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Static Tests of Jet Fuel Thermal and Oxidative Stability

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Jet fuels and a jet fuel surrogate have been thermally stressed to simulate the time/temperature history of aircraft fuel handling systems. Surrogate fuels were used to develop quantitative measurement techniques to assess fuel stability in static tests and compare the results with flowing tests. A variety of experimental techniques including Fourier transform infrared (IR), gas chromatography with atom-sensitive atomic-emission detection and high-pressure liquid chromatography have been used to study stressed and unstressed fuels. Quantitative and qualitative measurements of the deposits and the fuels are presented. In general, the static tests described here indicate that there is good agreement between static and flowing tests concerning the quality of a fuel. However, to adequately assess fuel stability, the availability of oxygen must be limited. Arbitrarily increasing the oxygen availability is likely to yield results which are not applicable to oxygen-starved stressing processes. Furthermore, contrary to expectations, the rate at which a fuel oxidizes is shown to be inversely related to the rate of formation of insoluble products.

Introduction

PROJECTIONS of future demands on jet fuels as a repository for excess heat generated in future aircraft indicate that the thermal stability of jet fuels must be increased by about 100°C.[1] One way to achieve such an increase is with the use of additives to the current fuel supplies. Fuels and additives have been supplied by a variety of manufacturers, and have been blended and shipped to several researchers to evaluate additive performance.[2]

The fuel was subjected to a variety of tests, each of which simulated some portion of the thermal history of the real fuel as it encounters different thermal environments in a jet fuel handling system. Stagnant heated-flask tests, as described here, were used to replicate onboard fuel storage systems, and to study the chemistry associated with the thermal degradation of fuel through the auto-oxidation process.

Among the goals of this study are the evaluation of jet fuel stability and the products of jet fuel breakdown by spectroscopic techniques, the chemical evaluation of the actual deposits formed, and the development of sufficient kinetics understanding to compare flowing tests, independent of operating conditions with nonflowing tests. In particular, Fourier transform infrared (FTIR) techniques are developed to quantify the amount of alcohol and ketone species in surrogate fuels. Gas chromatography with atomic emission detection (GCAED) is used to follow the production/consumption of oxygen/sulfur-containing molecules. Multielemental analysis is used to study the elemental makeup of the deposits.

This article describes the fuels used in the various experiments, the experiments used to stress the fuels, and the results of both qualitative and quantitative analysis techniques used to analyze the deposits and the fuels. In particular, the importance of the auto-oxidation process to the formation of deposit material is discussed.

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Experimental Work

Fuels Description

To assist in the development of analytic/spectroscopic tests, two systems (one consisting of the reference jet fuels, and one consisting of a surrogate jet fuel) were used. The reference fuels and some of their properties are listed in Table 1. These three fuels F-2799, F-2747, and F-2827 will be referred to as jet propellant thermally stable (JPTS), Jet A-1, and Jet A. Jet A-1 is a highly hydrotreated fuel, while JPTS is an Air Force specification fuel which has good thermal stability characteristics. The goal of this research program is to develop a fuel which exhibits the thermal stability characteristics of JPTS through the addition of additives to typical JP-8. The Jet A fuel is not hydrotreated, has a broader boiling range, and increased heteroatom concentration. It is expected that this fuel will exhibit lower thermal stability than Jet A-1. In addition, F-2814 is a JP-8 made by adding icing inhibitor, static dissipator, and corrosion inhibitor to Jet A-1. Finally, a JP-7 and two other JP-8 fuels and a surrogate fuel (JP-8S) were also tested.

