



Enhancement of Aviation Fuel Thermal Stability Characterization Through Application of Ellipsometry

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Abstract

ASTM D3241/Jet Fuel Thermal Oxidation Tester (JFTOT) procedure, the standard method for testing thermal stability of conventional aviation turbine fuels is inherently limited due to the subjectivity in the color standard for tube deposit rating. Quantitative assessment of the physical characteristics of oxidative fuel deposits provides a more powerful method for comparing the thermal oxidation stability characteristics of fuels, especially in a research setting. We propose employing a Spectroscopic Ellipsometer to determine the film thickness and profile of oxidative fuel deposits on JFTOT heater tubes. Using JP-8 aviation fuel and following a modified ASTM D3241 testing procedure, the capabilities of the Ellipsometer will be demonstrated by measuring oxidative fuel deposit profiles for a range of different deposit characteristics. The testing completed in this report was supported by the NASA Fundamental Aeronautics Subsonics Fixed Wing Project.

1.0 Introduction

Since the 1950's, many people and organizations have relied on ASTM D3241 for thermal stability rating of conventional aviation fuels. Although this method has been universally utilized since its inception, there have been numerous examples of people, academic discussions, and research that highlight issues regarding subjectivity and accuracy of the current method, namely the visual rating system. Despite a number of attempts to identify correlations between the color code and quantitative measurements, there has been little progress in this area overall. However, with an increasing emphasis on the development of more economical and ecological technologies, it is increasingly evident that there is a need for a more encompassing and advanced testing metric for quantifying the thermal stability characteristics of jet fuels. Improvements to the JFTOT visual rating system by way of a quantitative fuel testing metric may provide an improved tool for researchers and industry alike to facilitate advancements in fuel system design and explore the potential benefits of future fuels.

2.0 Background

2.1 Jet Fuel Thermal Oxidation Tester (JFTOT) Procedure

The Jet Fuel Thermal Oxidation Tester, as designated by ASTM D3241, is a standardized test procedure used to assess the thermal stability of conventional aviation fuels. JFTOT rates jet fuels utilizing two metrics: first, differential pressure (dP) caused by particulate formation in the fluid must lie within a certain

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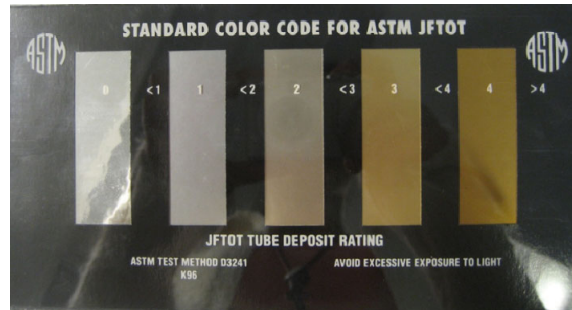


Figure 1.—ADJD3241 standard color code for JFTOT. [Visual ratings ranging from 0 to >4 are given. Only rate darkest spot of minimum size of 2.5 mm².]

range; second, tube discoloration due to hydrocarbon deposits must not exceed a certain color on the visual rating scale. This paper concerns itself primarily with the tube discoloration. The highest temperature at which the fuel passes in both respects defines the respective break point. JFTOT involves aerated fuel flowing over a resistively heated tube at 260 °C for 150 min to simulate jet fuel flow under engine operating conditions (Ref. 1). Once the test is complete, the operator utilizes a standardized Visual Tube Rater (VTR) to determine the color rating. The VTR is an internally lit black box with three 30 W incandescent bulbs and a color chart that allows the operator to rate tube deposits on a scale of 0 to 4, which can be seen in Figure 1. A rating of 3 or less constitutes a passing score for the color test (Ref. 2).

Numerous sources have found the standard visual rating method to be highly vulnerable to operator subjectivity (Refs. 3 and 4). Some studies have shown that reproducibility of results differed between operators on the order of 6.5 °C and up to a maximum of 15 °C, which is considered unacceptable by many in the research and fuel quality testing industries. The visual rating method fails to provide any information regarding thickness or volume of the deposits. The bulk and depth of deposits can disturb fluid flow and even cause blockages resulting in decreased engine performance. While the color of the engine components does not necessarily affect performance, fuel flow deposition and particulate formation plays an integral role. Thus, integrating such a metric into JFTOT will strengthen the test rating's value.

It is also known that thicknesses in relation to the JFTOT color scale vary with heater tube material, fuel, and temperature. This implies that a comparison, for example, between the colors of depositions created by a conventional jet fuel and an alternative fuel would not be directly comparable. For these reasons, it would be expected that different depositional patterns would manifest for each condition. This implies that it may be more useful to know absolute magnitude of deposits, not just discoloration.

In previously completed research, the thermal stability of Fischer-Tropsch (FT) fuel was compared to conventional Jet-A and various blends of Jet A and FT (Ref. 5). Fischer-Tropsch fuel was found to have a significantly higher break point temperature than conventional Jet A, though limitations in the JFTOT procedure inhibit the determination of the exact Fischer-Tropsch fuel break point temperature. It was reasonable to assume that the break point temperature is higher than 380 °C. It was also found that there was no added thermal stability benefit of 50:50 blends in comparison to pure Jet A. Researchers found Fischer-Tropsch fuel to fail based on the color test well before the differential pressure metric, potentially due to the use of stainless steel in place of aluminum. This leaves questions in the researchers' minds specifically on how accurately the JFTOT visual rating system depicts fuel fouling and its applicability across metal compositions. The limitations in temperature range for aluminum tubes lead to the need for a wider range of tube materials. It is important to recognize that other metals will have different mechanisms in which they interact and discolor in the presence of jet fuel. Implementing a more encompassing quantitative metric such as deposit thickness for thermal stability characterization will provide a means to expand the gamut of fuels, temperature ranges, and metal compositions that JFTOT can analyze. As non-petroleum based fuels progress in promise, both ecologically and economically, the ability to rate such fuel is of utmost importance. Through improvements in JFTOT, such capabilities can become feasible.

