THE LUBRICITY PROPERTIES OF JET FUEL AS A FUNCTION OF COMPOSITION PART 2: APPLICATION OF ANALYSIS METHOD

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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. These processes, however, tend to decrease the lubricity properties of jet fuel products. As a result, fuel lubricated engine components have been experiencing greater wear and mechanical failure. To alleviate this problem, a highly effective lubricity enhancer additive, based on mixtures of carboxylic acids, is mandatory in all U.S. military jet fuel. The additive, however, has been shown to interfere with the removal of water from jet fuel by coalescence. In addition, some fuels possess high levels of naturally occurring, lubricity enhancing carboxylic acids and, therefore, do not need the additive. This paper describes the application of an analysis method that distinguishes between fuels with and without the additive, and fuels that possess naturally occurring, lubricity enhancing carboxylic acids.

INTRODUCTION

In part 1 of this work, it was shown that a direct correlation exists between the presence of naturally occurring carboxylic acids and Ball-on-Cylinder Lubricity Evaluator (BOCLE) measurements.[1] This correlation was applied to a series of fuel samples that were used to determine the repeatability and reproducibility of the BOCLE instrument. Extensive BOCLE data had been generated to which the compositional analysis results could be compared. The compositional analysis method was found to be able to distinguish between naturally occurring and added lubricity enhancing carboxylic acids.

This paper applies the compositional analysis method to a series of Navy JP-5 jet fuel samples obtained from a worldwide survey of storage depots. BOCLE measurements were performed at the Naval Air Propulsion Center (NAPC), Trenton, NJ. As in the previous work, the presence of carboxylic acids in a fuel sample increased its inherent lubricity. The compositional analysis method also identified fuels which were deficient in the mandatory lubricity enhancer additive.

EXPERIMENTAL

<u>Reagents</u>- HPLC grade uninhibited tetrahydrofuran (THF) and HPLC grade methylene chloride were obtained from Fisher Scientific. Seven JP-5 fuel

samples, from the Navy's Second Worldwide Fuel Survey, were obtained from the Naval Air Propulsion Center.

Equipment and Materials- Samples were analyzed using a Beckman-Altex Microspherogel high resolution, size exclusion column, Model 255-80 (50A pore size, 30cm x 8.0mm I.D.). Uninhibited THF was used as the mobile phase. The THF was periodically sparged with dry nitrogen to inhibit formation of hazardous peroxides. The injector was a Rheodyne Model 7125. A Beckman Model 100-A HPLC pump was used for solvent delivery with a Waters Model 401 differential refractometer for detection. Peaks were identified using a Varian Model 9176 strip chart recorder. A Fisher Accumet pH meter Model 610A and a Fisher standard combination electrode Catalog Number 13-639-90 were used for pH adjustments. An Interav Model BOC 100 Ball-on-Cylinder Lubricity Evaluator was used for lubricity measurements. The cylinders were 100% spheroidized annealed bar stock, consumable vacuum melted AMS 6444 steel obtained from Jayna Enterprises, Inc., Vandalia, OH. The balls used were 12.7mm diameter, SKF Swedish Steel, Part Number 310995A obtained from SKF Industries, Allentown, PA.

Method- Fuel samples were analyzed for carboxylic acid concentration by a previously developed method.[2] For each sample, 100 ml were extracted with 100 ml of 0.2M aqueous sodium hydroxide. The aqueous phase was drained into a clean beaker and acidified dropwise with concentrated hydrochloric acid. The pH of the aqueous phase was lowered to pH 2.0 ± 0.03. The acidified aqueous phase was back-extracted with 100 ml HPLC grade methylene chloride. The methylene chloride was drained into a clean beaker and allowed to evaporate. After evaporation, the residue remaining was dissolved in 2.0 ml HPLC grade THF and transferred to a glass vial with a teflon-lined cap.

BOCLE measurements were performed in triplicate on each of the fuel samples. The method used was according to appendix Q of the Aviation Fuel Lubricity Evaluation published by the Coordinating Research Council, Inc.[3] The sum of the values obtained for each sample was averaged and the relative wear scar diameter measurements are reported in Table 1.

RESULTS AND DISCUSSION

As in previous work, the presence of carboxylic acids, both naturally occurring and added, correlates well with BOCLE measurements. The relative average wear scar diameter for each sample is listed in Table 1. The cylinders used for this work were somewhat softer than the Timken rings previously used in Part 1 of this work. As a result, the actual wear scar diameter measurements were somewhat lower with a narrower range.

It can be seen in Table 1 that five of the seven fuels analyzed possessed the lubricity enhancer additive. Four of these fuels had both the major constituent, dilinoleic acid (DLA), and a minor component present in some lubricity enhancer additives, trilinoleic acid (TLA). Two of the fuels analyzed, however, did not possess any appreciable amount of the mandatory lubricity enhancer additive.

