Oxidative properties of lubricants using thermal analysis

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Abstract

The development of automotive lubricants requires optimization of a number of performance parameters of both base fluids and additive systems. The final test of a lubricant requires that it perform well in a particular application or system. Prior to the final selection of a lubricant, a number of combinations of base fluids and additives need to be evaluated. The most practical way to do this is through inexpensive bench testing. The use of pressurized differential scanning calorimeter (PDSC), thermal gravimetric analysis (TGA) and thin-film oxidation tests will be described in the evaluation of several lubricants. Examples of some practical applications of the thermal methods to the evaluation of alternative fuels and lubricants, and to studies involving extended drain lubricants are reported. Incompatibility of alternative fuels and lubricants can result in significant extraction of some additives. Thermal analysis shows significant variation in stability of the fractions obtained from simulated crankcase tests. Results from some of the methods are compared. © 2000 Published by Elsevier Science B.V.

Keywords: Lubricants; Oxidation; Thermal analysis; Alternative fuels; Thin-film methods

1. Introduction

Development of an automotive lubricant, or a lubricant for any mechanical system, is a lengthy and complicated process. Some of the key steps in the process are: selection of a base stock, evaluation of additives, evaluation of combinations of additives, and formulation of the lubricant with best trade-off in performance and cost. Finally, engine or full scale tests are required to determine the performance of final formulation in the actual system.

The first critical step in the process is the selection of the right base stock or base fluid. The base stock is an integral part of a lubricant system. It is the last line of defense in a mechanical system once the additives are depleted. Depending on the application, the finished lubricant usually contains over 80% base fluids. The remaining 20% or less is made up of additives to enhance the performance of the base fluid. Environ-mentally friendly fluids may contain 5% or less additives.

Most lubricant manufacturers utilize a variety of chemical and physical laboratory bench tests to evaluate the components and the base stocks in a lubricant. The structure, size, polarity and stability of the molecules in the base stock and additives have to be determined. This information coupled with the accumulated data on various components and mixtures over the years allows rapid formulation of lubricants. A key ingredient in this process of developing new lubricants has been the advancement in analytical instrumentation. Improvements in thermal analysis methods and technology are a prime example of the changes in the industry that allow rapid assessment of base stocks and additives while reducing the number of expensive full-scale tests.

Applications of thermal gravimetric analysis (TGA), pressurized differential scanning calorimetry

(PSDC) and some thin-film oxidation tests in some lubricant studies are described in this paper. However, the primary focus is on the use of several methods in assessing the effect of alternative fuels on engine lubricants.

2. Experimental methods

The methods used to research the properties of base fluids and additives include: TGA, PDSC, thin-film microoxidation tests and remaining useful life evaluation regime (RULER[TM]).

2.1. TGA

The application of this method to lubricants was reported by Hsu et al. at NBS in 1982 [1]. The method is useful in comparing the volatility of lubricants under thermal and oxidative conditions. The procedure used in previous studies included using 10 mg of fluid in an inert sample pan which was heated at the programmed rate of $10°C/min$ under a gas flow of 20 cc/min. The sample is run under nitrogen or argon and then the test is repeated using air or oxygen.

The TGA method can also be used to compare the volatility of additives by using a programmed temperature sequence to determine the rate of loss at incremental increases in temperature. This is referred to as the I^2TGA method.

The TGA methods are useful in the development of lubricants. Studies reported earlier [2,3] utilized the method to evaluate both base stocks and additives. However, the TGA method was not used in the study of alternative fuels.

2.2. PDSC

This method is widely used and one of the earliest applications to lubricant research was reported by Walker and Tsang [4]. PDSC applications are run either in an isothermal or a programmed temperature mode. There are a number of modifications of the methods in use. Variations include sample size, flow rates, temperature sequence and type of sample pan.

The PDSC has also been used to study oxidation stability of engine oils. A correlation of the PDSC and the thin-film oxygen uptake test (TFOUT) used to screen lubricants for ASTM IIID and IIIE automotive tests is reported in the literature [5,6].

