaining recognition as a renewable alternative to diesel fuel. One step to realizing commercial Biodiesel is how well it stores and what affect storing for long periods has on the performance of the fuel. The problems of fuel deterioration with Biodiesel during storage are more severe than for commercial diesel fuel. Although vegetable oils contain natural antioxidants, their high degree of unsaturation makes them susceptible to gum formation. Since fuel deterioration occurs mainly by oxidative polymerization leading to gum formations one objective of this study was to determine the rate of oxidative polymerization for different fatty acid esters prepared from rapeseed, as effected by container types, and environments. Peroxide values measure the levels of the oxidation products in the samples. Another objective of this study was to use short term engine coking and torque test procedures to determine whether the presence of the oxidation products affected the engine performance.

LITERATURE REVIEW

Previous work on the storage stability of vegetable oil fuels includes a three year study reported by Klopfenstein and Walker (1984), Klopfenstein and Walker (1985), Klopfenstein and Walker (1986). In that study, samples of soybean methyl esters were stored in three different environments (indoor, outside and underground), two container types (steel and plastic) and two formulations (with and without antioxidants). Samples were analyzed initially and at four month intervals for: fatty acid composition, peroxide value, density and viscosity. Results favored underground storage, plastic-lined containers and the use of 0.5% butylated hydroxy toluene as an antioxidant.

A study performed at the University of Idaho by Korus (1983) and continued by Jo (1984) involved neat vegetable oils as fuels. Oil deterioration was measured as a function of storage conditions (aerobic and anaerobic at room temperatures) and vegetable oil composition (fatty acid saturation vs. unsaturation). Parameters measured at six month intervals over a two year period were peroxide values and fatty acid profiles. Engine testing was also performed using the stored oils to test injector coking as a function of fuel deterioration. Fuels tested were 50/50 blends of winter rapeseed, linoleic safflower and oleic safflower with diesel fuel and 100% 2-D as a reference. All vegetable oil fuel blends gave a statistically significant ($\alpha<0.05$) increase in carbon deposits relative to diesel fuel with linoleic safflower having an injector coking area of 7.57 cm^2 relative to diesel fuel, 50% oleic safflower 5.01 cm^2 and 50% winter rapeseed 3.93 cm^2. Results indicated that deterioration was reduced by anaerobic storage and by high levels of saturated fatty acids in the oil.

OBJECTIVES

1. Produce batches of RME and REE and characterize their properties according to ASAE EP552.

2. Store triplicate sets of vented glass and steel containers of RME and REE in flammable solvent storage cabinets at both inside and outside ambient temperatures.

3. Analyze fuel properties (peroxide value, acid value, density, viscosity, and heat of combustion) from each storage container every 3 months for a 24 month period and compare with the initial values.

4. Compare two year stored RME and REE in short term engine performance tests with new RME and REE.

MATERIALS AND METHODS

Fuel Preparation

Thirty five gallons of each fuel (RME and REE) were made at the beginning of the study. Samples of each fuel were taken for triplicate determinations in all of the 5 test procedures at the beginning of this test and at each 3 month interval thereafter.

The Biodiesel fuels were processed in a batch type reactor. The methyl ester process utilizes 100 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 potassium hydroxide (KOH) was used. Table I shows the equations used for the quantities of methyl ester processed.

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 on the amount of input oil by weight, 1.3 percent of KOH was used. Table I also shows the equations used for quantities of ethyl esters processed.

Table I. Equations for Processing Methyl and Ethyl Ester Fuels.

Methyl Ester Process

$$MeOH = 0.225 \times Oil \qquad KOH = Oil / 100$$

where;   Oil = desired amount of oil in liters (L)
                  MeOH = amount of methanol needed in L
                  KOH = amount of potassium hydroxide (kg)

Ethyl Ester Process

$$EtOH = 0.2738 \times Oil \qquad KOH = Oil / 85$$

where;   Oil = desired amount of oil in liters (L)
                  EtOH = amount of ethanol needed in L
                  KOH = amount of potassium hydroxide (kg)

The transesterification procedure used has been reported in several other University of Idaho reports (Peterson et al., 1990; Peterson et al., 1995).

Storage Containers

Fuel containers for the study were: 4-liter brown glass reagent bottles and 8-liter steel pails with crimp on lids. All containers were filled 3/4 full and vented to the atmosphere to simulate actual fuel storage. The study used triplicate samples of two esters, RME and REE, each fuel was arranged in four different configurations: glass and steel containers stored at

room temperature (inside) and at the local outside ambient temperature (outside) for a total of 24 samples.

Fuel Analysis

After each three-month storage period samples were analyzed according to the following procedures (AOCS, 1987; ASTM, 1991).

Property	Procedure
Peroxide Value	AOCS Cd 8b-90
Acid Value	ASTM Test D974
Density	ASTM Test D1298
Viscosity	ASTM Test D445
Heat of Combustion	ASTM Test D240

The fuels were characterized initially and after the two year storage study by evaluating the parameters in ASAE EP552. The tests for specific gravity, viscosity, cloud point, pour point, flash point, heat of combustion, total acid value, peroxide value, catalyst, and fatty acid composition were performed at the Analytical Lab, Department of Biological and 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 by Phoenix Chemical Labs, Chicago, Illinois.

Short Term Engine Tests

Each of the 24, one gallon samples from the storage study were combined into two large REE and RME samples, respectively, for use in the short term engine testing. New batches of REE and RME were produced for comparative purposes. Phillips 66 low sulfur number two diesel fuel (2-D) was used in this study as a reference. The test engine was a John Deere (4239T) direct-injection, turbocharged diesel. This is a four cylinder engine with a bore of 106 mm, a stroke of 110 mm, a displacement of 3.917 L and a compression ratio 16.2:1. It has a high RPM of 2650, with 61 kW (82 HP) at 2500 RPM and 290 N•m (214 lbf•ft) of torque at 1500 RPM. Attached to the engine was a General Electric 119 KW (159 HP) cradle type dynamometer.

Two short term engine performance test procedures were performed. The first was a rapid engine test to measure injector fouling in diesel engines using vegetable oil fuels (Korus, 1985). For this test the engine was operated at maximum power and 2500, 2300, 2100, 1900, 1700, and 1500 revolutions per minute (RPM) for 10 minutes at each RPM. Readings of ambient air, opacity, exhaust, fuel, lube oil and intake air temperatures and opacity were acquired every 30 seconds. After each fuel test the injectors were removed and the carbonaceous tips were measured using machine vision. There was only enough fuel for one replication of this test.

The second test was a SAE torque test (SAE J1349, 1990). This test was performed under full throttle and full load conditions at 100 RPM intervals from 2600 to 1300 RPM. This test was replicated once also. Both test procedures were set up in random order. For more information on engine test procedures and equipment refer to (Hammond, 1996; Perkins et al., 1991).

Statistical Analysis

This experiment was set up as a randomized complete block with replication. Blocks were inside and outside. Treatments were fuels (RME and REE) and containers (glass and steel). Each fuel and container type were replicated 3 times for a total of 12 containers inside and 12 containers outside. Statistical analyses were performed with SAS (SAS Institute, Cary, NC). This consisted of a statistical analysis (ANOVA) followed by a Tukey multiple range procedure to separate the means for each of the parameters, peroxide value, acid value, density, viscosity, and heat of combustion.

In addition a regression model was formulated for each parameter by using SAS. Initially a multiple regression was run on each parameter against the variables container, location, time, location and time, time squared and fuel. The variables in the models were coded as shown in Table 2.

Table 2. Storage Variables

Container - Listed from 1 to 2, glass = 1, metal = 2
Location - Listed from 1 to 2, inside = 1, outside = 2 (inside temp = 70°F, outside temp varied from 34°F to 72°F)
Time - Listed from 1 to 9
Fuel Type - Listed from 1 to 2, RME = 1, REE = 2

RESULTS AND DISCUSSION

In the following discussion the nomenclature used is as follows: G=Glass, M=Metal, ME=Methyl Ester, EE=Ethyl Ester, I=Inside and O=Outside.

Peroxide Value
Peroxide values, measured in milliequivalents of peroxide per kilogram of sample for each sampling period, are shown in Figure 1. There was a consistent increase in peroxides over time with an acceleration of that increase from the 6th through the 18th month.