2.2 Ellipsometry

It was determined that ellipsometry may be a viable method of determining fuel deposit thicknesses. This was due to many factors, including the fact that the method is not dependent on knowing exact physical properties of the film being examined. In fixed angle ellipsometry, light of known polarization is impinging upon the surface and analyzed at a specified angle. At each interface between different materials (i.e.: different layers on the JFTOT tubes), light is both reflected and transmitted, creating multiple reflected light waves. Electric field components parallel and perpendicular to the plane of incidence are transmitted and reflected differently at each of these interfaces depending on the refractive index (n) of each material. Transmitted light diminishes in intensity within each layer depending on the extinction coefficient (k) of the material. The resulting reflected light waves differ from the impinging light in both intensity and polarization and interference of these waves create elliptically polarized light. With spectroscopic ellipsometry, the intensity and phase change of the reflected light is measured over a broad spectrum of wavelengths. Mathematical models describing the depth and optical properties of the layer as a function of wavelength are assumed and through an iterative process, unknown constants are varied until calculated curves correlate well with measured curves. To obtain an accurate match, a quantitative estimate of the correlation between calculated and measured curves is generated using a type of error function. The large number of data points provided by the broad spectrum of the spectroscopic ellipsometer allows for highly accurate film thickness measurements with resolutions on the order of an angstrom (Ref. 6).

3.0 Experiment

3.1 Jet Fuel Thermal Oxidation Tester

JFTOT testing for this study was performed using a Hot Liquid Process Simulator (HLPS) model HLPS-400 manufactured by Alcor. The HLPS machine, shown in Figure 2, is designed to simulate testing conditions as outlined in ASTM D3241 (Ref. 7). All operating conditions (i.e., fuel flow rate, test time, fuel system pressure etc.) are set in accordance with ASTM D3241 except experimental temperature which is operator defined. JP-8 was chosen as the fuel for this study. Procedural details can be found in *Klettlinger 2010* (Ref. 5). JFTOT testing was conducted at temperatures ranging between 255 and 275 °C to obtain a wide range of color ratings. As JFTOT designates testing at a temperature of 260 °C for

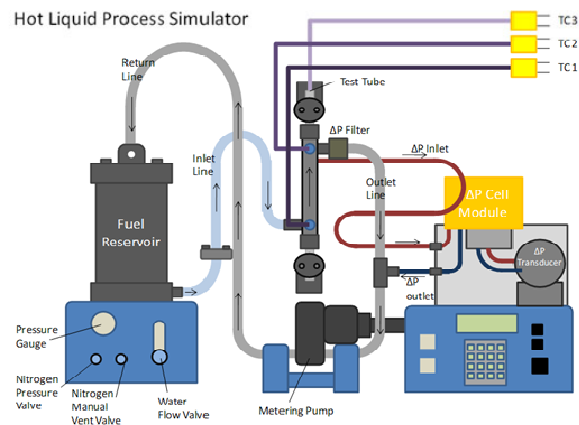


Figure 2.—Alcor HLPS-400 hot liquid. [Process simulator graphic. Fuel flows from a reservoir pumped at a constant rate to flow fuel over the tube at 3 mL/min. Three thermocouples provide point temperatures to roughly depict thermal profile.]

conventional aviation fuels, additional tests were conducted at this condition. However, to obtain data that would express probable correlation between temperature and deposit thickness, a range of temperatures was implemented into the test matrix. Following HLPS procedure, the heater tube specimen was visually rated in an Alcor Visual Tuberator, which corresponds to the rating method described in JFTOT protocol.

3.2 Ellipsometry Measurement

Once samples have been created through the JFTOT procedure, physical characteristics, specifically film thickness, can be attained using an ellipsometer. The sample can be mounted into a stand designed by HORIBA engineers to hold the JFTOT heater tube stationary. Ellipsometry was created on the pretense of determining film thicknesses of a flat surface, so due to the curved surface of a cylindrical heater tube, there were originally concerns that this would cause inaccuracies in readings. After testing these concerns were alleviated by finding variations to be insignificant in regards to either positioning or shape.

After the sample tube was mounted inside the ellipsometer, the motorized stage which holds the tube in position was manipulated so that the JFTOT tube was positioned correctly under the optical sensors. The spot size was then set to the minimum size necessary to obtain optical measurements using the ellipsometer. To be consistent, a spot of 250 by 250 μm was selected and ensured to be evenly centered over the curvature of the top of the tube. Once positioned here, the ellipsometer was used to obtain optical data on the full length of the tube—at 1 mm intervals. From this, raw information regarding the film’s optical properties was gathered and was ready to be fit to a dispersion model to determine the actual film thickness.