2.3. PSMO

The Klaus Penn state microreactor is described in numerous publications [7–10]. The Penn state micro-oxidation (PSMO) test is a thin-film test using as little as 20 µl of test fluid in which volatility loss, oxidized product formation and deposits can be measured. In this study, 20 µl samples were run in an air atmosphere at $225°C$ for 30 min and the volatility and deposit formation measured.

2.4. RULER[TM]

This is an electrochemical voltametric method that was used in this study to confirm the findings of the PDSC and PSMO in the alternative fuel study. The method was developed by Kaufmann to predict the remaining useful life of aircraft turbine lubricants and is described in the literature [11,12]. Basically, a small sample, 200 µl, is dissolved in a solvent containing an electrolyte and the additive response is determined by use of a controlled voltage ramp through an electrode inserted into the mixture. This results in a peak at the oxidation potential of the additive evaluated. The peak height is related to the concentration of the additive in the sample.

3. Alternative fuel: lubricant study

Environmental issues have resulted in the use of alternative fuels, such as methanol in trucks, busses and cars. With the exception of formaldehyde, the alcohol fuels produce less chemically reactive emissions than gasoline. Renewed interest in methanol fuels resulted in revisiting some of the issues regarding the used of alternative fuels. Part of the overall study, the effect of several blended fuels on the lubricant is reported in this paper.

During the oil crisis in the early 1980's, there was a considerable effort to increase the use of alcohol fuels in modified heavy duty diesel truck engines and automotive engines [13]. The diesel fleet tests resulted in problems with injector plugging and increased friction and wear in some engines [14,15].

In a diesel engine, the crankcase lubricant is used to lubricate the bearings, piston-ring and liner components and the fuel injector system. In the crankcase, there is fuel contamination due to blow-by products and condensed methanol fuel was found to exceed 20% in some engines. In the fuel injector, there is interaction between large quantities of fuel and a small amount of lubricant.

Klaus and others researched the problem [16,17], and found that the alcohol preferentially extracted additives from the lubricant leaving the remaining raffinate more susceptible to oxidation. In the fuel injector, deposits were forming on the injector tips as a result of increased oxidation. In the crankcase, the additives were similarly extracted causing both increased oxidation and wear in the system. Two bench methods were developed to simulate the diesel engine problems with the alcohol fuels. The two simulation methods were used to study the alternate fuels in this paper.

The study involves an evaluation of six methanol fuels and two commercial lubricants. An evaluation of the effect of the fuels on the lubricants was performed using the two simulation tests. PDSC, PSMO and the RULER^{TM} methods were used to evaluate the changes in the lubricant performance.
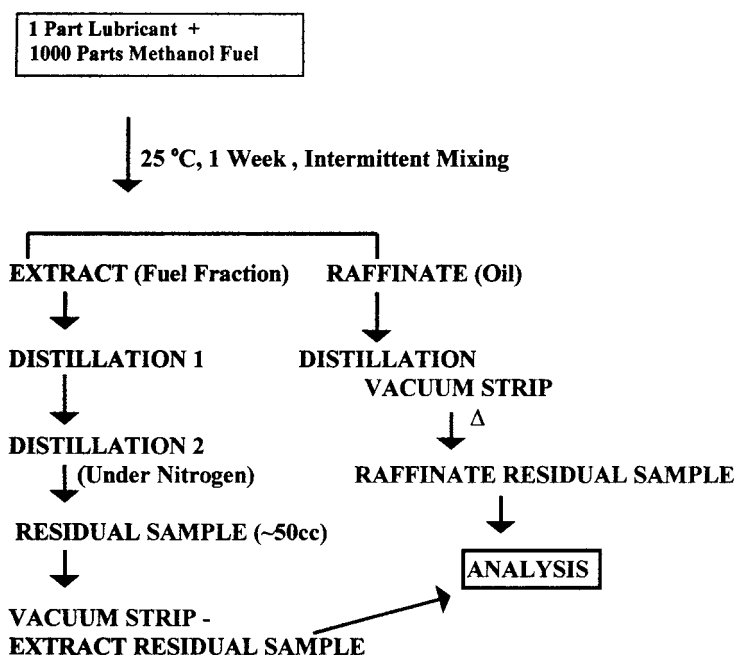
4. Fuels