Peroxide values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated EE was significantly higher between inside and outside storage for peroxide values. ME showed no significant difference for interactions between fuel and location for peroxide values. There was a significant increase for peroxide from initial readings with ME after six months. EE showed a significant increase after three months.
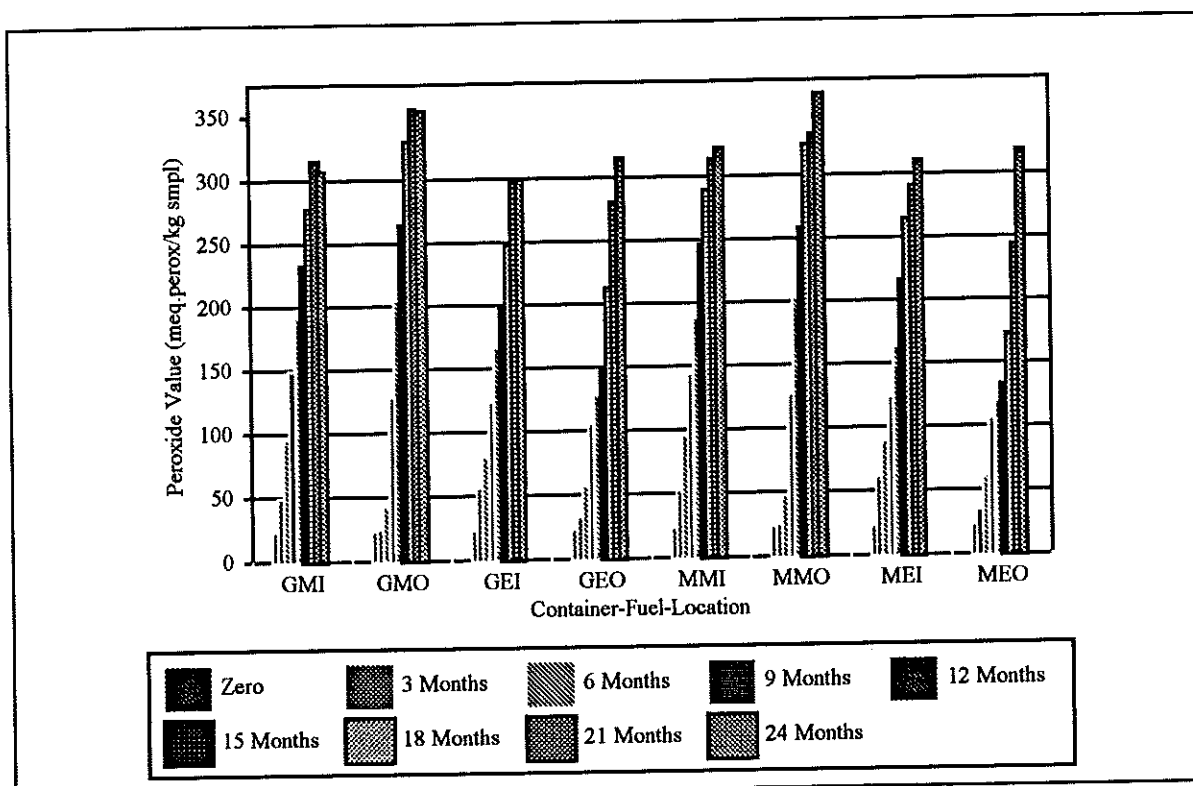
Figure 1. Peroxide value versus container type-fuel type-location for two years.

Figure 2 shows that after 6 months the peroxides in the RME increased at a faster rate than in the REE. Peroxide values at the outside location had a slower rate of increase than did the values at the inside location for the first six months (Figure 3). This was most likely due to an overall lower sample temperature during that time.

Figure 2. Peroxide value versus two year storage study for RME and REE.

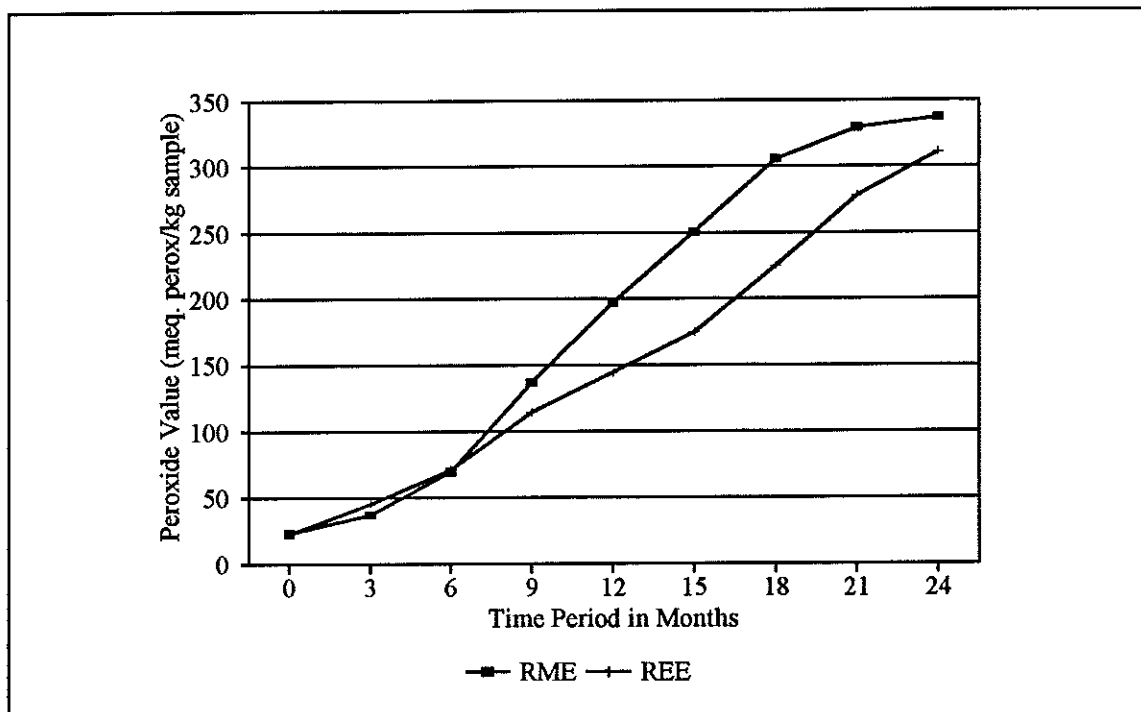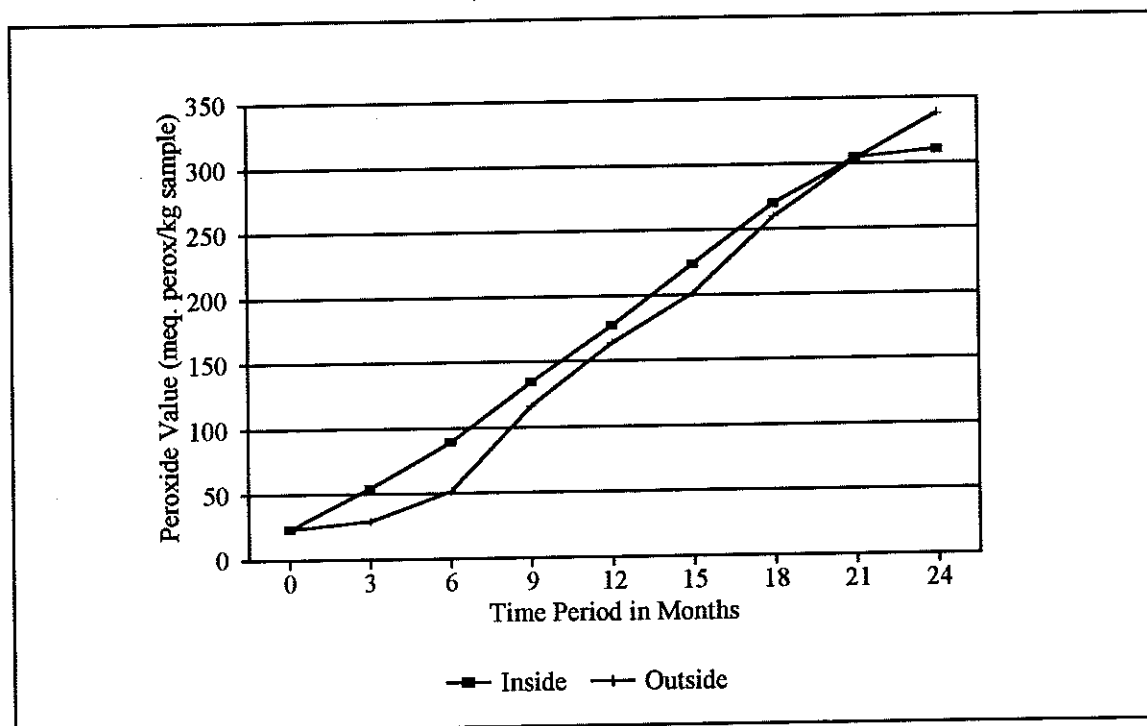**Figure 3**. Peroxide value for the two year storage period for inside and outside locations.

Table 3 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. A steady increase in Peroxide Value over time is observed. At 24 months the Peroxide Value was 14.5 times higher for RME and 13.7 times higher for REE compared to the beginning value. Fuel stored outside had a peroxide value 14.7 times higher while fuel stored inside was 13.5 times higher compared to the beginning value.

The best fit regression model for the change in Peroxide value were as follows:

$$P_{perox} = -30.906*loc - 33.41*fuel + 35.19*time + 3.95*loc*time + 61.624$$

The R^2 value for this equation is 0.94 using the values in Table 2.

This equation, over the 24 months, shows that fuel type affected Peroxide by a change of 33.41, each quarter of time increased peroxide by 35.19, outside location decreased peroxide value by 30.906, and there was a small location by time interaction.

Table 3. Results of ANOVA analysis for peroxide values on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

Peroxide Value (meq. peroxide/kg of sample)				
Sampling Period	RME Means	REE Means	Inside Means	Outside Means
Beginning	23.26 a	22.68 a	22.97 a	22.97 a
3 Months	37.27 ab	45.67 ab	54.15 b	28.80 ab
6 Months	69.63 c	71.25 bc	89.45 c	51.43 abc
9 Months	136.83 d	114.19 d	134.73 d	116.29 d
12 Months	197.13 e	144.33 de	177.33 e	164.13 de
15 Months	250.70 f	174.39 ef	223.75 f	201.34 ef
18 Months	305.59 g	224.42 g	270.06 g	259.95 g
21 Months	329.30 h	278.19 h	304.18 h	303.31 gh
24 Months	336.93 hi	310.88 i	309.97 hi	337.85 hi

* Numbers in the same column followed by the same letter of the alphabet are not significantly different (p<0.05).

Acid Value

The acid values (Figure 4), measured in milligrams of KOH per gram of sample, displayed the same trend as did the peroxide values. Since both of these values are related to autoxidation, the acid values naturally increase with an increase in peroxides because the esters first oxidize to form peroxides which then undergo complex reactions including a split into more reactive aldehydes which further oxidize into acids. Acids can also be formed when traces of water cause hydrolysis of the esters into alcohol and acids (Formo, 1979).