The software supporting HORIBA’s ellipsometer allows for numerous different dispersion models and algorithms for fitting to be performed. First, under the assumption that the aluminum alloy JFTOT tube was nearly uniform throughout, a profile of non-uniformity in thickness and chemical composition in the hydrocarbon deposits implied that a classical Lorentzian oscillator would not easily describe such a surface. After numerous iterations of absorbing disposition models, a “new amorphous” model derived by Horiba Jobin Yvon based on a Fourouhi-Bloomer formulation was chosen. The fitting equation used to describe this model can be seen below, and more information can be found in references (Ref. 8). The equations below display the models for the coefficient of extinction, k , and refractive index, n .

$$k(\omega) = \begin{cases} f_j \cdot (\omega - \omega_g)^2 & ; \text{for } \omega > \omega_g \\ \frac{(\omega - \omega_j)^2 + \Gamma_j^2}{\omega - \omega_j} & \\ 0 & ; \text{for } \omega > \omega_g \end{cases} \quad (1)$$

$$n(\omega) = n_\infty + \frac{B \cdot (\omega - \omega_j) + C}{(\omega - \omega_j)^2 + \Gamma_j^2} \quad (2)$$

Along with these equations, it is important to have general ranges and estimates for values of the unknowns that are being fit in the equations above. Table 1 list the approximate values for the unknown parameters contained in Equations (1) and (2). These unknowns describe different properties of the extinction coefficient; according to Horiba, ω_g is the energy band gap, f_j is related to the strength of the extinction coefficient peak, ω_j is approximately the energy where the extinction coefficient is at a maximum, and Γ_j is the broadening term of the peak of absorption.

TABLE 1.—OPTICAL PROPERTIES HYDROCARBONS.
[Listing of approximate optical properties of general hydrocarbons.]

Material	n_∞	ω_g	f_j	ω_j	Γ_j
Hydrocarbons	~1.650	~0.488	~0.084	~3.443	~1.839

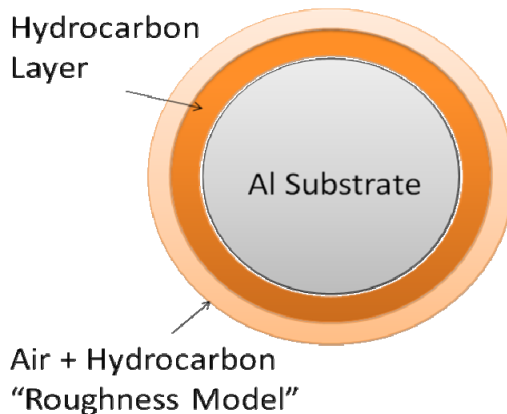


Figure 3.—Deposition model. [Aluminum substrate with two film deposit layers. Layer 1: hydrocarbon film. Layer 2: "roughness model"- air and hydrocarbon.]

To assess the performance of the models, the difference between the theoretical and experimental results was calculated, squared, and averaged across the range of the model, resulting in a statistical metric called chi-squared (X^2) that described the quality of fit. At first iterations, it was attempted to model the system as a simple aluminum substrate with a uniform layer of hydrocarbon deposits on top. This model resulted in X^2 values on the order of 50 to 500+, which was deemed unacceptably high. In seeking a X^2 value on the order of 0.01 to 1.00, the model was modified to better represent the realistic deposition patterns. After realizing the non-uniformity of the deposit thicknesses, it was desired to find a way of adding a layer that could model this surface roughness. This was achieved by incorporating a layer that represented a mixture of air and hydrocarbon material above a uniform hydrocarbon layer, see Figure 3. This would allow measurements of not only deposit height of the second layer, but also the respective percentage of hydrocarbons present. From this, one could determine an average thickness of the second layer which could be added to the first layer to determine total hydrocarbon deposit thickness.

Using this model, it was possible to achieve fits with chi squared values on the order of 0.05 to 0.20, which resulted in variations in coating thickness measurements on the order of 1 to 3 percent. An amorphous dispersion model was used, allowing highly accurate determinations of thicknesses with chi-squared values on the order of less than 1. From this, a relatively detailed profile for deposits could be created. To determine more precise heights, readings were taken every 1.00 mm around the maximum recorded heights from the first readings. Once one side was completed, the sample was rotated 90° and then retested. This process was repeated until there was a profile and maximum height for every 90°. The maximum height was then matched to the color rating taken from JFTOT testing. From this point, correlations between physical characteristics of the deposit thickness and colors could be observed.

4.0 Results/Discussion

4.1 Modified JFTOT

The data collected from performing a number of runs in HLPS following the modified JFTOT procedure as described in Section 3.1 was organized in Table 2 (For the complete set of experimental data collected refer to Appendix A, Table 4). Note a minor software system error systematically displayed temperature readouts 6 °C actual experimental temperature; this is applicable across the entire range. Unless otherwise stated, temperatures have been altered to reflect true temperature.

TABLE 2.—EXPERIMENTAL RESULTS
 [Test matrix showing different variables of successful JFTOT testing.
 Note temperatures have yet to be corrected for system error.]

