COMPARISON OF JF1OT HEATER TUBE DEPOSIT RATING METHODS FOR THE EVALUATION OF FUEL THERMAL STABILITY (U) NAVAL RESEARCH LAB WASHINGTON DC R E MORRIS ET AL. 29 DEC 07
Comparison of JFTOT Heater Tube Deposit Rating Methods for the Evaluation of Fuel Thermal Stability

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Quantification of deposits formed of heated metal surfaces is desirable for the evaluation of thermal stability by the JFTOT procedure. Empirical methods widely employed entail either visual comparisons or measurements of reflected light (TDR), both of which are sensitive to deposit color. We have examined these and several other measurement techniques for JFTOT heater tubes and have found that measurements of total carbon content by combustion were the most reliable. Two novel techniques, based on measurements of dielectric strength and interference effects of monochromatic light, have been examined. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, while the TDR often yielded misleading results. The correlations between the various methods will be discussed in addition to the consequence of method choice on the interpretation of experimental data.
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COMPARISON OF JFTOT HEATER TUBE DEPOSIT RATING METHODS
FOR THE EVALUATION OF FUEL THERMAL STABILITY

INTRODUCTION

The property of thermal oxidation stability describes the extent to which thermally induced decomposition occurs in the fuel. This process is often accompanied by the formation of insoluble reaction products, either as a precipitate or as a gum which adheres to container surfaces. Modern aircraft engine designs and aerodynamic heating of wing surfaces place more severe thermal stress on the fuel, increasing the likelihood of the formation of insoluble deposits. Aircraft fuel system deposits can be responsible for a variety of problems including decreased efficiency of engine heat exchangers, seizing of fuel control valves and injector fouling.

It is known that thermally initiated fuel degradation is accelerated by the presence of oxygen through autoxidative processes involving free radical chain reactions. The Jet Fuel Thermal Oxidation Tester (JFTOT) has been widely used for the characterization of thermal oxidation stability of a fuel. In the JFTOT, aerated fuel is pressurized with nitrogen and passed over a heated metal tube so that the fuel is stressed under conditions of high oxygen availability and slowly increasing temperatures. The quantities of insoluble products formed under these conditions constitute a measure of the deposit forming characteristics of the fuel. In accordance with standard ASTM D3241 test procedures, the formation of filterable insolubles is detected from changes in pressure differential across a standard test filter downstream of the heated tube and the adherent insolubles are characterized by visual comparison with color standards. The highly subjective nature of the visual method of rating heater tube deposits was revealed in a round-robin effort conducted by the Coordinating Research Council. The poor precision of visual ratings from unusual and highly colored deposits resulted in random errors which were in excess of the differences between the values, thus eliminating any statistical significance. To increase the reliability of the measurement, the Tube Deposit Rating (TDR) was developed. The TDR is based on the attenuation of reflected white light from the coated heater tube. From comparisons with measurements of deposit thicknesses by Auger spectroscopy, Martel and Bradley found that neither the Visual Rating method nor the TDR were adequate in rating tube deposits. While less subject to operator judgement than the visual rating method, the TDR can be influenced by the optical properties of the deposit.

Quantification of tube deposits by combustion of carbon to carbon dioxide has been investigated, with the assumption that carbon constitutes the majority of the deposits. Taylor utilized measurements of total
carbon contents per unit area per unit time to study the influence of dissolved oxygen on the rates of deposit formation from thermally stressed jet fuels on 316 stainless steel tubes. The studies were later extended by Taylor(5) to examine the effects of trace amounts of sulfur-bearing compounds on deposition rates and by Taylor and Frankenfeld(6) to include nitrogen compounds. Giovanetti and Szetela(7) employed combustion analyses to quantify deposition rates from jet fuels stressed under a wide variety of experimental conditions in a special test apparatus. Carbon was determined from deposits on sintered stainless steel filters and from the inner walls of heated 316 stainless steel tubes. A lower limit of 200 micrograms carbon on the tube sections was reported. Kendall and Mills(8) have shown that the precision of combustion analyses conducted on standard JFOT heater tubes has been limited by the difficulty with which quantitative removal of carbon from the aluminum surface could be attained. They found that the amount of carbon from stainless steel tubes generally exceeded that from aluminum tubes by a factor of two. In addition, migration of magnesium in 6061 T6 alloy aluminum heater tubes at elevated temperatures, has been reported to catalyze deposition. Heater tubes comprised of 304 stainless steel do not form porous oxide coatings, allowing much lower detection limits, nor is magnesium catalysis possible. Besides these limitations associated with the use of aluminum tubes, the tubes are destroyed during the combustion analysis and it provides no detailed information concerning the spatial distribution of the deposit.

Two novel techniques for determining the volumes of heater tube deposits have been developed. One technique, developed by Stavinoha, et.al.,(9), is based on measurements of the electrical insulating properties of the deposit. The other method, developed by Darrah, et.al.,(10), is based on the interference effect produced when monochromatic light is reflected off the tube surface through the deposit. Since these methods are non-destructive, we were able to obtain deposit measurements from the TDR, dielectric, interference and combustion methods on each JFOT heater tube. In this study, the results from the four methods are compared.