A total of six fuels were evaluated. The fuels evaluated included methanol (M-100) and methanol with additives. Two additives were commercial additives used to reduce carbon deposit formation. Gasoline, light naphtha and iso-pentane were added to methanol and were the remaining fuel mixtures evaluated.
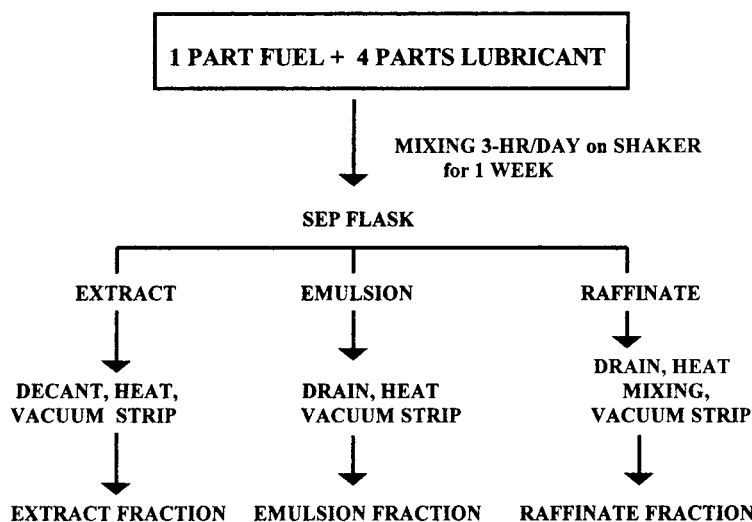
5. Lubricants

A commercial synthetic 10W30 Flex Fuel automotive engine oil, designated PRL 4723, and a commercial low ash 40 wt HDD (heavy duty diesel) engine oil, designated PRL 4713, were used in the study. Most work is with PRL 4713 due to difficulties in separating the emulsions formed with the synthetic oil.

6. Test methods

The analytical test methods were essentially the same as those described above. The samples analyzed were prepared using the two fuel contamination simulations, the fuel injector simulation (FIS, Scheme 1)

Scheme 1. Fuel injector simulation.

┌───┐
│ **1 PART FUEL + 4 PARTS LUBRICANT**   │
└───┘

**MIXING 3-HR/DAY on SHAKER
for 1 WEEK**

SEP FLASK

EXTRACT	**EMULSION**	**RAFFINATE**
DECANT, HEAT, VACUUM STRIP	**DRAIN, HEAT VACUUM STRIP**	**DRAIN, HEAT MIXING, VACUUM STRIP**
EXTRACT FRACTION	**EMULSION FRACTION**	**RAFFINATE FRACTION**

Scheme 2. Crankcase simulation.

and the crankcase contamination simulation (CCS, Scheme 2).

6.1. FIS

To simulate FIS situation in the laboratory, a 1000:1 fuel to oil mixture in a large flask was kept at 25°C in a water bath for a week with occasional mixing. The extract layer was carefully decanted and the alcohol removed by distillation. The remaining oil residue was transferred to a vacuum flask and any remaining fuel stripped off under vacuum with slight heating (70°C).

The raffinate layer remaining in the flask, along with a small emulsion layer, were also decanted and any fuel remaining stripped off. The sample was then poured into a vacuum flask and the remaining fuel removed.

The FIS results in an extraction fraction and a raffinate fraction that contains base oil and remaining additives from the original lubricant.