Run ID	Date	Fuel index	Test file	Tube type	Recorded temperature, °C	dP, mmHg	dP P/F	Color rating	Color P/F
1115	2011-07-25	JP8-ASCR-2011-05-27	AL-275C-500	AL	275	191	f	>4	f
1113	2011-07-21	JP8-ASCR-2011-05-27	AL-270C-500	AL	270	196	f	>4	f
1112	2011-07-20	JP8-ASCR-2011-05-27	AL-265C-500	AL	265	196	f	3,<4	f
1106	2011-07-12	JP8-ASCR-2011-05-27	AL-262C-500	AL	262	189	f	<3	p
1105	2011-07-11	JP8-ASCR-2011-05-27	AL-260C-500	AL	260	7	p	2	p
1104	2011-07-11	JP8-ASCR-2011-05-27	AL-257C-500	AL	257	1	p	2	p
1103	2011-07-05	JP8-ASCR-2011-05-27	AL-255C-500	AL	255	1	p	2	p
1102	2011-07-05	JP8-ASCR-2011-05-27	AL-260C-500	AL	260	192	f	2	p
1100	2011-06-30	JP8-ASCR-2011-05-27	AL-260C-500	AL	260	181	f	2	p
1097	2011-6-28	JP8-ASCR-2011-05-27	AL-260C-500	AL	260	7	P	2	P
1096	2011-6-27	JP8-ASCR-2011-05-27	AL-260C-500	AL	260	2	p	1	p

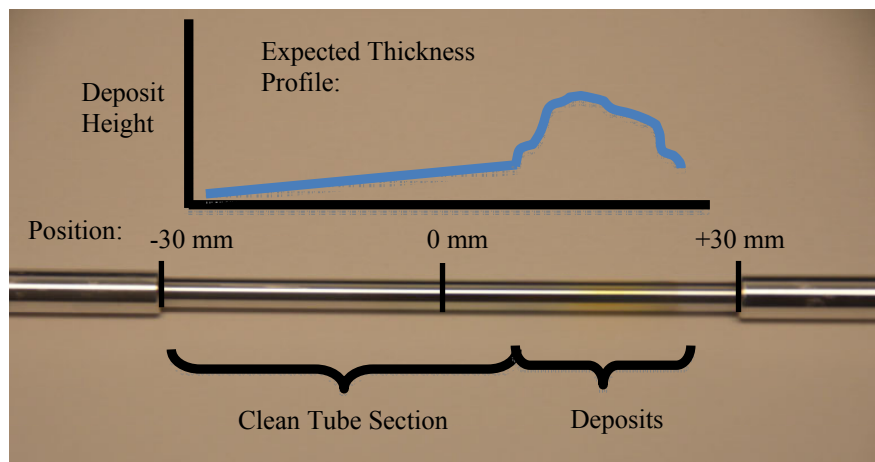


Figure 4.—JFTOT heater tube and deposition pattern. [A JFTOT tube run at 291 °C that yielded a “3” on the color scale can be seen above. An expected general deposition pattern that may be seen through thickness measurement is superimposed.]

Runs executed at 266 °C exhibited inconsistencies in differential pressure results. However, such inconsistencies are taken into consideration by JFTOT procedure. As JFTOT dictates, runs are to be performed at five degree intervals to definitively ascertain breakpoint. This accounts for potential fluctuations in fuel performance as temperatures approach the actual breakpoint. In addition some runs were deemed invalid and not included in data analysis. Regardless of failure with respect to differential pressure and visual rating, tests were considered invalid only when instrumentation/control system malfunctioned or the operator terminated the run prior to completion.

4.2 Angular Variation of Ellipsometer Profiles

Using the ellipsometric procedure outlined in Section 3.3, a profile for a JFTOT tube was attained. This graph showed the heights of the deposits measured at positions. To better understand what is represented, a picture of a JFTOT tube is contained below. It is important to see the maximum thickness of the color deposits, most importantly the dark areas on the tube. An example tube with depositions which were rated a “3” on the JFTOT color rating scale can be seen in Figure 4. Also included is a prediction of the expected thickness profile, showing the relatively low deposit height in the clean section of the tube, followed by the bumpy rounded deposition profile.

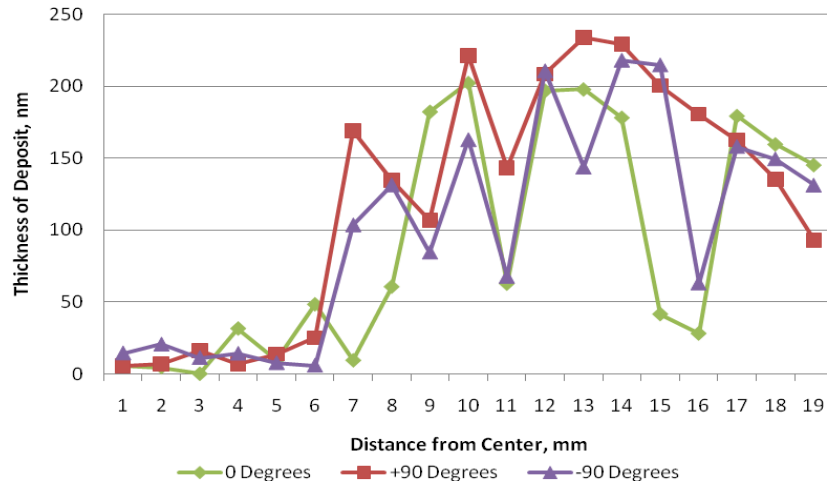


Figure 5.—Multi-angle film deposit profile of single aluminum heater tube. [This figure shows the relative profile of deposition along a JFTOT tube run at 291 °C that yielded a “<4” on the color test. The fuel type used for this case was JP8.]

It was expected that for the profile of the tube that along the discolored parts there would be the maximum deposition and along the parts that appeared clear, there would be relatively little deposition. This was verified as can be seen in the data seen above in Figure 5. The lower relative distances from the center, between ~0 to 5 mm represent the clean tube portion. These had maximum depositions on the order of 20 to 30 nm. Positions between 5 to 20 mm represent the visibly discolored area on the tube. It was expected that there would be a gradually rising rounded profile. What was found, in reality, was a rising profile that was not well-rounded and appeared to have irregular dips and peaks. This implied a need to validate results through another method, which is described in Section 4.3. It was verified, though, that the peak deposit heights were located in the darkest areas on the tube. Another encouraging result was that the maximum heights of depositions at different angles around tubes were similar, on the order of 15 percent variations. This allows for one to take measurements on only one side and know with relative certainty that the maximum height is close to the maximum height along the whole tube.

