THE LUBRICITY PROPERTIES OF JET FUEL AS MEASURED BY THE BALL-ON-CYLINDER LUBRICITY EVALUATOR

Bruce H. Black
GEO-Centers, Inc., Ft. Washington, MD 20744
Dennis R. Hardy
CODE 6181, Naval Research Laboratory, Washington, DC 20375-5000
and
Margaret A. Wechter
Southeastern Massachusetts University, North Dartmouth, MA 02747

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ABSTRACT

In recent years the quality of petroleum feedstocks used by refineries has decreased. This has necessitated the use of severe refinery processes in order to produce jet fuels of high thermal stability and cleanliness. Unfortunately these processes remove the compounds that are responsible for a fuel's inherent lubricity. As a result, fuel lubricated engine components are experiencing greater wear and mechanical failure. The Ball-on-Cylinder Lubricity Evaluator (BOCLE) was developed to predict a fuel's tendency to cause lubricity related problems. This paper discusses the influence of trace polar species on lubricity, the use of additives to increase lubricity, changes in a fuel's lubricity during storage, and inadequacies of the BOCLE. Finally, a suggested long term solution to lubricity problems by hardware modifications will be discussed.

INTRODUCTION

The incidence of lubricity related problems in commercial and military jet aircraft has increased over the past twenty years. This is a result of the need for more severe refinery processes to remove trace fuel species that adversely affect thermal stability and water removal by coalescence.[1-4] These processes also remove trace polar species that are responsible for a fuel's inherent lubricity properties.

Lubricity is a qualitative description of the relative abilities of two fluids, with the same viscosity, to limit wear and friction between moving metal surfaces.[2,4] It may be the most critical fuel property degraded by refinery processes.[5,6] The continued use of low lubricity fuel can lead to a decrease in the operational lifetime of fuel lubricated engine components. This leads to increased maintenance costs and down-time of aircraft. Furthermore, the use of low lubricity fuel has been implicated in the loss of certain military aircraft.

In the late 1960s, it was serendipitously found that a pipeline corrosion inhibitor had a significant effect on lubricity enhancement. The additive's original intended purpose was to decrease corrosion to fuel handling systems and transfer lines.[4] The additive is effective as a corrosion inhibitor due to its surface-active nature. The active ingredient in most corrosion inhibitors is a dimeric organic acid, usually dilinoleic acid (DLA). It is the surface-active nature of the dimeric acid that causes the corrosion inhibitor to be an effective lubricity enhancer.

The use of a corrosion inhibitor as a lubricity enhancer is now required in all military JP-4 and JP-5 jet fuel.[7] Unfortunately the additive can hinder water removal by coalescence. In other cases a fuel may have adequate lubricity initially and would preclude the use of the additive. Currently there is no lubricity specification for either commercial or military jet fuel. This has been due primarily to the lack of a test method; hence, the mandatory addition of the additive to assure adequate lubricity.

During the past fifteen years considerable effort has been made to develop a mechanical method to measure fuel lubricity. The current and most widely accepted method is the Ball-on-Cylinder Lubricity Evaluator (BOCLE). The lubricity of a fuel is determined by the measurement of an oval wear scar on a ball that has been in contact with a rotating cylinder partially immersed in a fuel sample under controlled conditions.[8] The reported value is the average of the major and minor axes of the oval wear scar in millimeters. Two limitations to this method are: First, the BOCLE is run at 25°C, a temperature that is not characteristic in aircraft environments. Second, the test is limited to a measurement of boundary lubrication, a lubrication regime not characteristic of currently used aircraft fuel pumps.[9,10]

In the United Kingdom a second method is being used. This method, developed and used exclusively by Shell Research, Ltd., is known as the Thorton Aviation Fuel Lubricity Evaluator (TAFLE). This consists of a stationery cylinder loaded onto a rotating cylinder both of which are completely immersed in the fuel sample. Measurements can be obtained at both ambient and elevated temperatures. This test also measures scuffing load which is generally characteristic of fuel system failures.[9,10]

EXPERIMENTAL

Reagents- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. JP-5 and Jet A jet fuel samples were obtained from the Naval Air Propulsion Center (NAPC). JP-4 jet fuel samples were obtained from Wright-Patterson Air Force Base (WPAFB). Carboxylic acid standards were obtained from a variety of sources including; Aldrich Chemical Company, Inc., LaChat Chemicals, Inc., and PolyScience, Inc. Trimethylsilyl ester derivatives of the carboxylic acids and jet fuel base extracts were prepared using Power Sil-Prep obtained from Alltech Associates, Inc.

Equipment and Materials- For HPLC analyses, samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30 cm x 8.0 mm i.d.). Uninhibited THF was used as a mobile phase. The THF was periodically purged with dry nitrogen to inhibit the formation of hazardous peroxides. The injector was a Rheodyne loop/valve Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer for detection. A Varian Model 9176 strip chart was used to record peaks. A Fisher Accumet pH Meter Model 610A and a Fisher Standard Combination Electrode Catalog Number 13-639-90 were used for pH adjustments.