JPTS has a jet fuel thermal oxidative tester (JFTOT) break-point of 399°C—indicative of its excellent thermal stability. Jet A-1 has a break-point of 332°C while Jet A has a break-point of 266°C. These fuels all pass ASTM D3241 and the break-points indicate the anticipated ordering of the stability. Also, the relative thermal stability of these three fuels has been established recently in several flowing systems including

Table 1 Properties of baseline jet fuels

		Fuel identification		
	ASTM method	Jet A-1	JPTS	Jet A
Sulfur mass, %	D4294	0	0	0.1
Aromatics vol, %	D1319	19	9	19
Gum, mg/ml	D381	0	0.4	0
Flash point, °C	D93	60	49	50
JFTOT break-point	D3241	332	399	266

Table 2 Composition of surrogate jet fuel-8S

Compound	Mass, %
Methylcyclohexane	5
m-Xylene	5
Cyclooctane	5
Decane	15
Butylbenzene	5
Tetramethylbenzene	5
Tetralin	5
Dodecane	20
Methylnaphthalene	5
Tetradecane	15
Hexadecane	10
Isooctane	5

single-pass heat exchangers,[3] multipass heat exchangers,[4] and hot-liquid-process simulators,[5] and they are all in agreement with the JFTOT break-point analysis.

Surrogate fuels comprise a mixture of selected hydrocarbons. The selection and mixture ratio of the hydrocarbons is designed to yield a solution which can mimic many of the properties of a real fuel, yet still have the simplicity of a pure hydrocarbon mixture. The great value of surrogate fuels is their simplicity, which allows for the observation of intermediate product formation. This formation is often obscured by the complexity of real fuels. The makeup of the surrogate fuel is listed in Table 2. This mixture exhibits a boiling range of 92–286°C, contains 22% aromatics, 0% alkenes, and a density of 0.8 g/ml.

Flask Test

Fuels were heated in round-bottom flasks under 0°C reflux at a temperature of 180°C. Oxygen was flowed into the heated fuel for two reasons. First, it was found that bubbling oxygen at 180°C was necessary to achieve significant (gravimetrically measurable) degradation in time periods approaching 4 h. Second, we hoped that maintaining oxygen saturation would remove the dissolved oxygen content as a variable in the system.

Deposits were collected by two separate methods. In one set of experiments, the entire 30-ml sample of fuel was cooled and decanted through a filter. Deposits were collected either in the filter or in an acetone wash. Deposits were then dried and weighed. In the second set of experiments 10 ml of a reacting 100-ml sample were extracted, filtered, washed, dried, and weighed. These filterable deposits were collected from the same samples used in the quantitative FTIR measurements.

FTIR

Surrogate fuel was used to show that the amount of oxidized product in the fuel could be measured quantitatively. Various quantities of alcohol (1-dodecanol), and ketone (2-octanone) were added to the fuel, and the integrated response of FTIR was determined. The spectrometer used for these tests was a Mattson Galaxy Series 4020. The surrogate fuel was described in Table 2 and all chemicals are 99% purity. A Nicolet model 740 FTIR was used for qualitative analysis of the fuels and the deposits.

Other Tests

Fuels (stressed and unstressed) and deposits were studied by following the total acid number of the fuel (ASTM D3242). The fuels were further analyzed by GCAED (Hewlett Packard HP5962a), and high-pressure liquid chromatography (HPLC). Elemental composition of the deposits was measured on a Leco CHN-932 elemental analyzer.

Results

Flask Tests

Table 3 shows the development of insolubles at constant time (5 h) and temperature (180°C), while allowing the flow rate of oxygen to vary for Jet A-1. Table 3 also lists values of total acid number of the fuel and the integrated FTIR absorption near 1700 cm^{-1}.

Table 3 Comparison of acid number, insolubles, and FTIR in fuel Jet A-1

Sample oxygen flow, cc/min	Acid number, mg, KOH/g of fuel	Deposit, mg/30 ml of fuel	FTIR 1722, cm^{-1} peak area
0	——[a]	0	——
15	8.03	62	——
30	10.6	154	11.9
60	14.0	200	14.2
90	16.4	321	16.0

[a]Not measured.

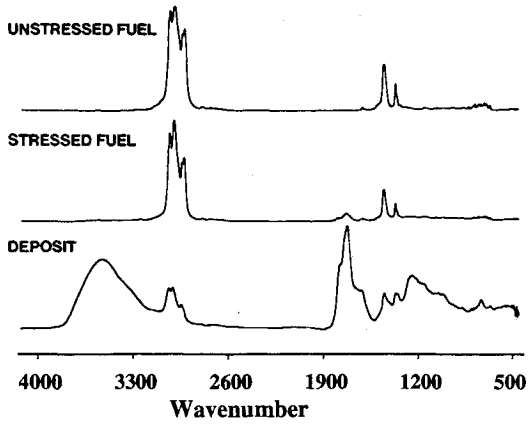

Fig. 1 Infrared spectra of Jet A-1 before and after stressing and the insoluble products.