6.2. CCS

It was found from an evaluation of field samples that the crankcase dilution would often exceed 20% by weight and could go as high as 30%. The crankcase simulation (CCS) developed by Klaus et al. was to add 25 g of alcohol fuel to 100 g of the crankcase lubricant in a 500 ml flask. The flask was stoppered and the

mixture swirled for a couple of minutes by hand. The flask was stoppered and placed on a wrist action shaker and shaken for 1 h. This was repeated two more times a day for 7 days.

The mixture was decanted into a separatory flask and the layers allowed to separate. First, the raffinate or lubricant layer was carefully drawn from the bottom of the flask into a vacuum flask containing a magnetic stirrer. This was placed under vacuum with stirring and heated until all dissolved fuel was removed.

The 25 cc fuel layer on the top was then carefully decanted or aspirated from the flask. The fuel layer was then carefully evaporated under vacuum with slight heating. The residue was the extract and contained mostly additive.

The remaining layer in the flask was an emulsion layer that does not readily break after standing for days unless heated. The emulsion was drained from the flask and placed under a vacuum with slight heating to remove any excess fuel. The layer is high in additives.

7. Experimental fractions

7.1. FIS fractions

Some typical FIS simulations are found in Table 1. The total recovery of the sample is shown. Earlier work [17] indicated at lower oil to fuel ratios, the

Table 1
Injector simulation (FIS) extraction and recovery data

Fuel	Oil (g)	Fuel (cc)	Extract (g) (%)	Raffinate (g) (%)	Recovered (%)
PRL 4717 (40 wt HDD oil)					
M100 (methanol)	35.23	3500	6.17 (17.5)	29.8 (84.7)	103
M100	4.98	4500	1.48 (29.7)	3.61 (72.5)	102
M100+0.06% add A	4.58	5000	1.71 (37.3)	2.88 (62.9)	100
M100+0.12% add B	4.40	5000	2.59 (58.8)	2.27 (51.6)	110
PRL 4723 (FFV synthetic oil)					
M100 (methanol)	6.66	4500	2.06 (39.0)	4.05 (60.8)	100
M100+0.06% add A	9.61	4500	4.69 (45.6)	6.55 (68.1)	114
M100+0.06% add B	6.62	4500	–	4.12 (61.9)	–

extraction was not at its maximum. The 1:100 ratio test appears to verify with this oil.

In the FIS method, the fuel additives do affect the extract-raffinate split and the removal of the fuel under vacuum. This is due to the relatively large amount of additive present the high fuel to oil ratio. Even at a 0.1% concentration, the additive level in the fuel is about equal to the amount oil used in the test.

7.2. CCS fractions

Typical CCS data are found in Table 2. The recovery is better than that found in the FIS due to the smaller quantity of fuel present in the CCS. The CCS tests were run in duplicate. The average recovery of the oil was about 98%. The extraction layer was small and the effect of additives was minimal on the recovery. However, the synthetic oil formed a very stable emulsion. This was probably due to relative solubilities of the additives in the more polar base stock and

the methanol. Unless heated, the emulsion is stable for 3–4 months.

To determine the effect of the heating and vacuum stripping steps on the processing of the base oil, a new sample PRL 4717 was placed under vacuum with heating for 6 h. The 10.00 g sample lost only 0.02 g or 0.2% by weight in the test.

8. Analysis of simulation samples

The fractions obtained from the FIS and CCS simulations were evaluated using thermal and electrochemical methods previously described. The objective of the testing was to compare the fractions against the original lubricant to determine any change in stability.

8.1. PDSC

A fresh sample of PRL 4713 was evaluated at a programmed temperature rate of 10°C/min using

