

Spectroscopic Study of Aviation Jet Fuel Thermal Oxidative Stability

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Aviation fuel is used as a coolant to remove waste heat loads from an aircraft in addition to its conventional role as an energy source through combustion. As the fuel temperature increases, several reactions involving hydrocarbon molecules, dissolved oxygen, and impurities take place, which ultimately lead to the formation of gums and solid deposits. Ultraviolet–visible light absorption and fluorescence spectroscopy were used to study the degradation of commercial Jet A-1 as it was thermally stressed. Both techniques were shown to be highly sensitive to the chemical reactions occurring in the thermally stressed fuel that led to the formation of oxygenate products.

Introduction

In modern aircrafts, jet fuel is generally used as a heat sink to remove waste heat in addition to its conventional role as an energy source for combustion. The use of aviation jet fuel as a coolant is problematic because the fuel temperature increases as it absorbs heat, resulting in several liquid-phase chemical reactions involving hydrocarbon molecules, dissolved oxygen, and impurities. These reactions can cause carbon deposits to build up within the fuel, constrict the fuel flow, potentially cause an engine shutdown, and decrease the effectiveness of the surfaces to act as a heat exchanger.¹

It is widely recognized that the fuel degradation process can be divided into two different temperature regimes with different reaction mechanisms: the autoxidation regime ranges from fuel temperatures of 150–300 °C, while the pyrolytic regime typically occurs for temperatures above 400 °C.

During autoxidation, the hydrocarbon fuel reacts with dissolved oxygen contained within the fuel to form free-radical species; air-saturated jet fuel contains about 70 ppmv of dissolved oxygen. The free-radical species then react with naturally occurring heteroatomic molecules, eventually leading to hydrocarbon polymerization processes accountable for gum formation.²

At fuel temperatures above 400 °C in the pyrolytic regime, the fuel instability mechanism is characterized by the breakdown of the hydrocarbon chemical bonds by pyrolytic cracking, which converts long paraffinic chains into smaller alkanes and alkenes that further develop into aromatic compounds and solid deposits.³

The thermal stability of aviation jet fuel has been examined in the present study. In particular, ultraviolet–visible (UV–vis) absorption and fluorescence spectroscopy measurements have been performed by comparing the thermally stressed fuel to fresh fuel samples. Furthermore, the fuel was stressed at

air-saturated dissolved oxygen levels and deoxygenated conditions, achieved by nitrogen sparging, to investigate both the effect of oxygen on the fuel thermal degradation process and the ability of the optical methods to follow the appearance of oxidative products within the thermally stressed fuel. Results from previous aviation jet fuel thermal oxidative studies that made use of optical and spectroscopic methods are also reviewed.

Review of Optical Diagnostics and Fuel Thermal Stability

Optical and spectroscopic techniques can be useful tools to better understand the jet fuel instability mechanism. Furthermore, optical diagnostics can be used as complementary tools for fast, *in situ* thermal stability tests instead of classical, time-consuming methods, such as the Jet Fuel Thermal Oxidation Tester (JFTOT; ASTM D3241). Fluorescence and absorption spectroscopies have already been shown to be successful techniques for the characterization of light and heavy crude oils by Mullins and co-workers.^{4,5} The first attempts to develop optical methods for jet fuel thermal oxidative stability analysis can be found in the early 1990s. Cheng et al.⁶ used UV–vis absorption spectroscopy in accelerated oxidation tests to measure the amount of soluble gums. Parker et al.⁷ studied the fouling phenomena of JP-4 fuel using a combination of optical measurements: light absorption spectra from 350 to 750 nm, elastic light scattering at 514.5 nm for particle size measurements, and monochromatic fluorescence collected in the visible spectrum. The authors concluded that all three techniques showed an ability to monitor changes within the thermally stressed fuel.