Acid values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated EE and ME had a significant difference between inside and outside storage for acid values. The effects of time on EE and ME show that after nine months, there was a significant increase in acid values from initial readings and the increase accelerated toward the end of the 24 month period.
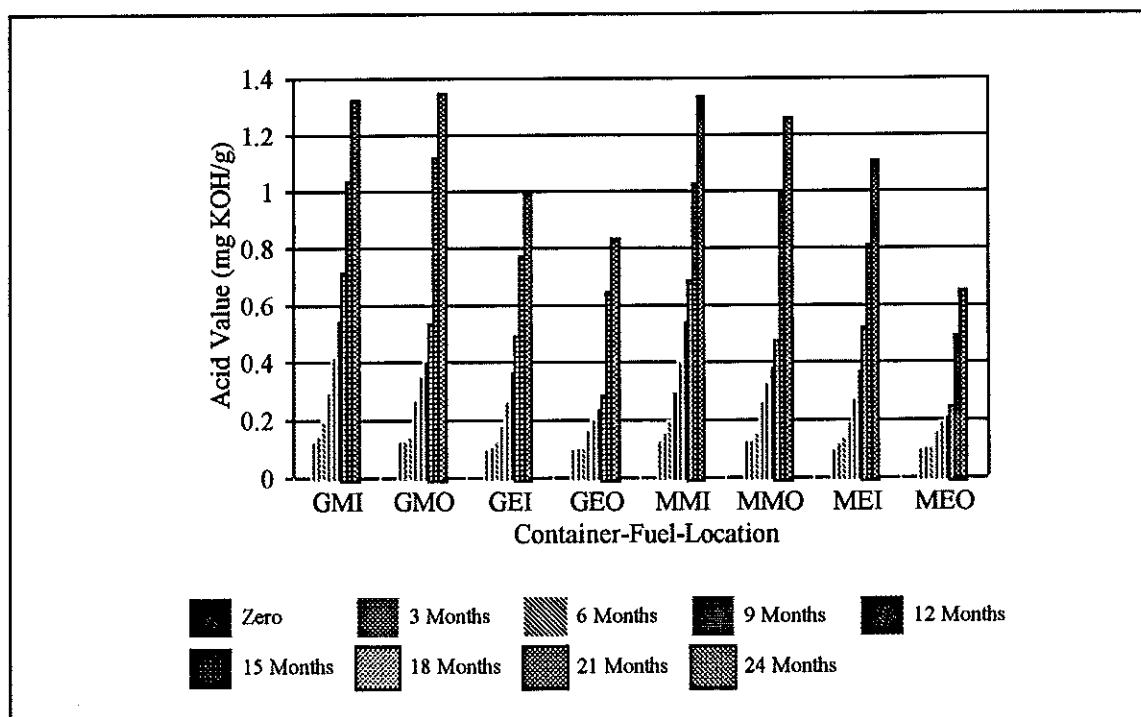

Figure 4. Acid value versus container type, fuel type, and location for two years.

Figure 5 shows acid value versus time for both RME and REE. The acid values were fairly constant for the first 6 months then took a significant upward trend. This is consistent with the hypothesis implied earlier that an accelerated increase in acid value is a natural progression of the oxidation process following an increase in peroxides. Supporting this statement even further is the fact that the RME acid values increased at a faster rate than the REE values after 6 months as was the case with peroxides. Figure 6 shows the acid value versus time for inside and outside samples. The acid value of the outside samples lagged behind the inside samples.
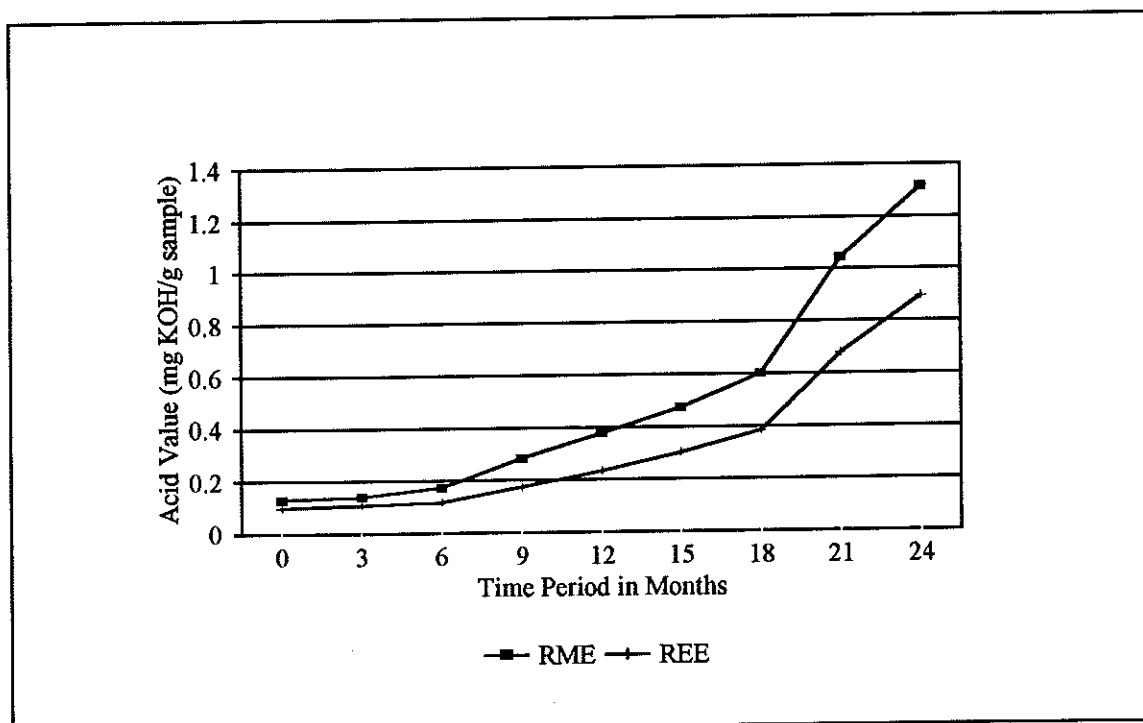
Figure 5. Acid value versus two year storage study for RME and REE.
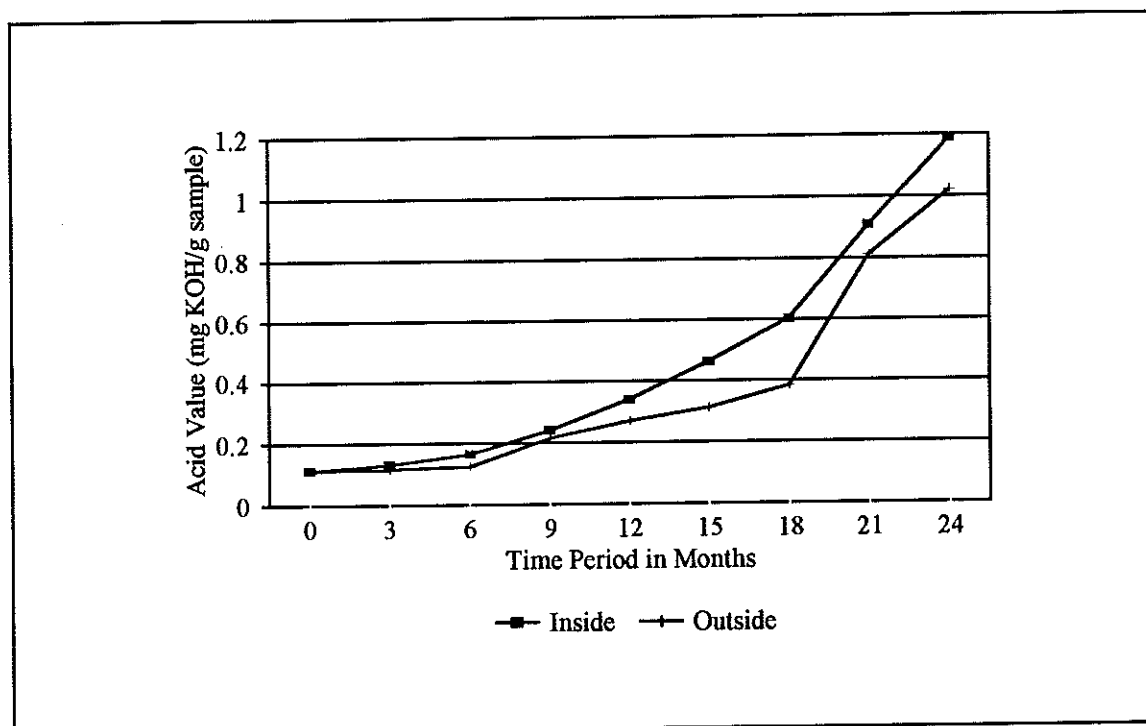

Figure 6. Acid value for the two year storage period for inside and outside locations.

Table 4 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. A steady increase in acid values over the 24 month storage time is noted.

At 24 months the acid value was 10.3 times higher for RME and 9.2 times higher for REE compared to the beginning values. Fuel stored outside had acid values 9.0 times higher while fuels stored inside had acid values 10.5 times higher compared to the beginning value. The best fit regression model for the change in acid levels was as follows:

$$P_{acid} = -0.064*time - 0.172*fuel - 0.0187*loc*time + 0.0209*time^2 + 0.473$$
The R^2 value for this equation is 0.93 using the values in Table 2.

This model shows a significant time to location interaction and a quadratic relationship for time. The acid value was -0.172 higher for fuel type (the negative sign indicates that REE was lower than the RME) and the outside samples had a 0.06 lower acid value than the inside samples.