4.3 Validation Techniques for Ellipsometer Results

It was determined that a secondary method for determining film thickness would be used in order to validate the ellipsometer’s results. Two readily accessible methods, interferometric microscopy and laser extensometry, were first explored. Interferometric microscopy only examines the surface profile of a small area on the surface of the sample, so the only way to obtain the thickness of the film is to create a step from the film to bare aluminum tube by removing some of the film and then measuring the height of the film layer. However, because of the surface irregularities of the tube it is hard to differentiate between the film and the bare aluminum at the step. This means thickness measurements made using this method are unreliable and inconclusive, and therefore interferometric microscopy would not be a viable method for determining film thickness.

Laser extensometry measures the width of an object placed between a laser and sensor; in the case of the JFTOT heater tubes the width corresponds to the diameter of the tube. Thus, determining the thickness of the hydrocarbon deposits using laser extensometry involves measuring the heater tube before and after JFTOT testing and then calculating the difference. The accuracy of this calculation requires that measurements be made in the exact same angular positions on the tube to avoid inaccuracies caused by non-uniform circumferential deposition and/or heater tube surface irregularities.

While the laser extensometer used has a claimed resolution of 50 nm (Ref. 9), initial results demonstrate relatively large variations in the overall heater tube profile as well as pronounced surface roughness. In Figure 6, a 200 nm thick line, representing a reasonable film thickness value, is superimposed upon a sample tube profile to exhibit the necessary resolution the instrument must be capable of achieving. While some of these surface features seemed to be reproducible, even small changes in angular position yielded much different profiles meaning differences calculated between pre and post test laser extensometer profiles may not represent actual film thickness. This demonstrates laser extensometry as an inadequate method for determining film thickness.

Scanning Electron Microscopy (SEM) was considered as another option to validate ellipsometer film thickness measurements. SEM provides highly magnified images which in our case can be used to measure the film height directly. Originally, we had intended to use a small diamond scribe to scratch the surface of the tube, image the area at different angles with the SEM, and then calculate the depth accordingly using the known angular orientations. However, after viewing the film surface on the heater tube, bare areas were present along the tube providing reference surfaces by which to measure film thickness as illustrated in Figure 7. These measurements were then corrected for the angular orientation of the area imaged. Film thickness at several points along a heater tube was measured using this method and

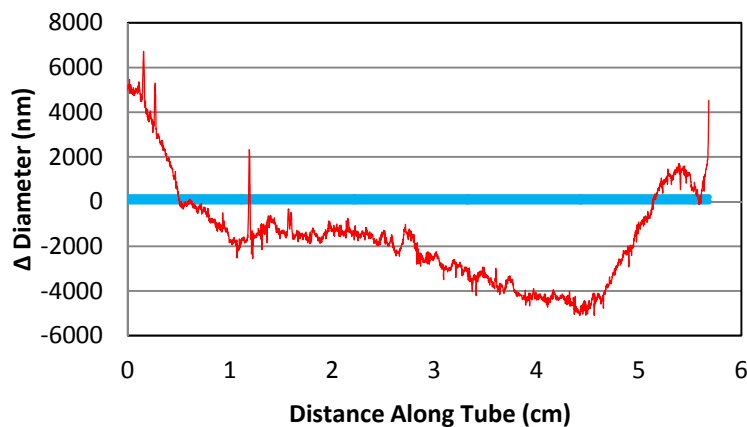


Figure 6.—Variations in JFTOT tube diameter. [A comparison between the tube diameter (red) and a 200 nm thick line (blue) demonstrates the considerable surface irregularities present on the tube.]

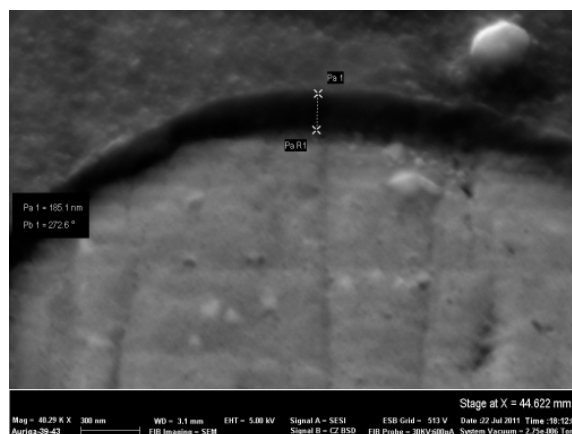


Figure 7.—SEM image of hydrocarbon film on aluminum. [The lighter area in the bottom of the figure represents the aluminum substrate while the hydrocarbon deposits are visible in the upper portion. Using the SEM the thicknesses of the deposits could be measured.]

the results were compared to the ellipsometer measurements. Figure 8 illustrates the film thickness profiles measured using SEM compared to 3 film thickness profiles measured using the ellipsometer. From this plot we see that the maximum heights from all three profiles agree well with one another. SEM analysis yielded a maximum thickness value of 233.3 nm compared to 233.8, 202.4, and 218 nm for the 0, 90, and -90° measurements respectively. These values correspond to percentage deviations from measured SEM maximum deposit thickness of 0.0, 13.2, and 6.6 percent respectively. The reasonable correlation between results from both methods suggests that the ellipsometer measurements are representative of actual deposit thicknesses.