EXPERIMENTAL

JFOT Runs

Thermal stressing of fuel samples was performed using the modified JFOT described earlier by Hazlett, et.al.(11). Five-inch 304 stainless steel heater tubes were employed to achieve a more gradual increase in temperature, greater reactive metal surface area and to facilitate the combustion analysis. In order to ensure sufficient quantities of material for combustion analysis, run times were increased to 300 minutes. Under these conditions, at a maximum fuel flow rate of approximately three milliliters per minute, the residence time of the fuel in the heater tube holder was approximately 28 seconds. Appreciable amounts of filterable insolubles would substantially reduce the fuel flow rate through the test filter and increase the contact time of the fuel with the heated tube surface. As a result, the stress on the fuel would be increased beyond the normal limits of the test and erroneously high levels of insolubles
could be produced. Fuel flow rates were therefore maintained at or above
2.5 ml/min by bypassing the test filter when the flow rate dropped below
that point. Tests were conducted at maximum heater tube temperatures of
260, 270, 280 and 310°C.

Tube Deposit Measurements

Spun TDR measurements were taken with an Alcor Mark 9 tube deposit
ingrating device. The TDR is based on the measurement of the attenuation of
reflected white light by a photocell; thicker coatings increase the TDR
while a clean tube surface gives a reading of zero. The instrument was
calibrated in accordance with the manufacturer's instructions, using a
calibration tube supplied with the instrument having known reflectance
coatings. Readings were taken on heater tubes before and after stressing
at two millimeter intervals over the 120 mm heated length. To obtain a
measure of the changes in reflectance due to the deposit, differences
between the initial and final TDR values at each location were
calculated. The sum of these TDR changes constituted the total delta TDR,
which was used as an indication of the total amount of deposit on the
tube.

Volume measurements were performed by Southwest Research, Inc., using
their dielectric measuring device. Central to this technique are the
assumptions that an organic deposit will behave as an electrical insulator
and that all typical deposits have similar dielectric strengths. When a
voltage potential is applied across the tube deposit, it acts as an
electrical insulator until the potential reaches the level at which the
organic material comprising the coating breaks down. At that point, the
coating ceases to act as a dielectric insulator and current begins to flow
through the coating. The dielectric breakdown was determined by
increasing an applied voltage potential across the coating at a controlled
rate while monitoring the current drain. Deposit thicknesses were
calculated from an empirically determined(9) proportionality factor, which
relates the dielectric breakdown voltage to deposit thickness. Since the
potential was applied through a stylus which is placed on the outside
surface of the coating, the precision of the measurement could be expected
to be reduced with very thin coatings. The nature of the measurement
precludes spinning of the tube to average out variations in thickness
around the tube, so the side of the tube with the thickest coating was
taken as a reference point i.e., zero degrees. Measurements were obtained
at 2 mm intervals down the tube at 0, 90, 180 and 270 degrees, providing
four sets of thickness measurements for each tube. At each location, the
readings were averaged and used to calculate the total deposit volume.

Deposit thickness measurements by interferometry were obtained by
Geo-Centers, Inc., using the apparatus they had developed. Monochromatic
light having a wavelength of 680 nm was directed onto the coated tube in a
direction perpendicular to the surface through a fiber optic assembly
which contained both the source and detector optics. The light intensity
measured in this technique represents the quantity of light which emerged
through the coating after reflecting off the metal tube surface. Since
there is a large difference in the refractive indices between the air and
the deposit, the reflected light wave undergoes a phase change. As a
consequence, the emergent wave interferes constructively or destructively with the incident wave, depending on the thickness of the deposit. As the detector was scanned across a deposit, the light intensity changed periodically as the deposit thickness passed through multiples of the wavelength of the incident light. At thicker deposit thicknesses, absorption of the light by the coating dominated, limiting measurement to thicknesses below approximately two microns. Like the dielectric method, the interference method is also a static measurement which is conducted at four quadrants down the tube length, using the side having the thickest coating as the reference. The thicknesses at each tube location were averaged and used to calculate the total deposit volume.

Total carbon contents of the tube deposits were determined after completion of the other measurements. Combustion analyses were performed with a Perkin-Elmer model 240 elemental analyzer. After calibration of the analyzer with known compounds, blank values were obtained from cleaned, unused heater tube sections. The grip ends of the heater tubes were removed and the heated section was cut into two equal lengths, cleaned by soaking in toluene, and analyzed.

DISCUSSION

The quantities of total carbon from each JFIT heater tube, the TDR values and the deposit volumes from the dielectric breakdown and interference methods are given in Table 1. The TDR values represent the summation of the differences between the spun TDR values along the heater tube before and after stressing. The entries in table 1 are arranged in order of decreasing carbon content and it can readily be seen that poor correlation was found between carbon content and TDR values. The scatter plot of TDR values vs total carbon in Fig. 1 illustrates that, although there is a tendency for the heavier deposits to exhibit higher TDR readings, there was a high degree of uncertainty. This illustrates the deficiency of the TDR when used quantitatively in research efforts undertaken with the JFIT.