Table 4. Results of ANOVA analysis for acid values on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

Acid Value (mg KOH/g of sample)				
Sampling Period	RME Means	REE Means	Inside Means	Outside Means
Beginning	0.128 a	0.097 a	0.113 a	0.113 a
3 Months	0.140 ab	0.108 ab	0.131 ab	0.116 ab
6 Months	0.173 abc	0.118 abc	0.165 abc	0.125 abc
9 Months	0.282 d	0.173 abcd	0.241 bcd	0.214 abcd
12 Months	0.377 e	0.233 cde	0.340 de	0.270 abcde
15 Months	0.472 f	0.301 ef	0.462 f	0.312 cdef
18 Months	0.601 g	0.385 fg	0.603 g	0.383 defg
21 Months	1.043 h	0.678 h	0.909 h	0.812 h
24 Months	1.315 i	0.894 i	1.183 i	1.021 i

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p<0.05$).

Density

It was found that the density of the esters (Figure 7) increased over time. Alcohol evaporation and polymerization could account for this phenomenon. Hydrolysis of the esters into acids and alcohols could have steadily liberated volatile alcohols that may have evaporated leaving a more dense product. Additionally, polymerization of the aldehydes could also result in an increase in the density of the fuel in storage.

Density values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated EE had a significant increase between inside and outside storage for density values. ME showed no significant difference for interactions between fuel and location for density values. The effects of time on ME show that after three months, there was a significant difference for density from initial readings. EE showed a significant difference after six months.
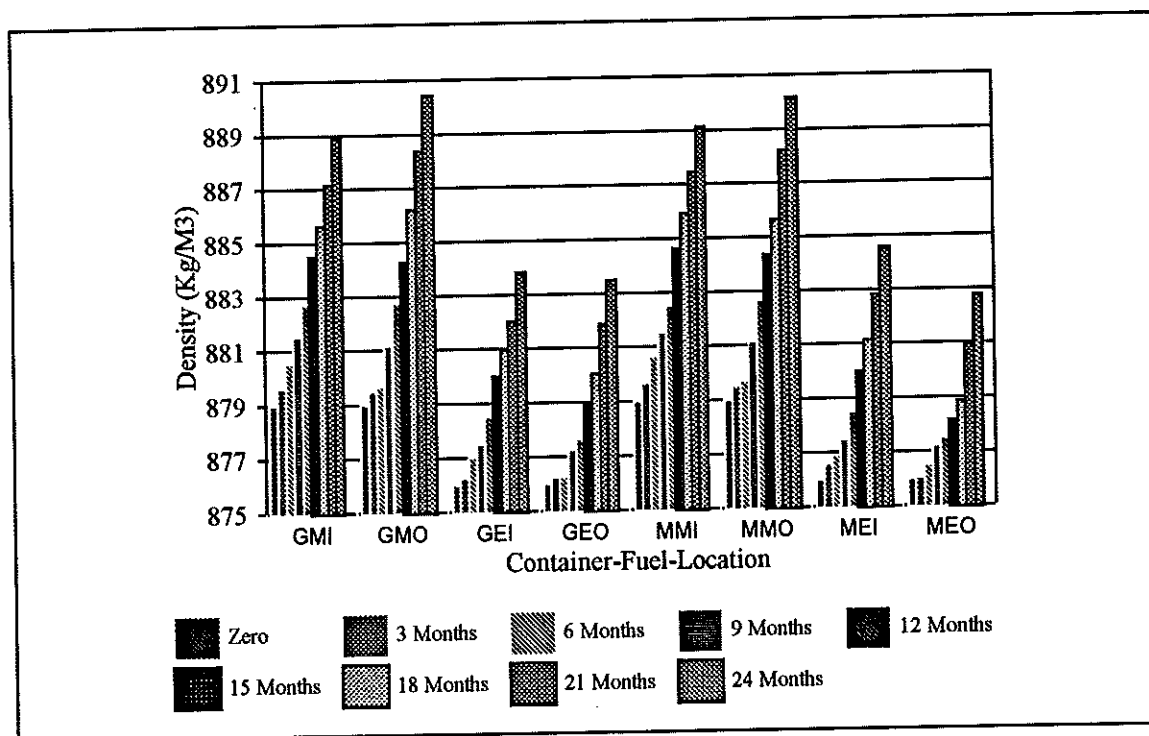

Figure 7. Density versus container type, fuel type, and location for two years.

Figure 8 shows density versus time for both RME and REE. The density of the RME at the beginning of the study was higher than that of REE and increased at a faster rate after 6 months. Significant differences were found among means from each sampling period with the exception of the density values of REE between 0 and 3 months. As can be seen in Figure 9, location was not a major influence in changing density values over time. Again the inside samples were higher than those of the outside samples. This may be accounted for by a lower outside temperature permitting less evaporation of the alcohol formed in the system due to hydrolysis. A significant difference was found only between the 0 and 12 month density readings for the inside samples.
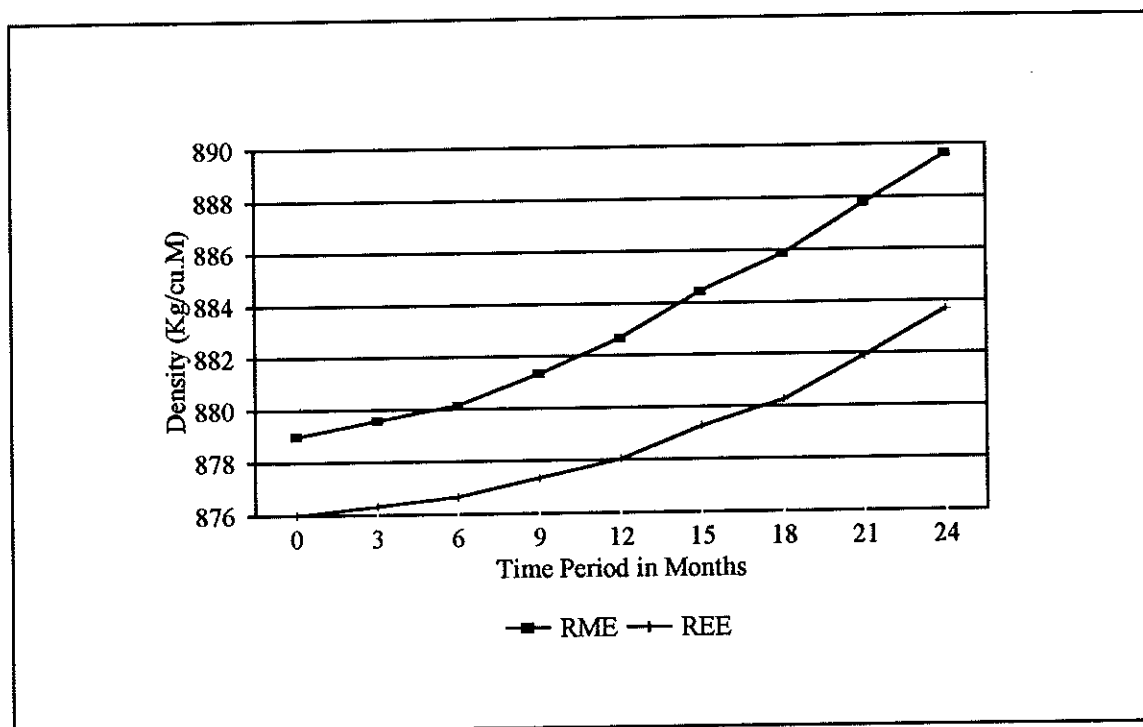

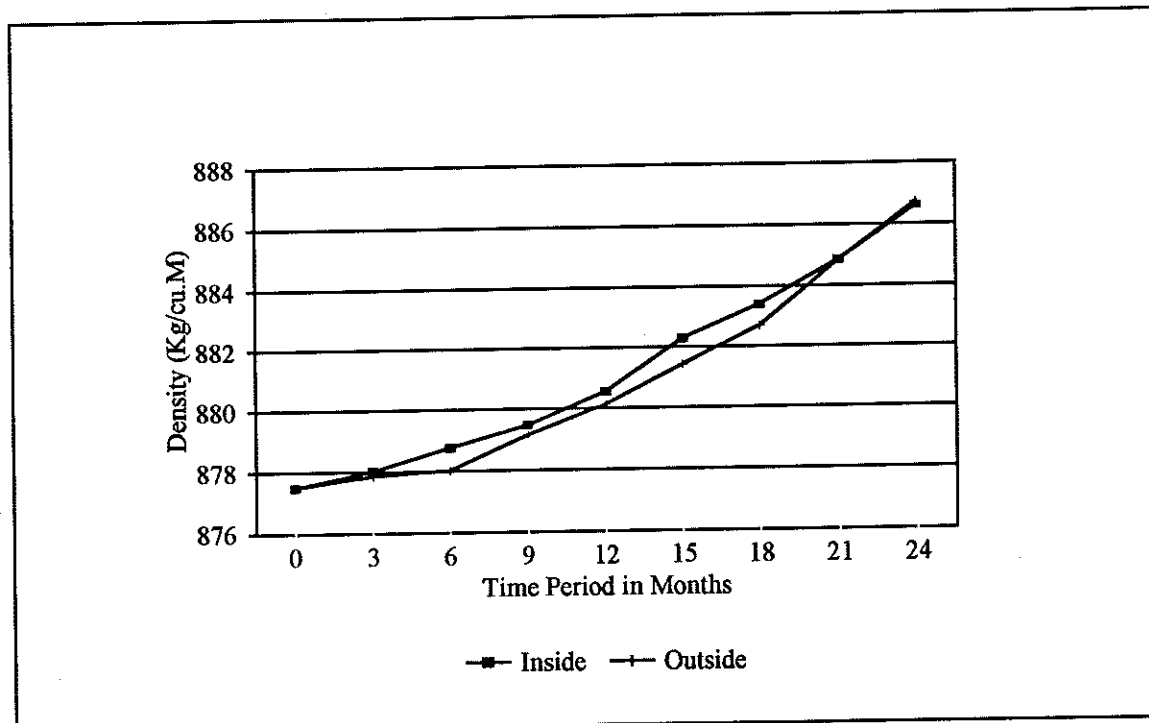**Figure 8**. Density versus two year storage study for RME and REE.