Table 2
Crankcase simulation (CCS) test results

| Fuel	Sample (g)	Extract (g) (%)	Emulsion (g) (%)	Raffinate (g) (%)	Total (%)
PRL 4713 (40 wt HDD oil)					
M100 (methanol)	100.51	0.76 (0.8)	10.01 (9.9)	87.62 (87.2)	97.9
M100	103.03	0.59 (0.6)	9.05 (8.8)	88.21 (85.6)	95.0
M100+0.06% add A	101.17	0.43 (0.4)	6.73 (6.6)	90.53 (89.5)	96.6
M100+0.06% add A	99.92	0.40 (0.4)	11.70 (11.7)	88.06 (88.1)	100.2
M100+0.12% add B	100.73	0.29 (0.3)	7.34 (7.32)	91.68 (91.0)	98.6
M100+0.12% add B	102.12	0.20 (0.2)	8.28 (8.11)	92.01 (90.1)	98.4
PRL 4723 (FFV synthetic oil)					
M100 (methanol)	100.13	[a]	[a]	79.22 (79.1)	–
M100+0.06% add A	100.11	[a]	[a]	79.47 (79.47)	–

[a] Emulsion layer stable for weeks. No analysis.
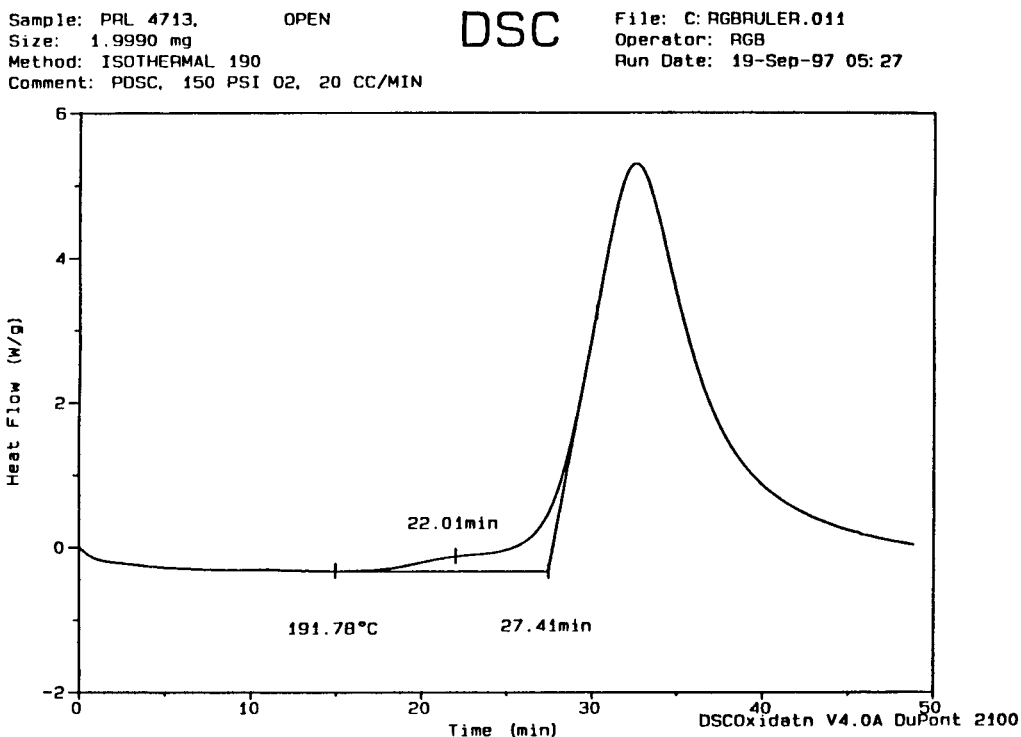
Fig. 1. Pressurized DSC-original oil sample.

approximately 2 mg of sample under 150 psi of air. The lubricant, based on the results of the test, an isothermal temperature of 190°C was selected for the remaining evaluations. At this isothermal temperature condition, the new oil had an oxidation induction period of about 28 min. The samples from the evaluations were similarly tested. Some examples of the thermograms from a CCS are found on Figs. 1 and 2. The data are typical in that the raffinate fraction that contained most of the oil had a shorter OIT than the original oil. The emulsion layers and most extraction layers had equal or higher OITs, indicating an increase in oxidation stability due to increase in additive concentration. A summary of the CCS samples are found on Fig. 3. The OIT of the raffinate samples were lower than the original oil.