In Figures 1 through 5, the major lubricity enhancer additive component, DLA, elutes at approximately 5.85 ml. The DLA component has a molecular weight of about 560 daltons. 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 believed to be the points of attachment to active surface sites.

In Figures 1 through 4, the peak corresponding to the TLA component is also present. This component elutes at approxmately 5.4 ml. The TLA component, which is also a product of the Diels-Alder reaction, has a molecular weight of approximately 840 daltons. It may possess either a partially unsaturated fused dicyclic ring structure or two isolated partially saturated cyclohexyl rings.

As expected, the fuels that possess the lubricity enhancer additive were found to have the highest lubricity. Those fuels that did not possess the lubricity enhancer additive, and were also deficient in naturally occurring carboxylic acids, were found to have the lowest lubricity. From what is known about carboxylic acids with respect to lubricity enhancement, continued use of these fuels could lead to lubricity related problems.

Table 2 lists the peak heights for the added and naturally occurring carboxylic acids extracted from the fuel samples. Fuel samples 1 through 3 each possessed similar amounts of the lubricity enhancer additive. Fuel sample 4 had slightly less than the first three fuel samples, while fuel 5 was devoid of the TLA component and had significantly less of the DLA component. Two sets of data for the naturally occurring carboxylic acids are listed. In previous work, it was found that some fuels possess two distinct molecular weight ranges of naturally occurring carboxylic acids.[1,2] These two ranges are designated regions 3 and 4. These components have retention volumes of approximately 6.5 and 7.0ml respectively and can be clearly seen in Figure 3.

High resolution, size exclusion chromatography separates components on the basis of molecular shape and size and, therefore, to an extent, molecular weight. In general, one would expect a normal distribution of straight chain alkanoic acids which parallels the distribution of normal alkanes present in a fuel. The presence of two separate peaks for the naturally occurring carboxylic acids indicates the presence of two distinct classes of constituents. Region 3 corresponds to the straight chain alkanoic acids, while region 4 corresponds to mono- and polycylic carboxylic acids. The maxima for regions 3 and 4 correspond to the molecular weight of tetradecanoic acid (C_{14}), and octanoic acid (C_8) respectively. The condensed size of a cyclic compound, as opposed to a straight chain compound, yields a calculated molecular weight lower than its actual molecular weight. For this reason, region 4 is most likely comprised of not only monocyclic carboxylic acids, but polycyclic acids as well.

Maxima for regions 3 and 4 are not as well defined in other fuels examined. For these fuels, the height was measured at a retention volume that corresponds to the maxima in Figure 3. In Figures 1, 2, and 5, the concentration of carboxylic acids present in region 3 increased gradually as the molecular weight decreased. In each case, there is a very rapid increase in carboxylic acid concentration in the region 4 molecular weight range. Similar results were found in earlier work.[1,2]

In each fuel previously examined, there was some minimum amount of carboxylic acids present in region 4. Not all fuels, however, possessed the carboxylic acids which correspond to region 3. Some had very low concentrations, some had approximately equal concentrations. These differences may be a result of crude source, refinery operations, or storage conditions.

CONCLUSIONS

The compositional analysis method has been applied to a series of field samples to determine the presence of naturally occurring and added carboxylic acids are known to enhance jet fuel lubricity. The concentration present in a given fuel sample correlates well with its inherent lubricity as measured by the BOCLE.

A number of molecular weight ranges of carboxylic acids are present in most jet fuels. Two of these regions correspond to the presence of an added lubricity enhancer, and two or more correspond to naturally occurring lubricity enhancing carboxylic acids. The relative effectiveness of each region has not yet been determined. It is believed, however, that the dimer of linoleic acid is more effective than the trimer. This is a result of steric hindrance between trimer molecules when attached to surfaces.[4-6]

The relative effectiveness of the naturally occurring carboxylic acids is believed to increase as chain length increases. Daniel found that, in general, the ease of adsorption increases with increasing chain length.[7] Boundary lubrication also increases as chain length increases.[8,9] The lubricity properties of jet fuel, therefore, may increase as the presence of longer chain carboxylic acids increases. At some point, however, there is probably a limit to lubricity enhancement by increasing chain length. The relative effectiveness of region 3 over region 4, therefore, may be substantially different due to the differences in structure.