Figure 9. Density for the two year storage period for inside and outside locations.

Table 5 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. A 1.046% increase of density with time was noted. RME density increased 1.22% and REE density increased 0.88%. Fuel stored outside increased 1.048% and fuel stored inside 1.037%. The best fit regression model for the change in density values was as follows:

$$P_{den} = -0.4815*loc - 4.61*fuel + 0.114*time^2 + 885.28$$

The R^2 value for this equation is 0.966 using the values in Table 2.

The model shows a quadratic relationship for time. The density increment for fuel type was -4.61 (the negative sign indicates a lower density for REE than RME) and a -0.48 reduction in density for the outside stored samples.

Table 5. Results of ANOVA analysis for density on test data with groupings according to sampling period.

Density (Kg/M³)			
Sampling Period	RME Means	REE Means	Inside Means	Outside Means
Beginning	879.0 a	876.0 a	877.5 a	877.5 a
3 Months	879.5 b	876.3 ab	878.0 ab	877.9 ab
6 Months	880.1 c	876.7 abc	878.8 abc	878.0 abc
9 Months	881.3 d	877.3 cd	879.5 abcd	879.2 abcd
12 Months	882.7 e	878.0 de	880.6 bcde	880.1 abcde
15 Months	884.4 f	879.3 f	882.3 def	881.4 cdef
18 Months	885.9 g	880.2 g	883.4 fg	882.7 defg
21 Months	887.8 h	881.9 h	884.9 fgh	884.8 fgh
24 Months	889.7 i	883.7 i	886.6 hi	886.7 hi

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p<0.05$) according to the Tukey Multiple Range Procedure.

Viscosity

Viscosity tended to increase over time (Figure 10) however the outside samples tended downward during the first half of the study before going up. This could be due in part to the lower average temperatures of the outside samples during the early period. Viscosity values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated EE had a significant difference between inside and outside storage for viscosity values. ME showed no significant difference for interactions between fuel and location for viscosity values. The effects of time on EE and ME show that after 24 months of storage, there was a significant difference for viscosity from initial readings.
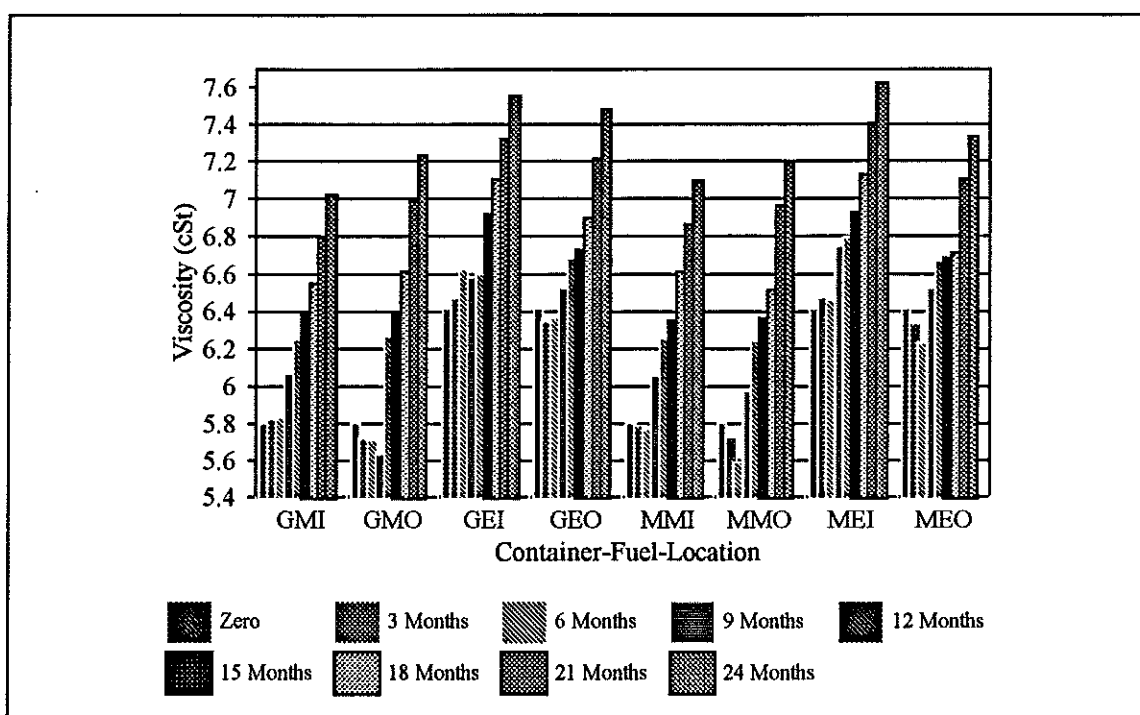

Figure 10. Viscosity at 40°C versus container type, fuel type, and location for two years.

The viscosity of REE (Figure 11) started out about 10% higher than that of RME but after a year of storage was only 5% higher. It can be seen from table 5 that RME experienced a significant rise in viscosity after 6 months of storage and continued to rise significantly over the 9 to 24 month periods. REE stayed fairly constant for the first 12 months and then increased at about the same rate as RME for the final 12 months.
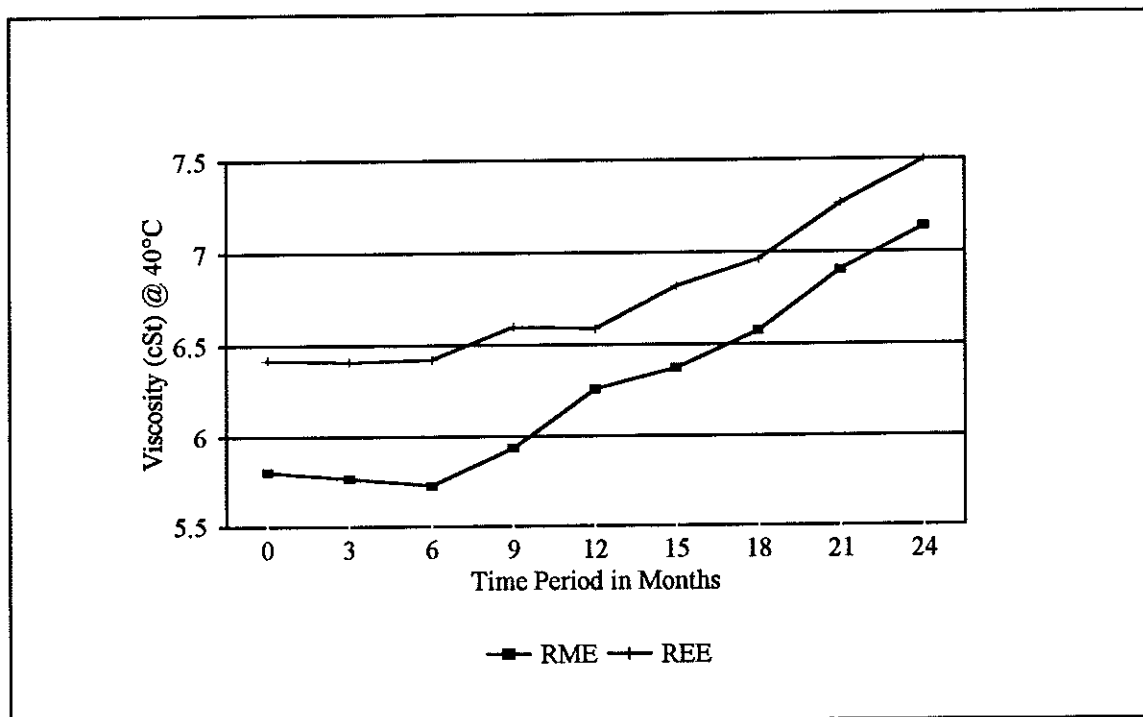
Figure 11. Viscosity at 40°C versus two year storage study for RME and REE.
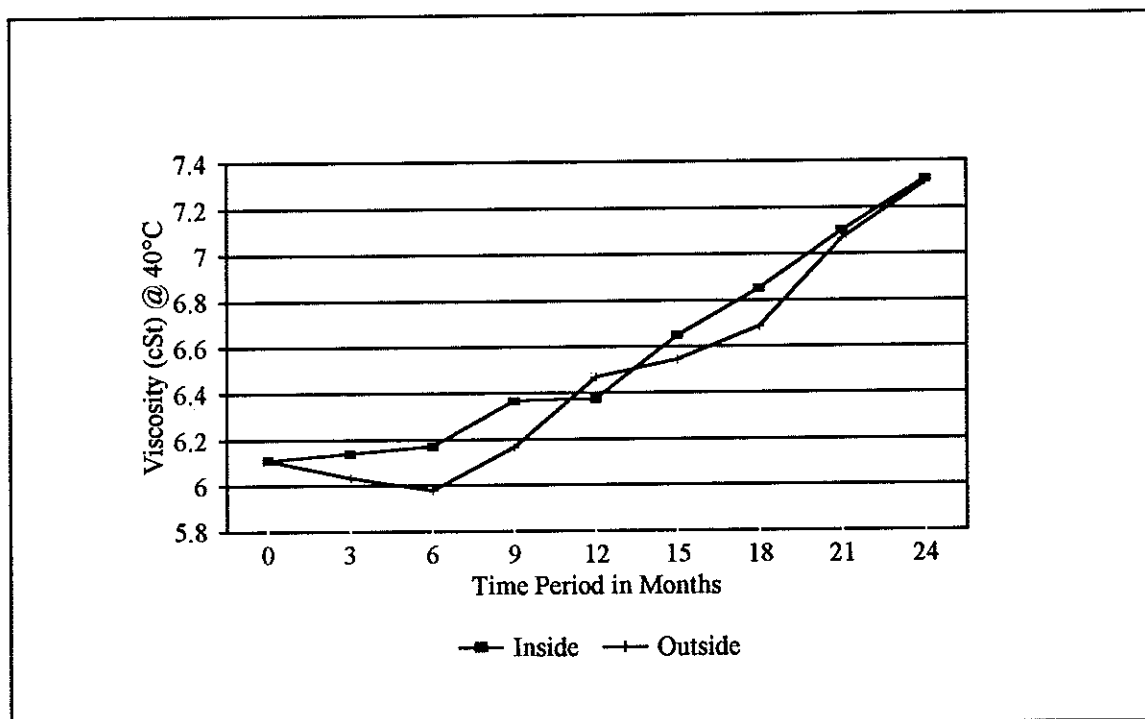

Figure 12. Viscosity at 40°C over the two year storage period for inside and outside
locations.