Gas Chromatography/Mass Spectrometry (GC/MS) analyses were performed using a Hewlett-Packard Model 5890 GC coupled to a Finnigan MAT ion trap detector. An all glass GC inlet was used in combination with a 0.2 mm x 50 m OV-101 fused silica capillary column. Data were collected using an IBM AT Personal Computer with ITDS software (version 3.0).

BOCLE analyses were performed using an InterAv Model BOC 100. The cylinders used were Timken Rings Part Number F25061 obtained from the Falex Corp., Aurora, IL. The test balls used were 12.7 mm diameter, Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Methods- HPLC analyses of fuel extracts were performed using a previously developed method.[11-13] This involved the extraction of 100 mL of jet fuel with an equal volume of of 0.2 M NaOH. The aqueous phase was drained and acidified with concentrated HCl. The acidified aqueous phase was subsequently back-extracted with 100 mL of HPLC methylene chloride which was then drained and allowed to evaporate. The residue was dissolved in 2.0 mL HPLC THF for analysis.

BOCLE measurements were performed according to the method described in appendix Y of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.[8]

RESULTS

Figure 1 is an HPLC chromatogram of a base extract from a typical JP-5 jet fuel. The active ingredient of the lubricity enhancer additive, DLA, has an elution volume of 5.85 mL. The DLA component has a molecular weight of 562. This material is prepared by a 1,4- cycloaddition (Diels-Alder) reaction of two linoleic acid molecules. The product is a monocyclic compound with a molecular weight twice that of linoleic acid. It possesses two carboxylic acid moieties which are the points of attachment to the active surface sites.

The peak that elutes at approximately 5.4 mL corresponds to trilinoleic acid (TLA). The TLA component, which is also a product of the Diels-Alder reaction, has a molecular weight of approximately 840. It may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings.

The components with elution volumes of approximately 6.5 mL and 7.0 mL correspond to naturally occurring base extractable materials. These peaks are designated regions 3 and 4 respectively. These peaks can be clearly seen in Figure 2. The components that elute in what are designated regions 3 and 4 are believed to play a significant role in the inherent lubricity of jet fuel as measured by the BOCLE. Earlier work has shown a relation between the presence of these components and BOCLE measured lubricity.[14-15] In general, as the concentration of components that elute in regions 3 and 4 increase, the lubricity of a fuel sample measured by the BOCLE increases.

While performing routine analyses of jet fuel samples, an interesting change in the fuel samples was noted. A series of JP-5 field samples were analyzed for base extractable material. After nine months of ambient storage, these same samples were analyzed a second time. It was found that the amount of base extactable material that elutes in regions 3 and 4 had increased. Table 1 lists the peak heights of regions 3 and 4 before and after nine months of ambient storage.

BOCLE analyses were run to determine if there had been a concomitant change in lubricity. Since these were actual field samples of JP-5 jet fuels and, therefore, contained the mandatory lubricity enhancer additive, these fuel samples were all considered to be high lubricity fuels originally. It was found, however, that lubricity had increased. Previous work with an early version of the BOCLE yielded similar results. The lubricity of eight additive-free JP-5 and Jet A fuel samples were measured before and after 18 months of ambient storage. The change in wear scar diameter measurements for these fuels are listed in Table 2. It can be seen that the lubricity had increased in most cases. The wear scar diameters measured are smaller than those that would be measured on the current version of the BOCLE. This is a result of a metalurgical change in the cylinders to increase repeatability and reproducibility.

The increase in base extractable material with a concomitant increase in BOCLE measured lubricity is probably a result of oxidative changes in the fuel. Free radical autoxidation mechanisms are well known and readily occur in some fuels. These mechanisms can lead to the formation of trace levels of carboxylic acids that are known to enhance BOCLE measured lubricity.

The relation between lubricity and fuel composition is of great interest. Attempts have been made to correlate a number of fuel properties to lubricity measurements with little or no success. Early work performed by Grabel showed that straight chain carboxylic acids were among the most effective lubricity enhancers at very low concentrations.[16] The effect of straight chain carboxylic acids on boundary lubrication is well known and well documented. It's not surprising that an corrosion inhibitor based on carboxylic acids is also an effective lubricity enhancer. Grabel attempted to correlate the total acid number of a fuel to its lubricity as measured by the BOCLE. It was found that there was a relation, however, it would not serve as a adequate prediction of a fuel's lubricity. The conclusion is that there are acids that contribute substantially to the total acid number that are not involved in lubricity.

Combined gas chromatography/mass spectrometry (GC/MS) was used to identify components present in regions 3 and 4. With the knowledge of the effect of carboxylic acids on BOCLE measurements, comparison between fuel extracts and carboxylic acid standards were made. Both the fuel extracts and standards were derivatized to form their trimethylsilyl analogs to facilitate GC/MS analysis. After analysis of a standard mixture of derivatized carboxylic acids, a variety of fuel extracts were analyzed. Carboxylic acids were found to be present at low concentrations. These were identified by both GC retention time and by their mass spectra. To aid in identification, multiple ion detection was also used for samples with overlapping peaks. The specific alkanoic acids found ranged from heptanoic acid (C_7) to undecanoic acid (C_{11}). The total concentration of the alkanoic acids varied with different samples. In most cases the total concentration was on the order of a few parts per million. Previous work has shown that as little as 2 ppm of added alkanoic acids can significantly improve BOCLE measured lubricity.