The oxidation rate of different hydrocarbon fuels was monitored by UV–vis absorption spectra by Li et al.,⁸ who also confirmed the presence of OH, C–O, and C=O groups in the

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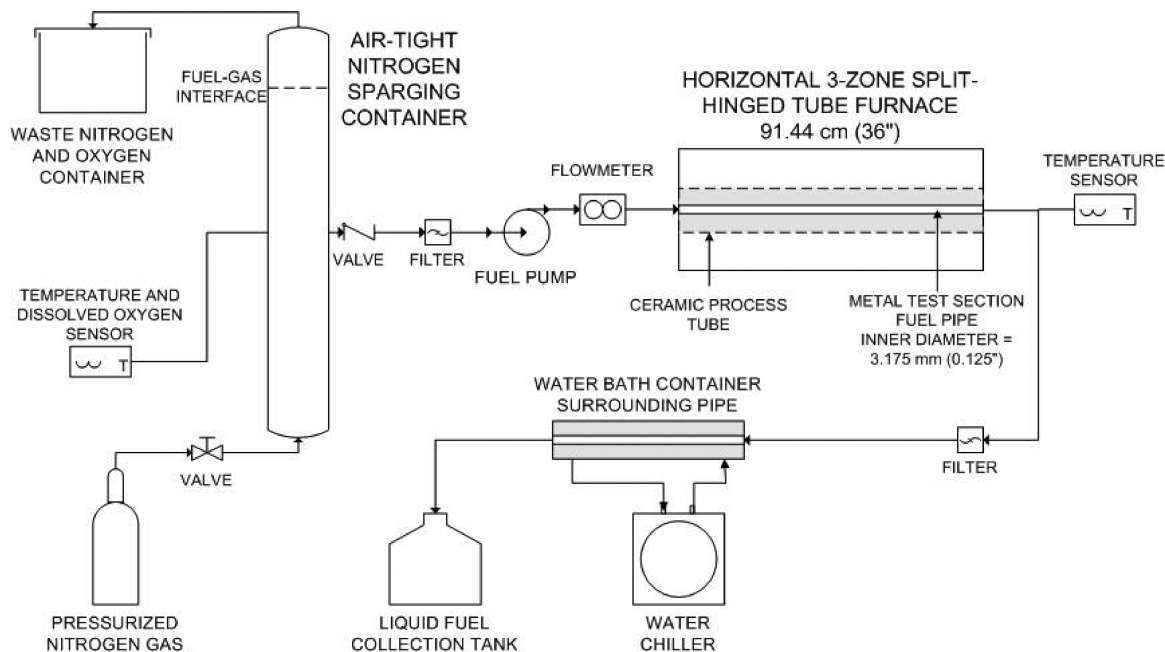


Figure 1. Schematic diagram of the experimental test facility used to thermally stress aviation jet fuel.

oxygenated products formed in the oxidized fuels and the deposit by infrared spectroscopy. Furthermore, Jeyashekar and Wilson⁹ addressed the capabilities of laser-induced fluorescence as a tool to quantify the thermal degradation of aviation jet fuel by performing experiments on several fuel samples with varying thermal stability. A near-perfect correlation was found between fluorescence intensity and the fuel breakpoint temperature measured by the JFTOT test.

Experimental Section

In the present study, we investigate the aviation jet fuel thermal stability in both flow and static conditions. In both types of tests, the fuel was heated within a horizontal, split-hinged, three-zone Thermcraft tube furnace with a heated length of 91 cm (36 in.), as shown in Figure 1. The aviation fuel was commercial Jet A-1 provided by Shell Canada.

For the flow test, fuel was introduced via a Teledyne ISCO A500 continuous flow syringe pump at a gauge pressure of 600 psi. A back-pressure control valve was used downstream to maintain the line pressure until the end of the apparatus. The fuel flowed through a 316 stainless steel tube with a $\frac{1}{8}$ in. outer diameter and 0.069 in. inner diameter. The apparatus was designed for a more general purpose and included a nitrogen-sparging system to evaluate the effect of the dissolved oxygen content of the fuel on the thermal oxidative mechanisms. The two different conditions investigated were with air-saturated dissolved oxygen and fully deoxygenated fuel, namely, 100% and 0% O₂, respectively. Fuel temperatures were measured upstream and immediately downstream of the heated test section by two resistance temperature detectors (RTDs) that allowed for highly accurate and stable data collection. After Jet A-1 was heated in the tube furnace, it was immediately cooled to quench the chemical reactions, prevent damage to valves and analytical equipment, and allow the fuel to be sampled. Thus, a thermal bath heat exchanger was built around and surrounded the fuel tube, with cold water continuously supplied from a Lytron Kodiak recirculating chiller. The aviation jet fuel was stressed over a range of temperatures from 120 to 220 °C. The line pressure and fuel flow rate were kept

constant at 600 psi and 1 mL/min, respectively, which corresponded to a 2 min stress duration.