Table 6 represents the results of ANOVA analysis on test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. The viscosity of RME increased 23.1% and viscosity of REE 16.8% over the 24 months. Inside and outside samples had nearly identical 19+% increases. The best fit regression model for the change in viscosity was as follows:

P_{visc} = -0.0807*loc + 0.0394*time + 0.5006*fuel + 0.0198*time^2 + 5.46
The R^2 value for this equation is 0.91 using the values in Table 2.

The model shows viscosity was 0.08 cSt lower for outside stored samples, the effect of fuel type changed viscosity by 0.5 cSt (REE higher than RME) and a quadratic effect of time.

Table 6. Results of ANOVA analysis for viscosity on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

Viscosity (cSt)				
Sampling Period	RME Means	REE Means	Inside Means	Outside Means
Beginning	5.80 a	6.42 a	6.11 a	6.11 a
3 Months	5.76 ab	6.41 ab	6.14 ab	6.03 ab
6 Months	5.73 abc	6.42 abc	6.17 abc	5.98 abc
9 Months	5.93 ad	6.60 abcd	6.37 abcd	6.17 abcd
12 Months	6.26 e	6.59 abcde	6.38 abcde	6.47 de
15 Months	6.37 ef	6.82 df	6.65 def	6.54 ef
18 Months	6.57 g	6.96 fg	6.86 fg	6.69 efg
21 Months	6.91 h	7.26 h	7.10 gh	7.07 h
24 Months	7.14 i	7.50 i	7.33 hi	7.31 hi

* Numbers in the same column followed by the same letter of the alphabet are not significantly different (p<0.05).

Heat of Combustion

The values for heat of combustion (Figure 13) tended to decrease over time. This was most likely due to the breakdown of the fuel by oxidation which was verified by the increase in the peroxide and acid values.

Heat of combustion values for either fuel were not significantly affected by the type of container. Statistical analysis of the interactions between fuel and location indicated EE had a significant difference between inside and outside storage for heat of combustion values. ME showed no significant difference for interactions between fuel and location for heat of combustion values.
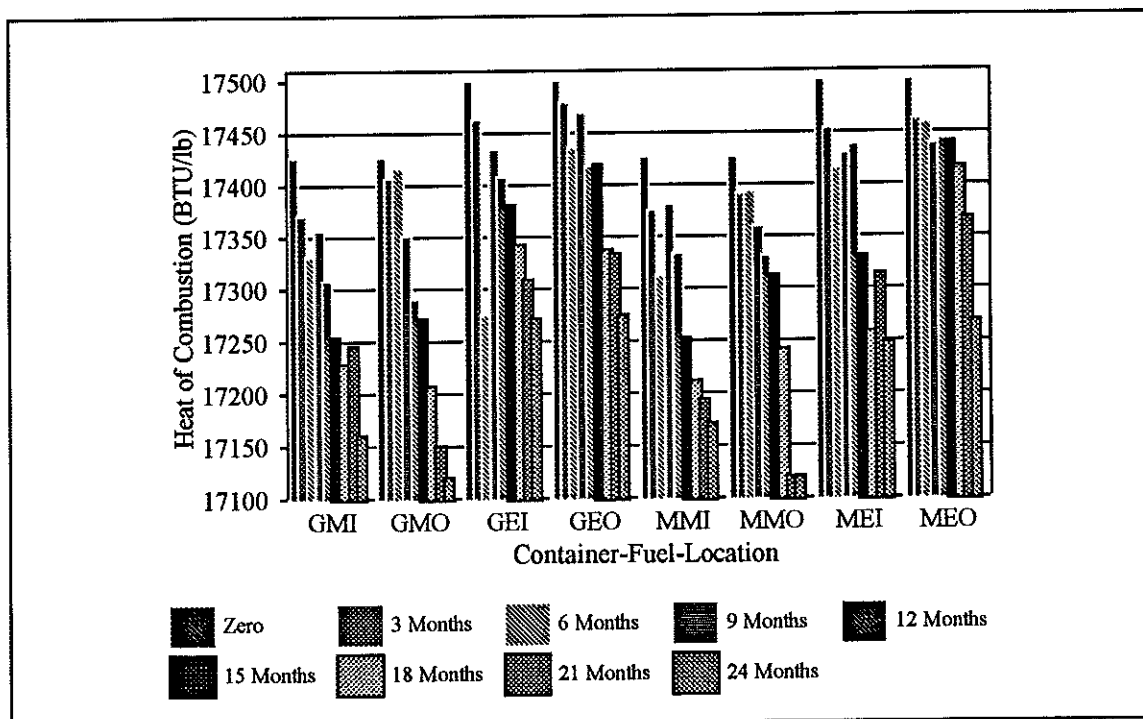

Figure 13. Gross heat of combustion versus container type, fuel type, and location for two years.

Figure 14 shows a decline in the heat of combustion of the two fuels with the exception of REE between month 6 and 9. From Table 6 it can be seen that heat values for RME at 12 months were significantly lower than values at both 0 and 3 months. The REE heat of combustion values on the other hand showed a significant drop at 6 months which corresponds with a rise in the other four parameters at 6 months, however it then increased at 9 months although not significantly. The final reading at 24 months was significantly lower than the beginning value for heat of combustion.
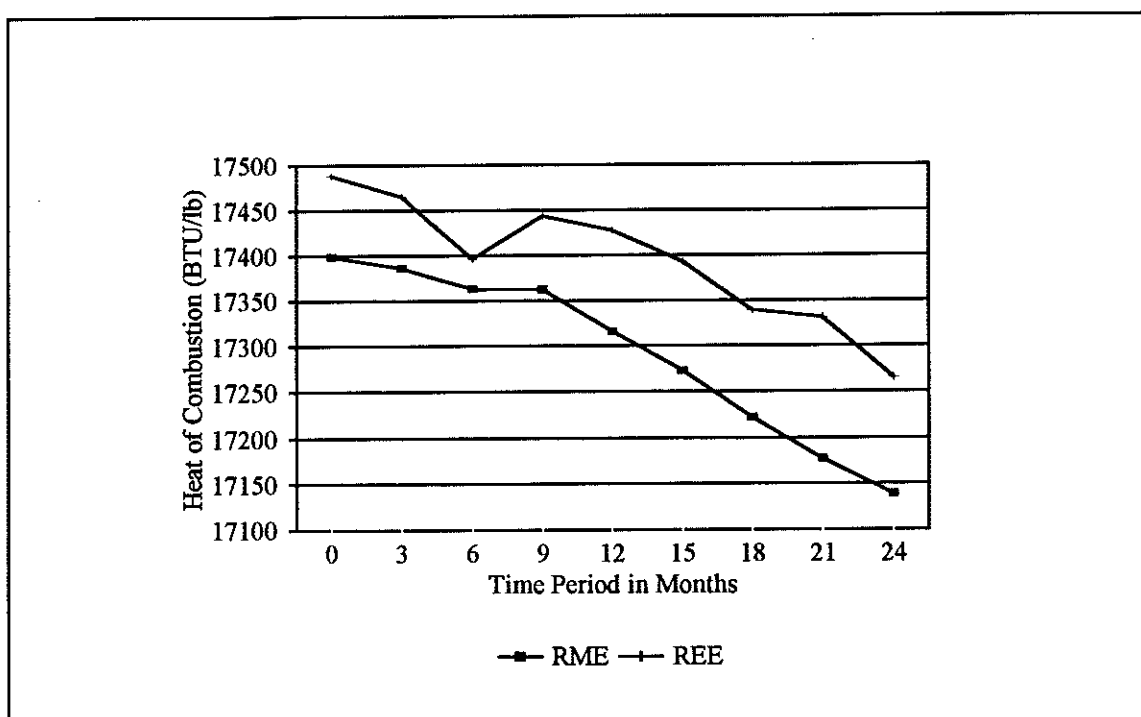