Under similar conditions of stressing, JPTS produces essentially no insoluble materials, despite having an elevated acid number and showing absorption in the 1722 cm^{-1} region. Similarly, Jet A produces only 3–7 mg of insoluble product, essentially independent of the oxygen flow. It shows no other signs of being strongly oxidized.

Qualitative IR

The IR spectra of products from Jet A-1 show a similar qualitative behavior (Fig. 1). The absorption pattern is typical of an organic acid, with absorptions in the region of 1700 cm^{-1} from the carbonyl group and the broad absorptions near 3000 cm^{-1} from the OH moiety. Again, JPTS stressed fuel shows similar features, whereas the stressed Jet A fuel shows almost no absorption in the 1700 cm^{-1} or 3100 cm^{-1} region.

Quantitative IR

The surrogate fuel was used to establish the ability of FTIR to quantitatively measure the amount of oxidized product in fuel. After determining the integrated response factors for 2-octanone and 1-dodecanol in surrogate fuels, seven different fuels were stressed under oxygen-rich conditions for 2 h at 175°C. The amount of alcohol and ketone was determined by assuming the response of all ketones and alcohols formed were identical to the standards used in the surrogate fuel. Organic acids would show up as an increase in the measured concentration of both the alcohols and ketones. The amount of filterable solid deposits formed (in 10 ml) was also determined. Table 4 lists the results of the concentration of alcohol, ketone, the sum of oxidation products, and the amount of filterable solids.

Other Tests

The HPLC of stressed and unstressed Jet A-1 shows that there has been a significant change in the unsaturated fraction of the fuel. Figure 2 shows the dielectric constant detection of Jet A-1 before and after stressing at 180°C with bubbling

Table 4 Analysis of the oxidation products of various fuels

Fuel	ID no.	Insoluble, mg	Alcohol, mole/l	Ketone, mole/l	Sum, mole/l
JPTS	F-2799	0.1	0.312	0.278	0.59
JP-7	F-2818	10.0	1.853	0.588	2.441
JP-8	F-2814	12.5	1.142	0.875	2.017
Jet A-1	F-2747	13.7	1.140	0.636	1.776
JP-8	F-2813	18.0	0.022	0.013	0.035
JP-8		34.8	0.029	0.020	0.049
JP-8S	Surrogate	38.3	0.352	0.253	0.605

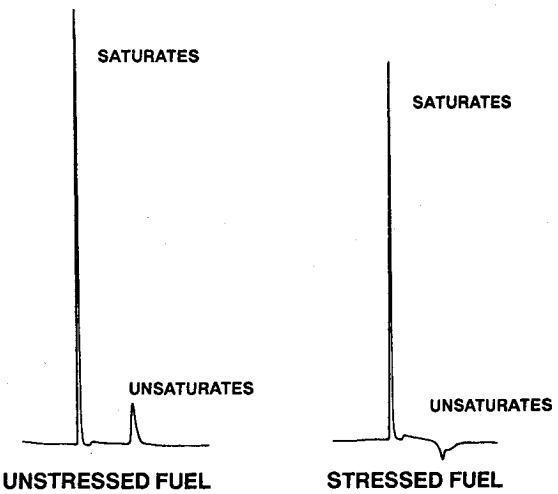

Fig. 2 Dielectric constant detection of HPLC of Jet A-1 before and after stressing.