8.2. PSMO

If there is a depletion of additives including the antioxidants then the deposit forming tendency of the extracted lubricant should increase. The volatility of

the fractions would also vary depending on the nature of the additives extracted. The volatility of the CCS fractions, Fig. 4, indicate increased volatility for the raffinate and correspondingly heavier deposits. The deposits formed at 225°C in 30 min are summarized on Fig. 5. The emulsion layers contain extracted additives and exhibit lower volatility and lower deposits. The data show a significant increase in the deposit forming tendencies of the raffinate and a decrease for the emulsion fraction. The increase in the volatility of the raffinate samples is due to an increase volatile oxidation products and some residual fuel in the sample. The emulsion layer was less volatile than the original oil, suggesting that the extracted additives in the emulsion layer may be less volatile, higher molecular weight dispersant or detergent molecules.

8.3. RULER^{TM}

This method is used to determine changes in additives in used oil samples and has been used to study

Sample: SAMPLE 13-2-1, OPEN
Size: 2.0040 mg
Method: ISOTHERMAL 190
Comment: PDSC, 150 PSI O2, 20 CC/MIN

DSC

File: C:RGBRULER.024
Operator: RGB
Run Date: 13-Oct-97 00:21

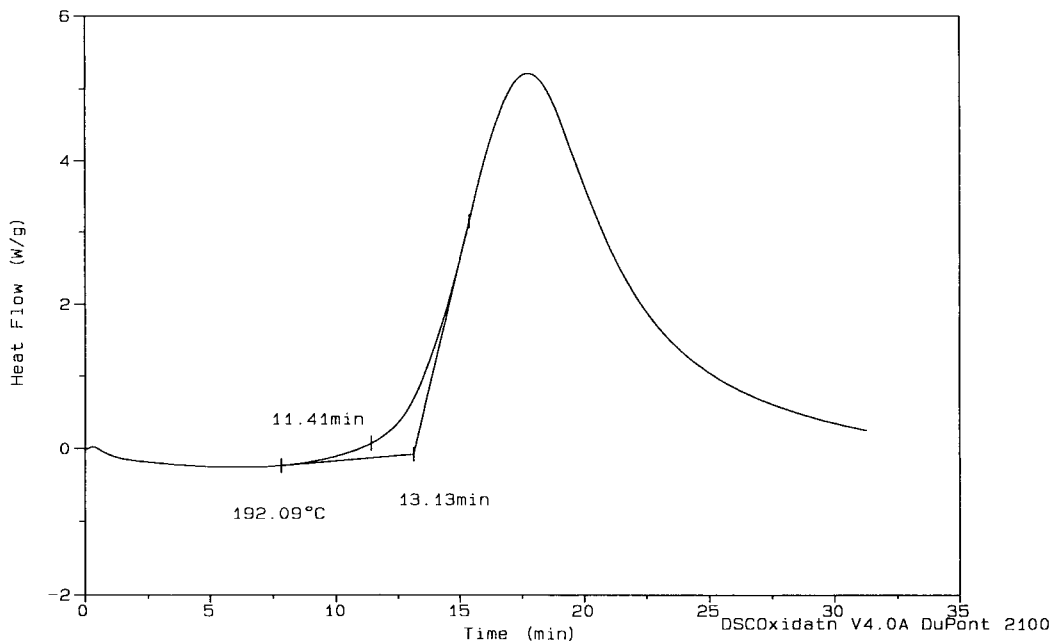11.41min

192.09°C

13.13min

DSCOxidatn V4.0A DuPont 2100

Fig. 2. Pressurized DSC-raffinate sample.

extended drain tests [16]. A small amount of sample, 200 μl in this study, is mixed in a selected solvent containing an electrolyte and a three electrode probe is immersed in the solution. The voltage of one of the electrodes, the auxiliary electrode, is increased linearly with time. The current produced at the surface of a second electrode, the working electrode, is recorded as a function of the voltage. When the voltage reaches the