Figure 14. Gross heat of combustion versus two year storage study for RME and REE.
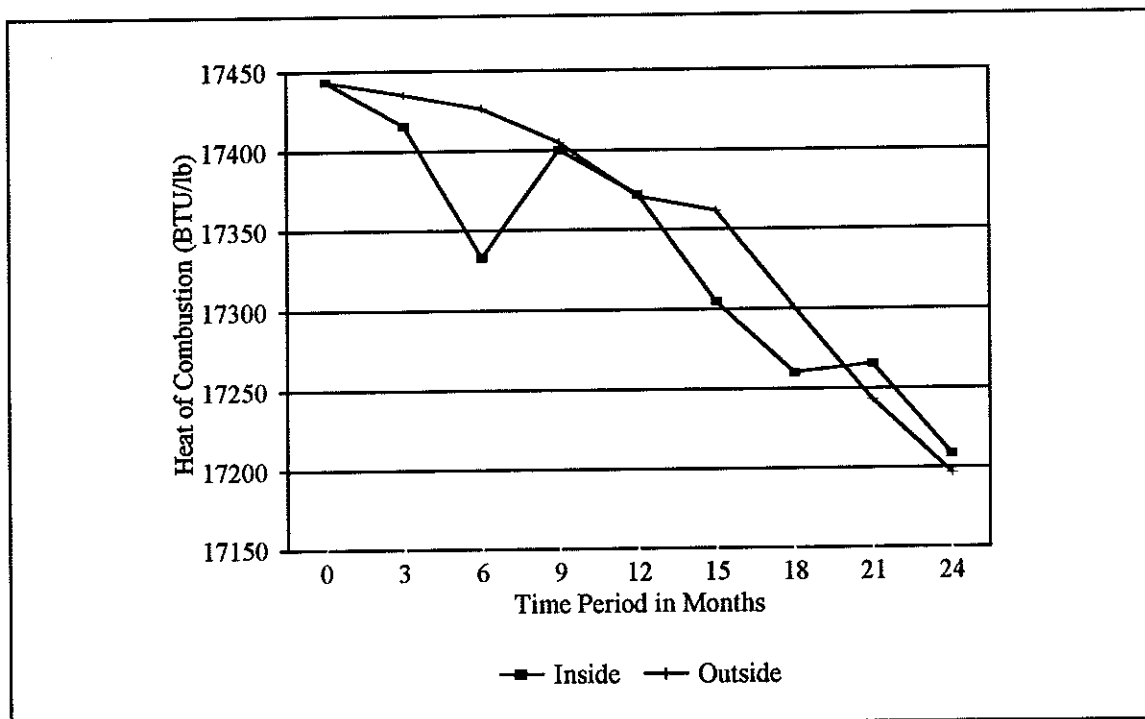
Figure 15. Gross heat of combustion for the two year storage period for inside and outside locations.

Table 7 represents the results of ANOVA analysis on heat of combustion test data over time with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among group means. Heat of combustion declined about 1.4% over the 24 months of storage. RME declined 1.50% and REE 1.27%. Inside and outside samples declined at about the same 1.4% rate. The best fit regression model for the change in heat of combustion was as follows:

$$P_{HoC} = 19.94*loc + 101.231*fuel - 2.89*time^2 + 17254$$

The R^2 value for this equation is 0.747 using the values in Table 2.

The model shows a quadratic change in heat of combustion with time, 101.2 Btu/lb less energy for RME than for REE and 19.94 Btu/lb more energy for samples stored outside compared the inside stored samples.

Table 7. Results of ANOVA analysis for heat of combustion on test data with groupings according to sampling period. The Tukey multiple range procedure was used to find differences among groups.

Heat of Combustion (BTU/lb)				
Sampling Period	RME Means	REE Means	Inside Means	Outside Means
Beginning	17399 fghi	17488 efi	17444 efhi	17444 defghi
3 Months	17386 fgh	17465 efh	17416 efh	17435 defgh
6 Months	17363 efgh	17396 bcdefg	17333 bcdefg	17426 defg
9 Months	17362 efg	17444 def	17401 ef	17405 cdef
12 Months	17315 de	17427 de	17372 de	17371 cde
15 Months	17273 cd	17393 bcd	17305 bcd	17362 cd
18 Months	17222 bc	17339 bc	17260 abc	17301 abc
21 Months	17178 ab	17331 ab	17266 ab	17243 ab
24 Months	17139 a	17266 a	17208 a	17197 a

* Numbers in the same column followed by the same letter of the alphabet are not significantly different ($p < 0.05$).

Fuel Characterization

Table 8 is the fuel characteristics for the initial and two year stored fuel. The SREE and SRME are the REE and RME fuels, respectively, stored for two years.

Table 8. Fuel Characterization Data

	REE	SREE	RME	SRME
Fuel Specific Properties				
Specific Gravity, 60/60	0.8760	0.8837	0.8790	0.8897
Viscosity, cSt @ 40°C	6.42	7.50	5.80	7.14
Cloud Point, °C	-2	0	0	1
Pour Point, °C	-10	-9	-15	-15
Flash Point, °C	170	148	179	148
Boiling Point, °C	273	254	347	271
Water and Sediment, % Vol.	<0.005	<0.005	<0.005	<0.005
Carbon Residue, % mass	0.06	0.12	0.08	0.07
Ash, % mass	0.002	0.011	0.002	0.003
Sulfur, wt%	0.014	0.008	0.012	0.009
Cetane Number	64.9	>72.7	61.8	>72.7
Heat of Combustion, Gross, MJ/kg	40.51	40.16	40.54	39.86
Copper Corrosion	1A	1A	1A	1A
Karl Fischer Water, ppm	761	949	757	1077
Particulate Matter, mg/L				
Total	1.9	48.45	1.1	57.00
Non-Combustible	0.9	8.10	<0.1	2.05
Elemental Analysis				
Carbon, %	76.83	78.85	78.7	77.76
Hydrogen, %	11.8	12.49	12.66	12.49
Oxygen, % (by difference)	11.36	8.64	9.22	9.74
Iodine Number	96.7	90.1	91.9	93.9
Peroxide Value	22.68	310.88	23.26	336.93
Acid Value	0.097	0.894	0.128	1.315

The cetane number increased more than 12%, viscosity increased more than 16%, and particulate matter all increased during storage as did the peroxide value. The increase in peroxide value is due to the oxidation of the double bonds.

From test results the following trends emerged: In general no effect was found for container type. Test values compare very closely for both metal and glass containers. Significant differences were, however, found in the values for the 5 parameters for both fuel type and storage location with the passage of time. For both fuels the peroxide and acid values, density, and viscosity tended to increase over time. The heat of combustion, on the other hand, tended to decrease slightly over time. Fuels tended to degrade at a slightly faster rate,

particularly as indicated by the peroxide and acid values, at the indoor location. This was evidently due to the higher average temperature at the indoor location.

Initially, and over the 24 month storage period, properties of the two fuels displayed slightly different values. The ethyl esters were higher in viscosity and heat of combustion, but lower in density, peroxide and acid values than the methyl esters. Over time, degradation occurred at a different rate for the two fuels. The RME increased in peroxide value, acid value, and density at a faster rate than did the REE.

Short Term Engine Tests

<u>Coking Tests</u>

Figure 16 shows the injector tip coking index for the 2-D, new RME and REE, and the stored RME and REE fuels. Dividing each of the fuels coking area by the diesel coking area gives the injector tip coking index. The coking on the injector tips for the stored fuels was 7.8% more for RME and 2.8% more for REE. The coking observed for RME in this test was extremely low and for REE was at or below other tests for Biodiesel reported by the authors recently. The effect due to storage was extremely small in both cases.
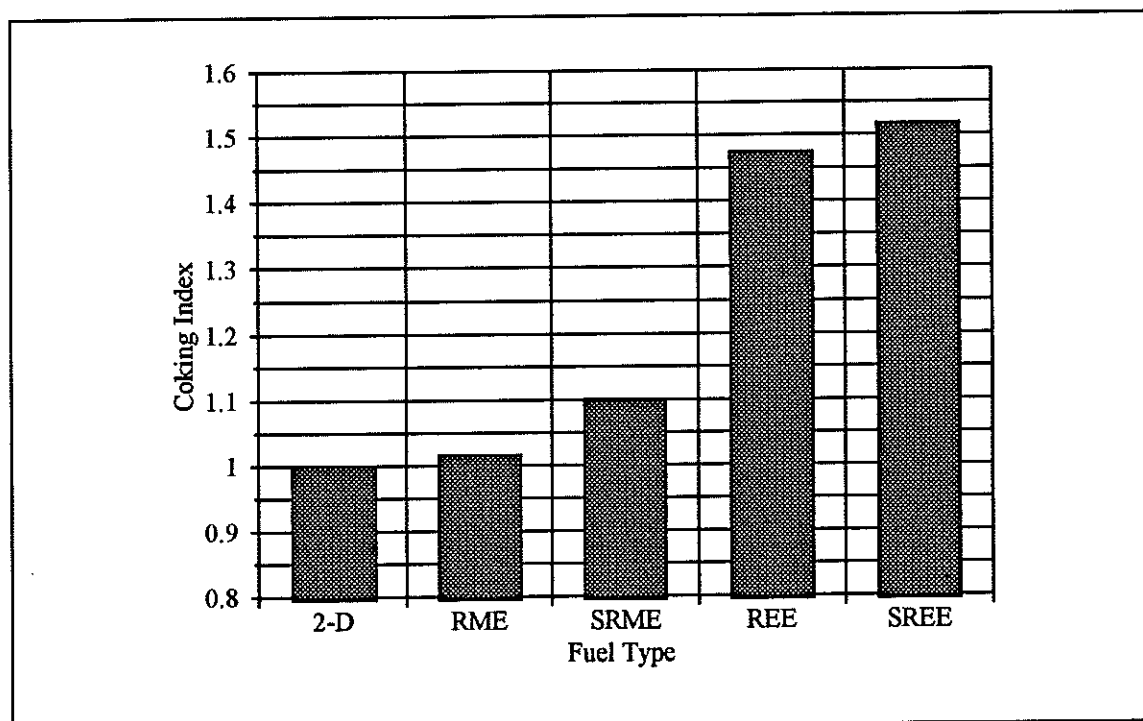
Figure 16. Injector coking for the new and stored fuels and 2-D.