Figure 9 shows the chemical characterization of tube deposits using scanning electron microscopy energy-dispersive x-ray (SEM-EDX) spectroscopy. These two images show the results at two different locations along the tube surface. On the left, position 0, the film shows very little carbon deposition and a high quantity of aluminum from the tube surface. This indicates that position 0 is expected to be a very thin film. On the right, position B, the film is analyzed to have a high quantity of carbon as well as an increased deposition of oxygen. Visual observation is consistent with the SEM analysis as point 1 is darker in color.

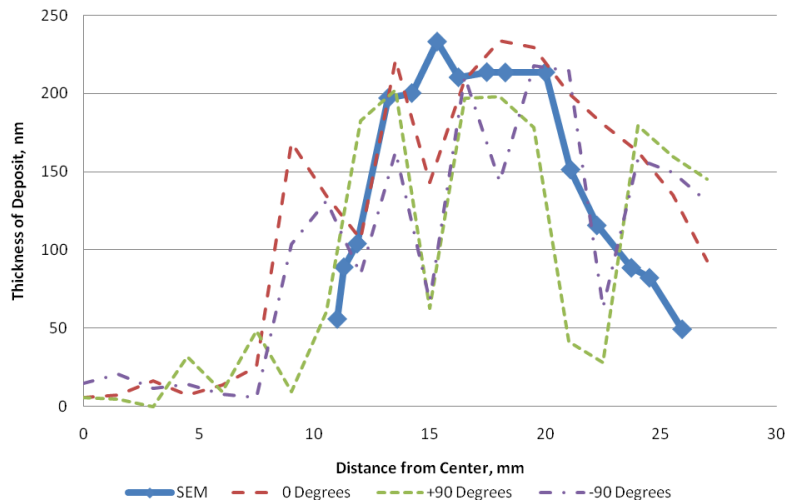


Figure 8.—SEM versus spectroscopic ellipsometer. [Deposit thickness measurements from SEM are superimposed onto previous ellipsometry measurements. These profiles are similar, providing evidence that ellipsometry is representative of actual deposit thickness.]

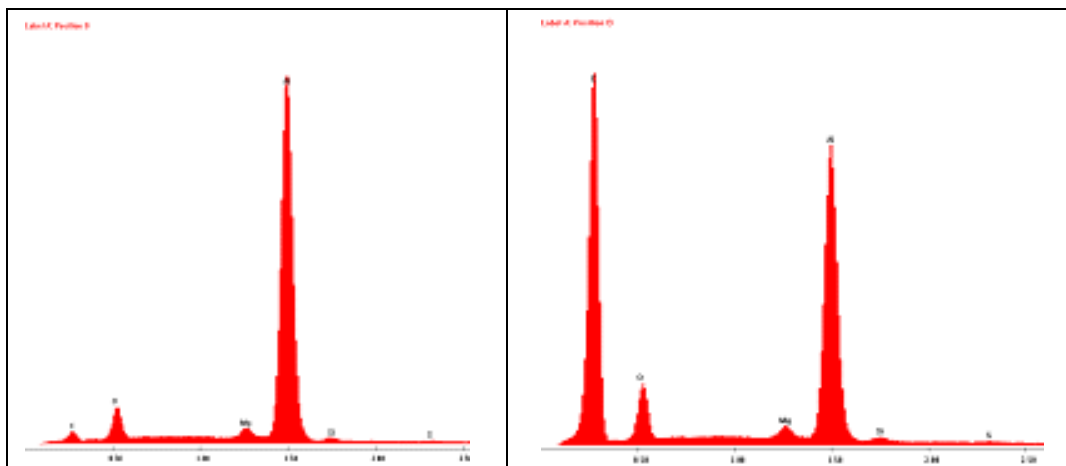


Figure 9.—Scanning electron microscopy energy-dispersive x-ray (SEM-EDX) spectroscopy results. [This figure shows the chemical characterization of the tube deposits at two different points along a tube surface: “position 0” is on the left and “position B” is on the right.]

4.4 Ellipsometry Results

After finding the relative profile along the tube to be relatively accurate and independent of measurement angle, it was desired to show that the maximum height of deposits was reproducible between specific tests at specific temperatures. For this reason, 11 data points were taken, ranging from 255 to 275 °C. This can be seen below in Table 3. In taking this data, it was desired to both obtain a range of temperatures and color ratings, and also it was deemed beneficial to obtain measurements at one temperature to assess precision. The resulting maximum thicknesses found can be seen in the Table 3 and ranged from 52 nm for a “2” on the color scale to 250.1 nm for a “>4” on the color scale. The general correlation between thickness and temperature can be seen in Figure 10.

TABLE 3.—EXPERIMENTAL RESULTS
[Temperature Range HLPS was run and the respective metrics measured post JFTOT.]