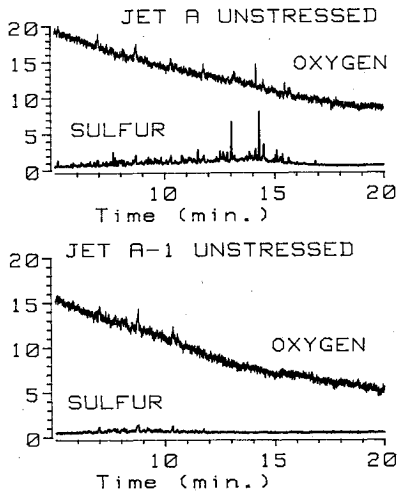

Fig. 3 GCAED sulfur and oxygen analysis of Jet A-1 and Jet A fuels.

oxygen for 4 h. The negative response of the second (the unsaturated fraction) peak after stressing indicates that the dielectric constant of that fraction has significantly increased. As a result, changes in the amount of unsaturates cannot be determined. The HPLC of Jet A does not show the same type of major change in the dielectric constant of the stressed fuel.

A GCAED analysis of two fuels, the hydrotreated Jet A-1 and the nonhydrotreated Jet A, provide additional data on the oxidation of fuels. Jet A shows the presence of sulfur (Fig. 3), whereas Jet A-1 does not. In the stressed fuels (Fig. 4), Jet A shows that the sulfur has been intimately involved in the reactions, yet the oxygen level is barely visible. Jet A-1 shows significant oxidation.

Finally, the deposits formed in stressed Jet A-1 have been analyzed for elemental composition. The deposits are greater than 20% oxygen by mass and nearly 0.2% sulfur. As yet, the elemental composition of the deposits for Jet A has not been measured.

Discussion

Table 3 indicates that the amount of insoluble material was directly related to the amount of oxygenated product in the fuel. However, this is true for only one fuel (Jet A-1—the highly hydrotreated fuel). JPTS also forms oxygenated fuel soluble products (according to the IR spectra), but produces almost no deposits. Jet A produces very little insoluble product, and the total insoluble solids formed are not a strong function of the amount of oxygen available.

The GCAED traces (Figs. 3 and 4) verify the FTIR observations that some fuels do not form soluble oxidative products. Jet A has sulfur atoms present, and these compounds are significantly involved in the chemical reactions which take place under stressing. The level of sulfur atoms in the stressed fuel has decreased by nearly 75%. This fuel, however, does not form significant amounts of soluble oxidation products. Jet A-1 contains no detectable sulfur. This fuel consumes oxygen, forming a large number of detectable oxygen-containing compounds, including a large "humptanol" peak near 13 min (Fig. 4).

The HPLC traces of Jet A-1 (Fig. 2) are consistent with a large increase in oxygen-containing molecules. Jet A does not show a similar increase in the dielectric constant of the unsaturated fraction. This is consistent with the GCAED observations that fewer oxygen-containing species are present in stressed Jet A relative to Jet A-1, as highly oxygenated species are likely to be more polar and exhibit a greater dielectric constant than nonpolar compounds.

The sulfur atoms which are involved in reactions in the stressed Jet A probably show up in the insoluble products. The number of sulfur atoms in the fuel has decreased by more than a factor of 2 (note the change of scale in Fig. 4). Sulfur atoms tend to concentrate in the deposits as shown by the elemental analysis of Jet A-1 deposits. The deposits formed by Jet A-1 contain nearly 0.2% sulfur, despite having less than 50-ppm sulfur in the fuel. The large amount of oxygen in the solids is also consistent with an easily oxidized fuel.

Conventional wisdom holds that fuels which are more easily oxidized will exhibit less thermal stability.[6] That is, fuel stability as measured by deposits on metal surfaces and oxidation are strongly and positively correlated. This notion is based on the observation that the deposition of solid material, the consumption of oxygen, and the production of peroxides are seemingly all related. For instance, in single pass or multiple heat exchangers,[3,4] the amount of deposit is known to decrease if oxygen is removed from the fuel. However, all of the tests on the baseline fuels showed that the more thermally stable fuel (Jet A-1) was also less oxidatively stable. We therefore decided to look at a variety of fuels, using the FTIR to measure the amount of oxidized species.