Static tests were performed using a slightly modified heating configuration. A $\frac{1}{4}$ in. outer diameter, 0.18 in. inner diameter, 316 stainless-steel tube was used instead to allow for enough fuel to be collected for the optical measurements. The tube was partially filled with Jet A-1 and then pressurized with oxygen to limit a situation where the autoxidation reaction rate would be oxygen-limited.

UV-vis fluorescence spectra were obtained on a Perkin-Elmer model LS-50B luminescence spectrophotometer. The emission spectra were collected in the range of 300–700 nm, with a scan speed of 240 nm/min and a resolution of 0.5 nm. Excitation and emission slit widths were fixed at 5 nm. Also, the fluorescence spectra were corrected for self-absorption. A Perkin-Elmer UV-vis spectrometer Lambda 12 was used to measure the UV-vis absorption spectra of thermally stressed Jet A-1. All of the stressed fuel spectra were compared against a reference sample of unstressed Jet A-1 fuel. The absorption measurements were spectrally resolved from 330 to 630 nm, where the lower wavelength limit corresponded to the optical absorption edge of the Jet A-1 used in the present investigation. In all optical measurements, a 10 mm path-length quartz cuvette was used.

Results and Discussion

The formation of solid deposits in the autoxidative regime is a complex process involving liquid-phase chemical kinetics, polymerization or clustering reactions to form high-molecular-mass compounds, solubility, and mass transfer, as shown by Watkinson and Wilson.¹⁰ Specifically, the oxidation of the fuel is the result of a free-radical mechanism, which involves fuel hydrocarbon molecules, dissolved oxygen, and heteroatomic species containing oxygen, nitrogen, and sulfur in aromatic functional groups. These heteroatomic molecules, also known as antioxidants, can easily lose a hydrogen atom because of their weak O–H, N–H, and S–H bonds. As a result, antioxidants can interfere with the free-radical oxidative mechanism, resulting in a slower oxidation rate and a

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greater amount of solid deposits.¹¹ Furthermore, it is well-known that reducing the dissolved oxygen content in the fuel results in a general improvement of the fuel thermal stability (i.e., less solid deposits).

UV–vis absorption spectra of thermally stressed Jet A-1, with and without oxygen (100% O₂ and 0% O₂, respectively), are shown in Figure 2. The absorbance values, for the air-saturated Jet A-1 samples, showed a structureless broad line profile with increasing intensity at shorter wavelengths. It is possible that the measured absorption band could be attributable to the $n \rightarrow \pi^*$ transition of the carbonyl C=O, which is formed as a result of the oxidation process, as reported by Li et al.⁸ and Friedel and Orchin.¹² The maximum measurable value was at 330 nm, which corresponded to the optical absorption edge of the commercial Jet A-1 used in the present study. This optical property is closely related to the concentration and chemical identity of the constituent aromatic hydrocarbons in the fuel, as shown by Mullins and co-workers.^{4,5} Typically, the presence of larger aromatics in the fuel would shift the electronic absorption edge to longer wavelengths. Furthermore, the absorbance values for the stressed fuel became negligible for wavelengths longer than 500 nm, as shown in Figure 2. This leads to the conclusion that only the spectra range between the electronic absorption edge of the fuel, at 330 nm for our Jet A-1, and 500 nm is available for such spectroscopic analysis. It may be possible that, for heavier fuel samples with a longer absorption edge wavelength, the use of absorption spectroscopy for fuel thermal stability studies would be quite unpractical. Therefore, the feasibility of using such a method to investigate the thermal oxidative stability of aviation jet fuel is strongly affected by the aromatics content in the pristine jet fuel.

Further analysis showed that the difference in the absorption spectra between deoxygenated and air-saturated fuel samples not only confirmed the importance of dissolved oxygen on the thermal stability of aviation fuel but also showed that this technique was able to detect the presence of oxygenated products or deposit precursors in the fuel, which are likely to be responsible for deposit formation. This was further confirmed by the spectra of Figure 3, where flow tests with short residence times were compared to static tests with longer residence times at the same fuel temperature. Note that the absorbance values in Figures 2 and 3 are all measured using the unstressed Jet A-1 sample as a reference.