In addition to the acids, the majority of the species present in the fuel extracts were substituted alkyl phenols. Earlier work by Grabel has shown that these materials are not effective lubricity enhancers at low concentrations. At higher concentrations they may, however, contribute to BOCLE measured lubricity.

SUMMARY

The BOCLE is a useful tool in the laboratory for jet fuel lubricity measurments. Its limitations, however, must be recognized. The test is performed at 25°C, well below the operating temperature of aircraft fuel systems. Compounds that exhibit a beneficial influence on lubricity in the BOCLE test may fail at higher temperatures. The BOCLE analysis is performed in a different lubrication regime than is found in current aircraft fuel systems. This may lead to erroneous conclusions about a fuel's ability to impart lubricity in actual fuel systems. For instance, the BOCLE measured lubricity of a fuel is not influenced by the presence of sulfur compounds. Jet fuel lubricity as measured by the TAFLE, indicates that sulfur compounds increase the load limit of a fuel before scuffing occurs. This means that the BOCLE may fail a fuel that is capable of high loads in an actual fuel pump.

Lubricity related problems have been associated with only certain specific aircraft. The use of the lubricity enhancer additive has been found to adequately alleviate these problems. Other aircraft have not been found to exhibit any lubricity related problems. One may ask why there is a concern about lubricity. In the past the Navy has had problems with lubricity as a result of shipboard fuel handling practices. As JP-5 fuel is depleted from shipboard storage tanks, seawater is pumped in for ballasting. Seawater has been shown to effectively remove the lubricity enhancer additive by forming dicationic salts of the DLA.[12,13] This results in jet fuel with inadequate lubricity.

Another cause for recent lubricity problems is the lack of a lubricity specification. Additives used for lubricity enhancement are used, not for their ability to enhance lubricity, but their ability to inhibit corrosion. Of the additives qualified for use in jet fuel[17], some are not effective surface active lubricity enhancers.

Two recommendations as an approach to short term and long term lubricity concerns are as follows: First, delete the additives from the Qualified Products List that are not found to enhance lubricity. Of the additives remaining, select those additives that are most effective for lubricity enhancement, are most cost effective, and are readily available.

Second, design aircraft components that are not affected by the continued use of low lubricity fuel. Long term problems with jet fuel lubricity should be approached by hardware modification not by the continued use of additives.

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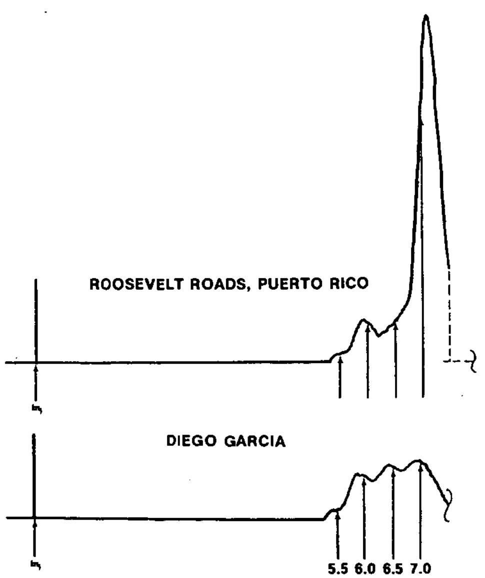

FIGURE 1

FIGURE 2

HPLC CHROMATOGRAMS OF JP-5 FIELD SAMPLES

TABLE 1

SAMPLE	Reg. 3 Pk Hgt Before	Reg. 3 Pk Hgt After	Reg. 4 Pk Hgt Before	Reg. 4 Pk Hgt After
Roosevelt Roads	14.5	26.0	126.0	55.0
Guantanamo Bay	11.0	26.0	25.0	>200
Diego Garcia	20.0	22.0	22.0	65.0
Iorlaki, Japan	4.0	4.0	3.5	11.0
Gatun, Panama	12.0	15.0	24.0	>250
Cartagena, Spain	5.0	12.0	8.5	29.0
Azorea	7.5	7.0	6.5	13.0

CHANGE IN CONCENTRATION OF BASE EXTRACTABLE MATERIAL AFTER NINE MONTHS OF STORAGE

TABLE 2

SAMPLE	ORIGINAL WSD	REMEASURED WSD
1	0.28 mm	0.23 mm
2	0.32 mm	0.26 mm
3	0.26 mm	0.27 mm
4	0.43 mm	0.26 mm
5	0.31 mm	0.34 mm
6	0.62 mm	0.35 mm
7	0.53 mm	0.36 mm
8	0.52 mm	0.41 mm

CHANGE IN WEAR SCAR DIAMETER MEASUREMENT FOR ADDITIVE-FREE JET FUELS AFTER 18 MONTHS OF STORAGE