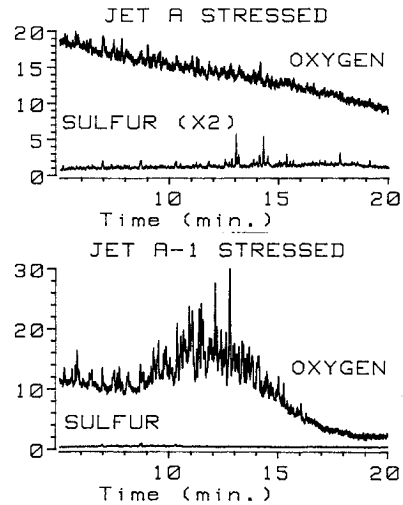

Fig. 4 GCAED sulfur and oxygen analysis of stressed Jet A-1 and Jet A fuels.

Figure 5 is a plot of the oxygenated fuel-dissolved products vs the filterable solid materials formed (Table 4). There is good agreement between the observed amount of ketone and alcohol produced. Interestingly, some fuels produce deposits, while not forming any oxygen containing products at all. In fact, if JPTS and surrogate jet fuel (JP-8S) are not considered, the general conclusion is that fuels which oxidize easily will, in general, not form large amounts of insoluble solids. JPTS seems to not oxidize sufficiently to follow this trend, but it has an added antioxidant which may account for the low level of oxidative products. There is also added antioxidant in JP-7 and the Jet A-1, but these two fuels oxidized the most in this test. The discrepancies may be indicative of the relative effectiveness of the antioxidants. JP-8S oxidizes too much given the large amount of solids formed. However, JP-8S is not really a fuel, therefore, its comparison here may not be appropriate.

The general behavior of ease of oxidation being inverse to ease of solid formation has been observed recently by Hardy.[7] His observation was based on measurements in 13 jet fuels. He measured the ability to oxidize by measuring the resulting peroxide number after an accelerated storage test under oxygen overpressure at 100°C for 48 h, and the deposits in a flowing gravimetric JFTOT test. Hardy's results are shown in Fig. 6. Jet A-1 and Jet A have been measured and are also shown in Fig. 6. These conclusions are identical to ours in that fuels which oxidize easily are invariably stable when measured by filterable deposits. Conversely, Hardy noted that

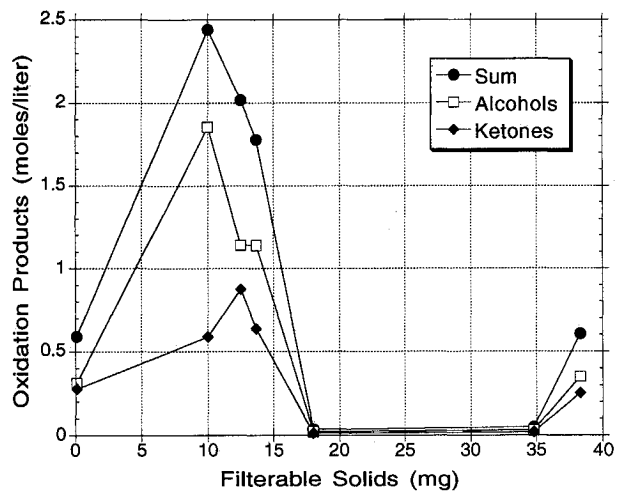

Fig. 5 Comparison of the oxidation products concentration and the filterable solids from seven different fuels.

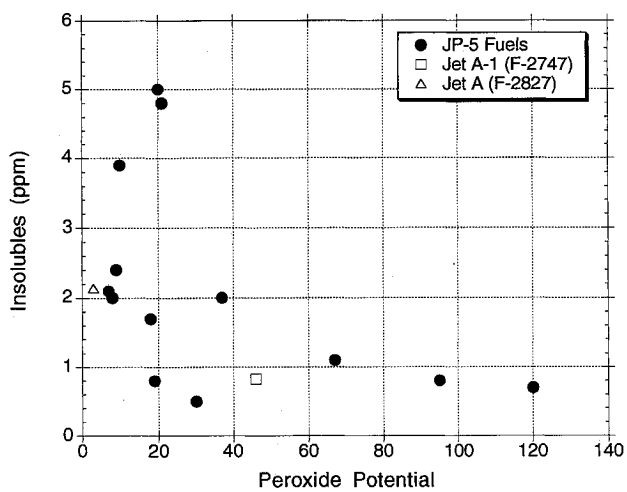

Fig. 6 Peroxide potential vs gravimetrically measured deposits (from Ref. 7).