There may be some question as to why the mandatory lubricity enhancer additive is absent from two of the fuels examined. There are possible explanations for this. First, the lubricity enhancer additive was originally added to the fuel to inhibit corrosion to fuel handling and storage systems which resulted from dissolved oxygen and free-water present in fuel. The carboxylic acid based corrosion inhibitors were serendipitously found to enhance the lubricity properties of low lubricity fuels.[10-13] As lubricity related problems became more prevalent, the primary purpose for the corrosion inhibitor was lubricity enhancement. Unfortunately, the military specification for jet fuel was not modified to include lubricity properites. Second, the additives are accepted and used, not for their ability to enhance lubricity, but to inhibit corrosion. Some of these additive are based on acylated glycols and acylated alkanolamines. the compositional analysis method described in this paper is not suitable for analysis of these materials. It should be noted that these materials have been shown to be relatively ineffective lubricity enhancers. Third, the additive was not added at the refinery as it should have been.Additive loss due to adsorption in fuel handling has been found to be insignificant. Previous work has shown that as little as 3% is lost due to adsorption on the surfaces of a 100 mile pipeline.[14]

The compositional analysis method can be used as a supplement to the BOCLE. The BOCLE can determine if a fuel has sufficient lubricity characteristics. The compositional analysis method can determine if the lubricity is a result of naturally occurring or added carboxylic acids or both.

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TABLE 1

SAMPLE	Relative WSD	TLA Present	DLA Present
1. Roosevelt Roads, P.R.	0.67	YES	YES
2. Guantanamo, Cuba	0.70	YES	YES
3. Diego Garcia	0.71	YES	YES
4. Iorizaki, Japan	0.77	YES	YES
5. Gatun, Panama	0.79	NO	YES
6. Cartagena, Spain	0.86	NO	NO
7. Azores	1.00	NO	NO

The Relative Lubricity of Fuel Samples as Measured by the Ball-on-Cylinder Lubricity Evaluator.

TABLE 2

SAMPLE	TLA Pk Hgt	DLA Pk Hgt	Reg. 3 Pk Hgt	Reg. 4 Pk Hgt
1	4.0	15.5	14.5	126.0
2	4.0	15.0	11.0	25.0
3	4.0	16.0	20.0	22.0
4	1.5	11.0	4.0	3.5
5	0.0	7.5	12.0	74.0
6	0.0	0.0	5.0	8.5
7	0.0	0.0	7.5	6.5

The Results of the Compostional Analysis of Fuel Samples for Natural and Added Carboxylic Acids.

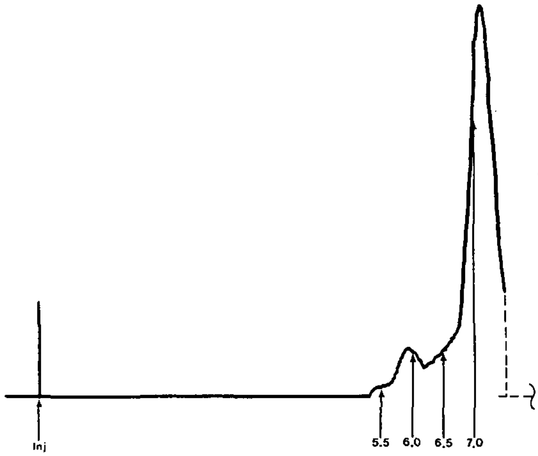

FIGURE 1: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Roosevelt Roads, Puerto Rico.

FIGURE 2: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Guantanamo, Cuba.

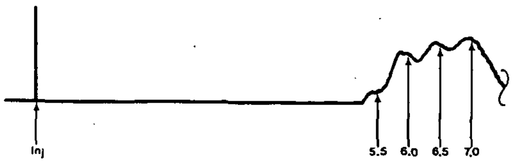

FIGURE 3: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Diego Garcia.

FIGURE 4: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Iorizaki, Japan.

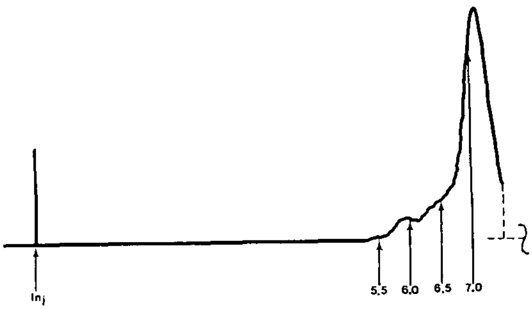

FIGURE 5: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from Gatun, Panama.

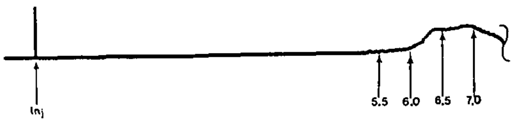

FIGURE 6: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel From Cartagena, Spain.

FIGURE 7: HPLC Chromatogram of Base Extracted JP-5 Jet Fuel from the Azores.