ADDITIVE EFFECTIVENESS IN OIL FRACTIONS
COLD CRANKCASE SIMULATION TESTS
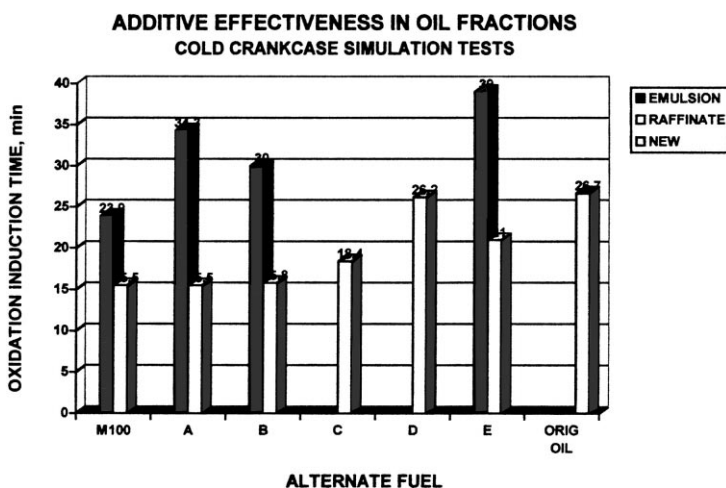
Fig. 3. Pressurized differential scanning calorimeter (PDSC) tests: additive effectiveness in oil fractions, cold crankcase simulation tests.
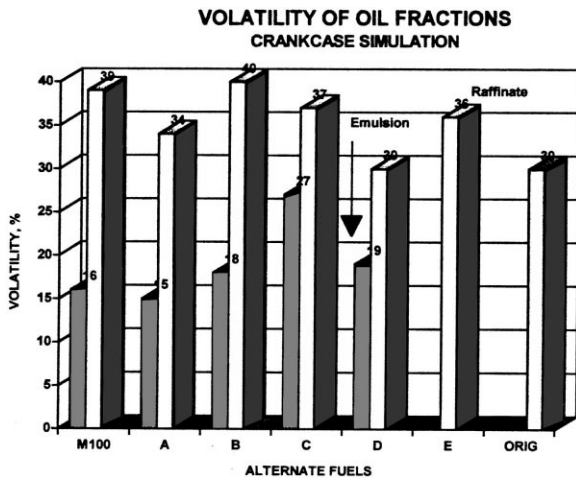
Fig. 4. Penn state microoxidation test: volatility of oil fractions, crankcase simulation.

oxidation potential of the additive, the additive undergoes electrochemical oxidation increasing the current flow at the working electrode. The voltage of the peak generated on the voltammogram is related to the type of additive in solution and the area under the curve is related to the concentration of the additive present in

solution [10,11]. A typical set of curves is found on Fig. 6. Data for the FIS samples obtained using the RULER[TM] method are found on Fig. 7. The CCS data are summarized on Fig. 8. The additives in the extract increase several hundred percent, while the raffinate are reduced. The high values are due to the relative sizes of the sample fractions. The extract, after removing the fuel, contains mostly additive and in some cases some oil. The raffinates are mostly the original oil stripped of additives and in some cases containing traces of fuel.

9. Conclusions

- Thermal analysis methods are basic to the science of formulating lubricants.
- Bench test methods can give significant results, reducing the number of full-scale tests required for the certification of lubricants.
- Use of alternative fuels requires evaluation of compatibility of fuels and lubricant.
- Alcohol fuels can significantly deplete the additives in a lubricating oil by extraction. This can be shown by both thermal and electrochemical methods.
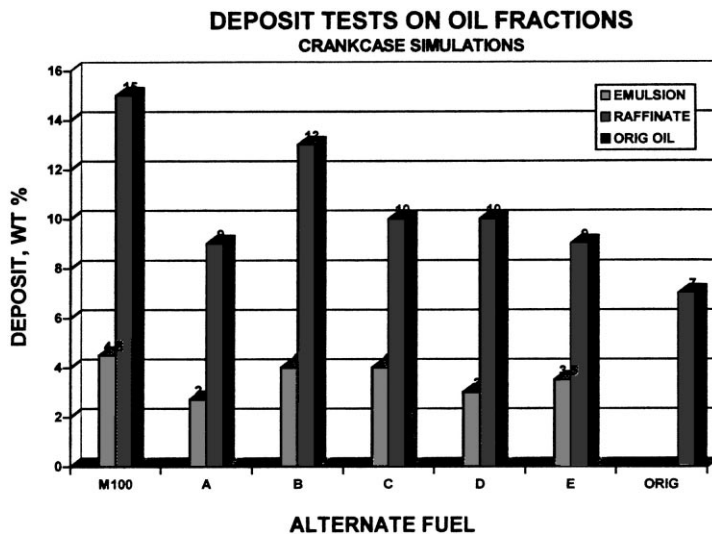