Table 5 Oxidation vs deposits in single-tube heat exchanger[3]

Fuel ID	Oxidation T, K	Ease of oxidation, $10^3/T$, K	Deposits, μg
JPTS	458	2.18	300
Jet A-1	463	2.16	450
Jet A	488	2.05	2800

fuels that do not oxidize easily exhibit a wide range of thermal stability as measured by deposits.

Using the same three reference fuels (Jet A-1, 2827, and 2799) Heneghan et al.[3] showed that the amount of solid formed on the walls of a single-pass heat exchanger was inversely related to the temperature that the fuel consumed oxygen. Since the "ease of oxidation" is inversely related to the temperature at which the fuel consumes oxygen, this is a repeat of the general behavior observed here and by Hardy. The behavior of the three baseline fuels for oxidative and thermal stability is shown in Table 5, where ease of oxidation is shown as the inverse temperature in Kelvin (K). Again these data are consistent with an inverse relation between ease of oxidation and thermal stability.

Finally, Biddle[5] showed that the amount of deposit formed in a hot liquid process simulator was inversely related to the onset temperature of the oxidation exotherm in differential scanning calorimetry. Biddle used the same three fuels as Heneghan,[3] thereby confirming the previous observations.

As indicated above, it was originally hoped that use of the FTIR to monitor oxygenated compounds would help monitor the initial buildup of precursors to deposit formation. The data of Fig. 5, as well as the observation that JPTS and the hydrotreated Jet A-1 consume oxygen more easily than Jet A, suggest that the relation between the formation of oxygen-containing products in the fuel may be related to the production of solids in a much more complicated manner than previously believed. The additional evidence presented by Heneghan, Hardy, and Biddle are consistent with a more complicated relation.

The oxygen was originally bubbled into the fuels to maintain a saturated oxygen level and thus remove it as a variable. However, the results indicate that only Jet A has been maintained in the saturated oxygen condition. The increase of deposits with the increse of oxygen flow in Jet A-1 indicates that the fuel has not reached and maintained a saturated oxygen level despite the oxygen flow rate reaching 3 cm^3/min of oxygen/ml of fuel. The unsaturated condition of Jet A-1 is probably caused by the rapid consumption of oxygen.

Trying to correlate the results of our flask test to other tests designed to measure the thermal stability (JFTOT, single-tube flowing heat exchangers) showed that the correlation depended upon either the amount of oxygen flowing or how the solids were collected. The fuels exhibit the expected order of stability if the oxygen is limited, or as in the FTIR experiments, the filterable solids are collected. Since the condition of bubbling oxygen into heated fuel is not indicative of any real system, the milder oxygen conditions are deemed more useful in predicting fuel thermal stability.

Conclusion

FTIR, HPLC, GCAED, elemental analysis, tests of fuels, and deposits for a hydrotreated and a nonhydrotreated fuel have shown that the level oxidation in the more thermally stable fuel (as determined by JFTOT break-point and other flowing tests) is significantly higher than in the less stable fuel.

An extension of the FTIR oxidation measurements to seven different fuels confirm that there is an inverse relation between the thermal stability as measured by solid deposits and the stability as measured by oxidation. The inverse relationship of these two values, thermal and oxidative stability, has now been shown by at least four research groups using a total of 20 different fuels and eight separate techniques. The oxidation of these fuels have been measured by following the

consumption of oxygen, the appearance of peroxides, the appearance of ketones, and the onset of an oxidation isotherm. The thermal stability has been measured by JFTOT, a gravimetric JFTOT, a single-pass heat exchanger, and a hot liquid process simulator. While it is not neccessarily true that the slow oxidation reactions which lead to deposit formation will follow this inverse behavior, a model which can account for the observed relation between the rapid oxidation steps and slow deposit forming steps would be useful. Until such a model exists, the general relation should be interpreted with caution.

FTIR can be a useful tool in following the onset of oxidation products and is quantitatively useful in following the buildup of acids, aldehydes, and ketones in real fuel samples. However, the evaluation of fuels and additives in a static flask test will yield results which are strongly dependent on the availability of oxygen.

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