A plot of the deposit volumes calculated from the dielectric and interference measurements vs total carbon (Fig. 2), indicates that these quantities are more linearly related to carbon content than the TDR. Light absorption by the thicker deposits limited the useful range of the interference measurements to coatings containing less than 400 micrograms of carbon. Close examination of Fig. 2 reveals that deposit volumes calculated from dielectric breakdown measurements from thin deposits were somewhat less than corresponding determinations by the interference method. It is not possible on the basis of these data, to determine which method provides the best result for the thinner coatings.

Both of these two new non-destructive techniques provide a convenient means of measuring deposit thicknesses at known locations on non-spinning tubes. Such techniques could be employed to determine the relationships between deposit thickness variations and experimental variations. Thickness profiles from interferometry along four sides of a typical heater tube are illustrated in Fig. 3. In this example, the thickness measured at 0° was nearly twice that at 90 and 180°, where the side of the
tube having the thickest deposit was designated as 0° and the other
profiles were taken by indexing the tube in 90° increments. In those
instances where there are large radial variations in thickness, increasing
the number of measurements around the circumference would increase the
precision of the volume calculation. However, the high degree of
correlation with the combustion data indicates that, in these experiments,
the precision of the deposit volumes from measurements at four locations
was comparable to that of the combustion data.

The degrees of correspondence between tube deposit measurements from
these methods can be quantitatively expressed by performing regression
analyses and considering the linear correlation coefficients. From the
regression correlation coefficients given in Table 2 the deposit volumes
by the dielectric breakdown and the interference methods are shown to
correlate extremely well with total carbon contents and with each other.
The TDR values did not correlate with any of the other measurements.

Typical TDR profiles from two heater tubes having maximum TDR values
of 47 and 28 at the locations of maximum tube temperatures, are shown in
Fig. 4. The TDR scan of the heavier deposit also contains a secondary
maximum at approximately 80 mm. Comparison of the TDR plots with the
maximum dielectric breakdown potentials of 828.3 and 17.2
volts from the same two tubes (Fig. 5) illustrates the increased range of
the measurement over the TDR. This illustrates a case in which changes in
TDR were not proportional to the actual quantities of tube deposits.
Carbon contents of the entire deposits on these two tubes was 381 and 27
micrograms, respectively. The random nature of the correlation between
TDR and carbon contents or deposit volumes renders the existence of any
systematic non-linear relationship very unlikely. The secondary maximum
at 80 mm was also not apparent from the dielectric measurements. This
type of effect may have been caused by light absorption by a thin, highly
colored deposit which resulted in an erroneously high TDR. There is also
the possibility of interference effects arising from thin coatings with
thicknesses in multiples of the dominant wavelength of the incandescent
lamps used in the TDR rating device.

CONCLUSIONS

Excellent agreement was obtained between JFTOT heater tube deposit
volumes calculated from measurements of dielectric breakdown and from
optical interference and the total amount of carbon measured by
combustion. Tube deposit volumes calculated by the two non-destructive
measurements could be used in place of total carbon measurements to make
quantitative comparisons from 304 stainless steel heater tubes.

As practical alternatives to combustion analyses, the dielectric and
interference methods may allow the use of aluminum JFTOT tubes in
quantitative studies. These new techniques could also provide a
convenient and practical means with which to study the relationships
between fuel flow and deposit characteristics and to determine the
influence of heater tube composition without resorting to combustion
analyses to quantify deposits. The thickness profiles obtained by these
two new methods have also demonstrated instances where the TDR values were...
disproportionately influenced by thin, highly colored deposits. The failure of the IDR to respond proportionately to certain types of deposits poses limitations on its usefulness as a tool for quantitative measurements.

The precision of the volume calculations by the dielectric and interference methods can be affected by extreme radial variations in deposit thickness. Therefore, in those instances where higher precision is desired, it may be necessary to increase the number of measurements taken around the tube circumference.

REFERENCES


<table>
<thead>
<tr>
<th>Total Carbon, micrograms</th>
<th>Total Delta TDR</th>
<th>Interferometry</th>
<th>Dielectric Breakdown</th>
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<tr>
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<td>587.9</td>
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Table 2 - Linear Correlation Coefficients from Comparisons of Post-Run JFOT Heater Tube Deposit Evaluation Methods

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<td>Total Carbon</td>
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<td>Optical Volume</td>
<td>0.707</td>
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Fig. 1. Total Carbon vs Total $\Delta$TDR
Fig. 2. Total Carbon vs Deposit Volume
Fig. 3. Post-Run Spatial Measurements of Deposit Thickness by Interferometry Along Four Sides of the Tube
Fig. 4. Post-Run Spatial Measurements by Spun TDR
Fig. 5. Post-Run Spatial Measurements by Dielectric Breakdown
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