Fig. 5. Penn state microoxidation test (PSMO): deposit tests on oil fractions, crankcase simulations.
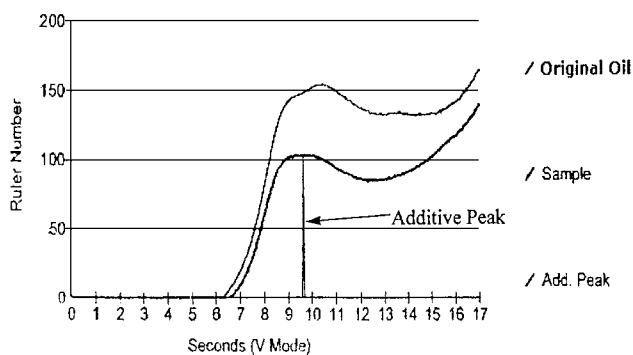
Sample Ruler® Output

Fig. 6. Remaining useful life evaluation routine: sample RULER^{TM} output.
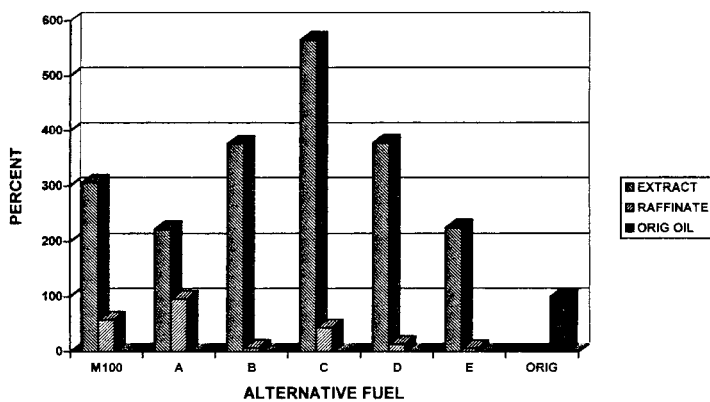
ANTIOXIDANT IN OIL FRACTIONS

Fig. 7. RULER^{TM}-fuel injector simulation (FIS) data: antioxidant in oil fractions.
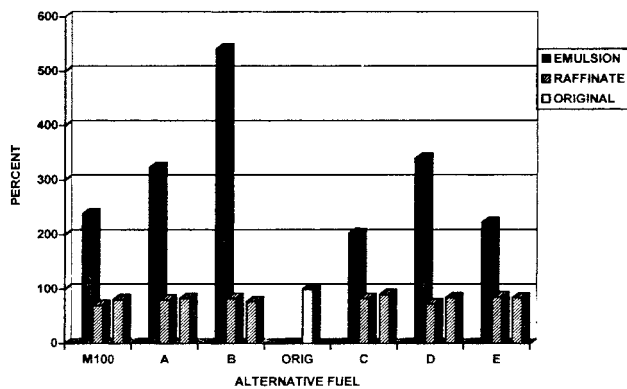
ANTIOXIDANT ADDITIVE IN OIL FRACTION

Fig. 8. RULER^{TM} crankcase simulation: antioxidant additive in oil fraction.

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Acknowledgements

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