Run ID	Temperature, °C	Max height, nm	Color rating	Differential pressure, mmHg
1103	261	52	2	1
1104	263	70	2	1
1100	266	96.6	2	183
1102	266	110	2	192
1105	266	72.3	2	7
1097	266	64	2	7
1096	266	63.7	1	2
1106	268	94.5	<3	189
1112	271	219.7	<4	195
1113	276	230.9	>4	196
1115	281	250.1	>4	190

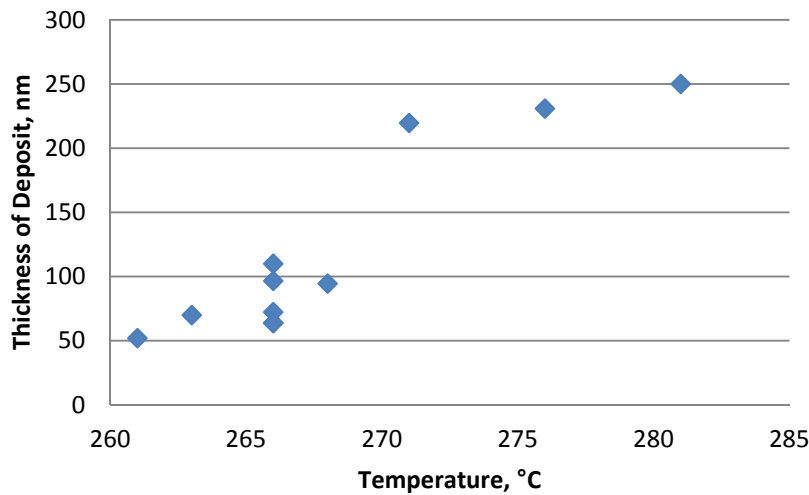


Figure 10.—Temperature versus deposit thickness. [This figure shows some degree of thickness reproducibility around lower temperatures and a positive correlation between temperature and thickness.]

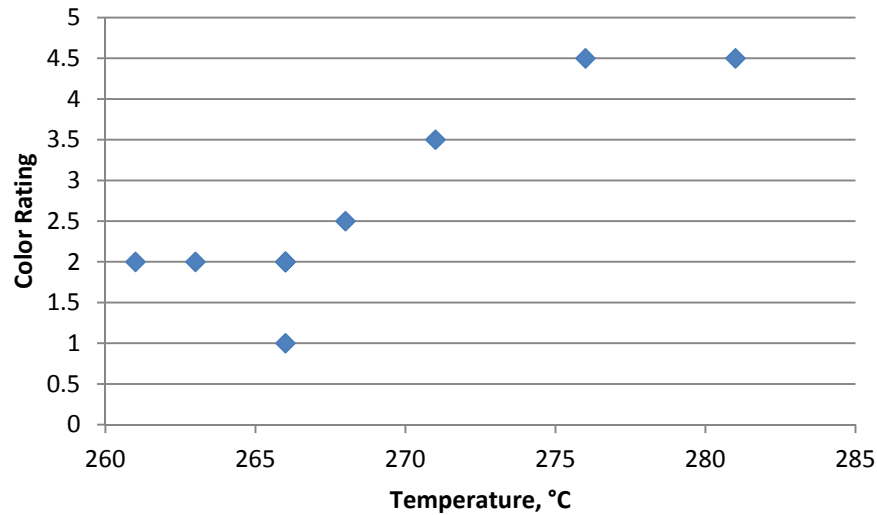


Figure 11.—Temperature versus color rating. [This figure shows the correlation between color rating and temperature.]

From these results, it was seen that there was a positive trend between temperature and thickness of deposits. As temperature increased, so did the relative maximum thickness of deposits. This was expected, as higher temperatures typically correlate with darker color scale results, and in Section 4.1 it was found that darker areas of deposition yield greater thicknesses. These two relationships imply that higher temperatures should correlate with a greater maximum deposit thickness. It was also seen that results were relatively tightly grouped for similar temperatures. Using the ellipsometer yielded relatively similar results for the same temperature, as can be seen by the tightly grouped points in the bottom temperature range of the data. Both of these trends were necessary in validation of ellipsometry results, and it was promising to see both reproducibility around singular temperatures and an upward trend over the range.

4.5 Color Test Results

To obtain a comparison of this new method as compared to the current color metric, the results for the tests run were also given color ratings. These are contained in Table 1 and can be seen graphically in Figure 11 (In these graphs, <ratings were graphically represented by taking the numbers they were between and averaging them; e.g., <3 would be between 2 and 3, so it would be graphically represented as a 2.5; “>4” is a 4.5).

From these results, one can see that there is an upward trend with temperature, but there are many differences from those of ellipsometry measurements. First, the maximum color rating was achieved at 275 °C, as the color scale does not specify specific steps above a “>4” on the scale. This may be one way in which the ellipsometry measurements outperform the color rating metric. Also, the points around specific temperatures do not fall neatly into a specific grouping, implying that the precision of this metric may be less than that of ellipsometry.

4.6 Performance Comparison

Within this temperature range and testing conditions, the relationship between temperature and both thickness of deposits and color rating has comparable shape, accuracy, and usefulness. In the color method, there are observed increases in darkness of deposits with an increase in temperature. With ellipsometry measurements, there are obvious increases in thickness as temperature is increased. The results demonstrate that with both methods there are increases in either deposit thickness or color rating

with an increase in testing temperature. These trends seem to be reasonably consistent throughout the testing temperature range for both methods, lending credibility to the validity of each.