Fuel economy was also taken from this data set. Figure 17 shows the fuel economy for each of the five fuels tested. At 1500 RPM the stored RME used 1.13 percent more fuel than did the new RME and the stored REE used 1.2 percent more fuel than the new REE.
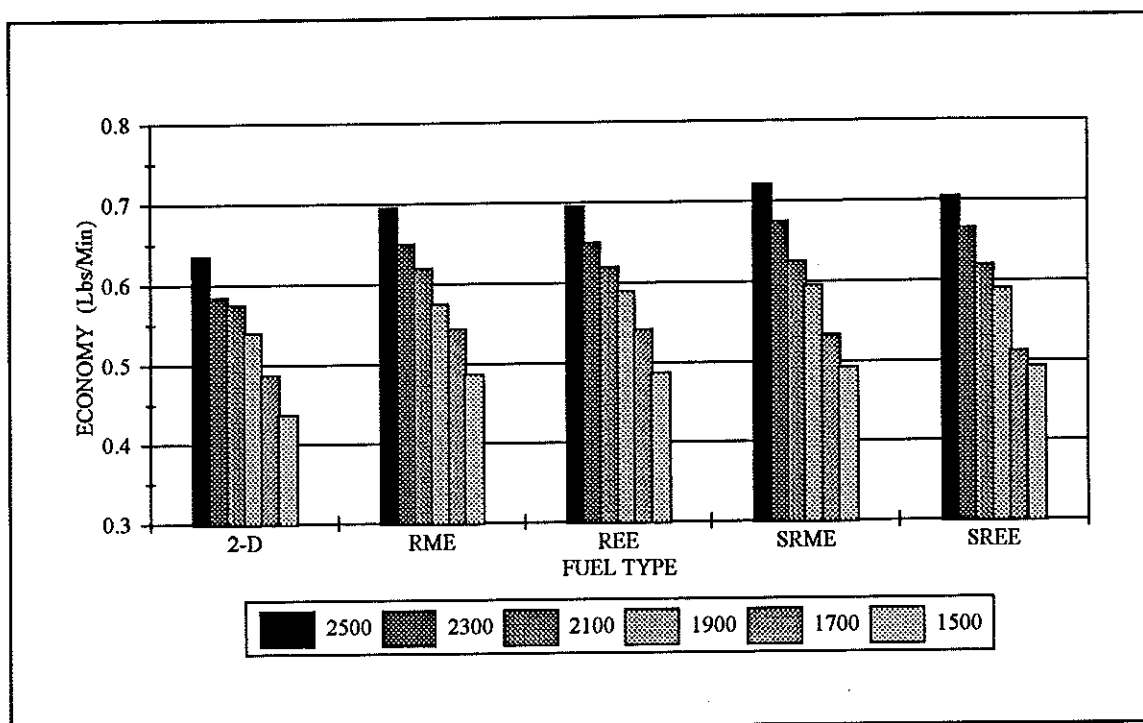

Figure 17. Fuel Economy from the fuel storage test at six different RPM's.

<u>Torque Tests</u>

Power and torque are plotted on Figure 18. At maximum power output the fuel stored for two years increased 1.9% for REE and 1.5% for RME. At maximum torque output the stored fuels had a 0.9% increase. The new fuels had 3.4% less power than 2-D at maximum power and 1.4% less torque than 2-D at peak torque RPM. Differences between stored and non-stored fuels were small.
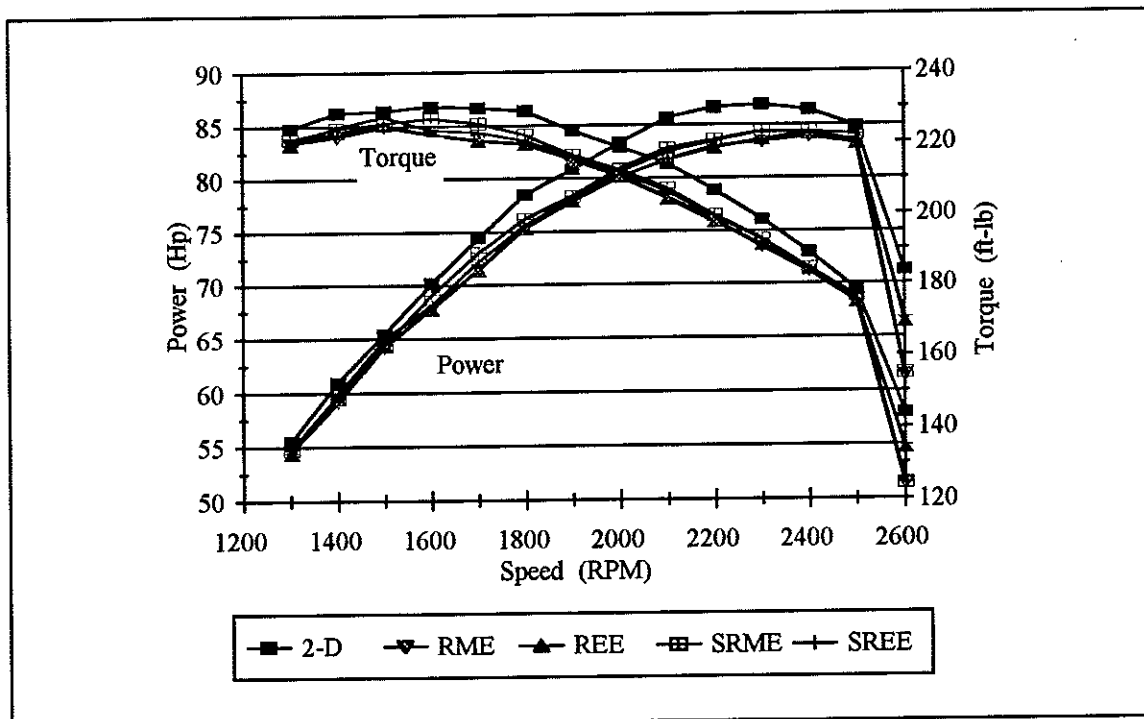

Figure 18. Power and Torque plotted against engine speed for five fuels.

<u>Smoke Density</u>
Smoke density (Figure 19) for the Biodiesel fuels varied from 1.7 to 3.6 times less than that of 2-D. The smoke density for the stored REE was 1.175 times more that of the new REE and the stored RME produced 3% less smoke than the new RME.
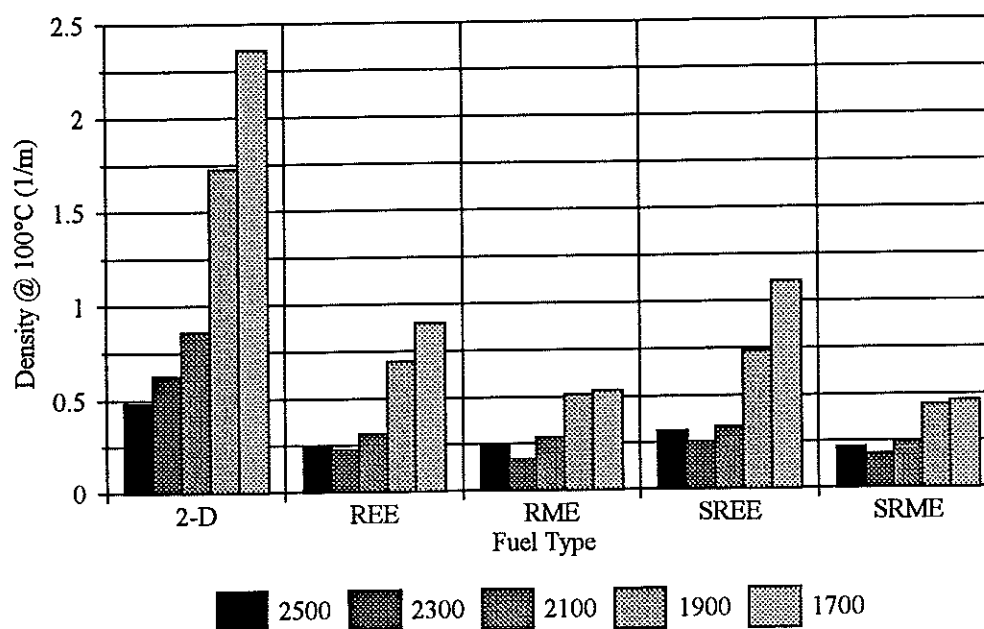

Figure 19. Smoke density at the standard temperature of 100°C for five fuels at five different RPM's.

CONCLUSIONS

According to test results from this 24 month study of rapeseed methyl and ethyl esters, there was a slight deterioration of the fuel over time. Oxidation occurred resulting in an increase in peroxide and acid value with a subsequent drop in heat of combustion. Other values that increased over time were viscosity and density. The container type had no effect on fuel storage, however, indoor samples degraded at a somewhat faster rate than did the outdoor samples. This can be accounted for by the higher overall average temperature of the indoor samples.

1. Peroxide values were increased 14.5 times for RME and 13.7 times for REE after 24 months compared to the beginning values.

2. Acid values were increased 10.3 times for the RME and 9.2 times for REE after 24 months compared to the beginning values.

3. Density increased 1.22% for RME and 0.88% for REE after 24 months compared to beginning values.

4. Viscosity increased 23.1% for RME and 16.87% for REE after 24 months compared to the beginning values.

5. Heat of Combustion declined 1.50% for RME and 1.27% for REE after 24 months compared to the beginning values.

6. The cetane number increased on the average from 63.4 to more than 72.7 and particulate matter increased on the average from 1.5 mg/L to 52.7 mg/L during storage.

7. Regression models showed location effects (due to temperature differences in storage) for peroxide, density, viscosity and heat of combustion.

8. Regression models showed second order time effects for acid value, density, and viscosity.

9. In general outside samples stored slightly better than indoor samples. It was noted that during the fall and winter the change in samples stored outdoors was less than those inside. In the summer when outside temperatures were higher the changes were more equal.

10. The short term engine tests, including torque, power, and fuel economy, and coking test showed very small amounts of change between the stored fuels and the new fuels. The high peroxide and acid values of the stored fuels had little effect on the performance of the engine in short term tests. Long term durability tests would be the next step needed to determine if these changes affect engine life. The small amount of fuel stored in this study precluded such testing.

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