Another important comparison is the relative precision and repeatability of each method. For these tests, because they were performed in the same circumstances with the same fuel, it would be expected that when temperature is held constant, similar results would present themselves. For ellipsometry, there were mixed results. Looking at the numerous data points taken at 266 °C, the reproducibility is marginal, showing a range from 63.7 to 110 nm. This shows that for one temperature there can be a range of >50 nm, which implies potential issues with resolution. However, when the data is separated into two sets representing passing and failing differential pressure (dP), the precision of the ellipsometry measurements improves considerably. Differential pressure passes at 266 °C ranged from 63.7 to 72.3 nm which represents a variation of only ~14 percent. At the same temperature, dP failures ranged from 96.6 to 110 nm, exhibiting an equal percentage of deviation. As dP pass/failure characterization is important in describing a fuel's thermal stability performance, these results may actually further support the usefulness of ellipsometry. It is possible that the measurements are capturing a phenomenon that is not well understood or found through simple color measurements, and this general ability to capture the thicknesses of films without alluding to color may show promise in research settings. For the color test, there was some precision and reproducibility, but the small scale of the test was shown to be limiting. Finding results within the 261 to 268 °C range resulting in "1" to "2.5" in a scale that only measures from 0 to 4 represents an excessively wide range of results and highlights the difficulty in using the color test as a performance or comparison metric. Without precise measurement, one must rely on statistical methods; ellipsometry may improve research and data acquisition by decreasing the necessary trials to find accurate, widely applicable results.

Overall, ellipsometry performs comparably to the color test in many ways, at least within the temperature range tested. Accuracy and precision have both been demonstrated by each method, with ellipsometry measurements showing potential to improve each. One other potential unexplored benefit is the extension to the range of the color test. Within the framework of this research, no sample is rated lower than a color rating of "2," and only 2 samples achieved ">4" rating, leaving the data within the range that the color test performs well. In reality, the color test has nearly reached the limits of its usefulness in these tests, while ellipsometry should still allow for a quantitative analysis of the fouling characteristics of the tested fuel at temperatures much higher than the point where the fuel would be rated ">4." Also, at lower level tests achieving around a "1" on the color rating scale, ellipsometry may be able to provide more precise information on the performance for specific tests. It is within the framework of these broad ranges that are not captured by the color test that ellipsometry will truly be useful.

5.0 Conclusion

Film thickness determination through ellipsometry has been demonstrated to be accurate, precise, and quantitative, potentially providing many benefits over the conventional color test in characterizing or comparing the thermal stability of fuels. As exhibited by the non-reproducibility of results in color testing, the visual rating method utilized in ASTM D3241 possesses inaccuracies. The inherent subjectivity in rating conventional jet fuel through the qualitative color measure diminishes the credibility of the visual standard. In addition, the color code is limited to a rating of ">4," forcing a wide range of different results into one specific level. Meanwhile as expected, there exists a positive correlation between temperature and deposit thickness. This, in conjunction with the repeatability of thickness measurements, displays the validity of using film thicknesses as a supplement to the discoloration to rate fuels. As JFTOT is utilized mainly for a small gamut of conventional jet fuels, other potential fuels may exhibit discoloration in a manner not understood or represented by the ASTM Color Standard. In these cases where comparability of color ratings is absent, the film thickness measurements can proffer information relating to thermal stability. Thus this metric can be used in a research setting and provide more meaningful fuel characterization methods for the implementation of future generations of fuels.

Appendix—Hot Liquid Process Simulator Raw Data

TABLE 4.—HLPS DATA SET

[Data collected with HLPS for each run including JFTOT metrics ΔP and visual rating.
Note * indicates test is invalid due to equipment malfunctions and early run termination.
Temperatures are not yet corrected.]

Run ID	Fuel index	Recorded temperature, °C	Tube type	dP, mmHg	dP, P/F	Color rating	Color, P/F
1120	JP8-ASCR-2011-05-27	260	AL	197	f	<4	f
1119*	JP8-ASCR-2011-05-27	270	AL	194	f	1	P
1116	JP8-ASCR-2011-05-27	262	AL	0	p	>4	f
1115	JP8-ASCR-2011-05-27	275	AL	191	f	>4	f
1114	JP8-ASCR-2011-05-27	270	AL	177	f	>4	f
1113	JP8-ASCR-2011-05-27	270	AL	196	f	>4	f
1112	JP8-ASCR-2011-05-27	265	AL	196	f	3,<4	f
1111	JP8-ASCR-2011-05-27	262	AL	171	f	3,<4	f
1110	JP8-ASCR-2011-05-27	275	AL	171	f	>4	f
1109	JP8-ASCR-2011-05-27	270	AL	189	f	>4	f
1108	JP8-ASCR-2011-05-27	280	AL	199	f	>4	f
1107	JP8-ASCR-2011-05-27	265	AL	190	f	2	p
1106	JP8-ASCR-2011-05-27	262	AL	189	f	<3	p
1105	JP8-ASCR-2011-05-27	260	AL	7	p	2	p
1104	JP8-ASCR-2011-05-27	257	AL	1	p	2	p
1103	JP8-ASCR-2011-05-27	255	AL	1	p	2	p
1102	JP8-ASCR-2011-05-27	260	AL	192	f	2	p
1101	JP8-ASCR-2011-05-27	260	AL	39	f	<3	p
1100	JP8-ASCR-2011-05-27	260	AL	181	f	2	p
1099	JP8-ASCR-2011-05-27	260	AL	194	F	<3	p
1098*	JP8-ASCR-2011-05-27	265	AL	45	f	2	p
1097	JP8-ASCR-2011-05-27	260	AL	7	P	2	P
1096	JP8-ASCR-2011-05-27	260	AL	2	p	1	p
1095*	JP8-ASCR-2011-05-27	270	AL	197	f		
1094*	JP8-ASCR-2011-05-27	282	AL	0	p	3	p
1093	JP8-ASCR-2011-05-27	282	AL	191	f	>4	f
1092*	JP8-ASCR-2011-05-27	282	AL	194	f	>4	f

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