Fluorescence emission spectroscopy led to similar results. The fluorescence spectrum of deoxygenated Jet A-1 fuel thermally stressed at 160 °C was the same as the unstressed Jet A-1 spectrum, which are shown by a red solid line and black dotted line, respectively, in Figure 4. In comparison, the air-saturated fuel emission spectrum was red-shifted, shown by the solid black line in Figure 4. The red shift in the fluorescence spectra was even more pronounced for the fuel sample stressed in the static test shown by the blue solid line, which had a longer residence time.

The ability of the emission spectroscopy to follow fuel oxidation under different temperatures was also investigated, and fluorescence spectra of thermally stressed Jet A-1 for several temperatures are shown in Figure 5. The fluorescence intensities increased as the fuel was heated to higher temperatures.

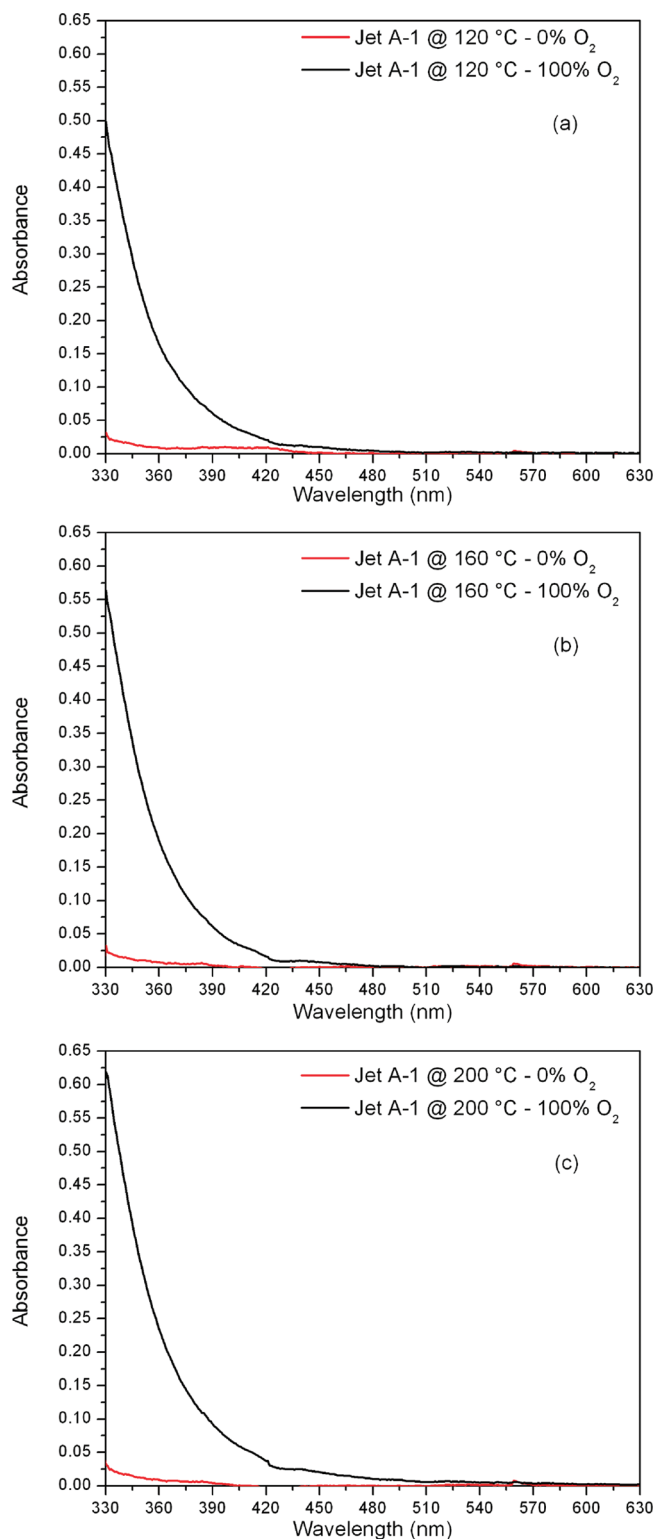


Figure 2. Absorbance spectra of thermally stressed Jet A-1 with and without dissolved oxygen for three different temperatures. Data are relative to flow test conditions.

To analyze the observed red shift, a deconvolution method based on multiple Gaussian fitting was used to mimic the behavior of the measured spectra, as shown by Patra and Mishra.¹³ For simplicity, only three Gaussian functions were

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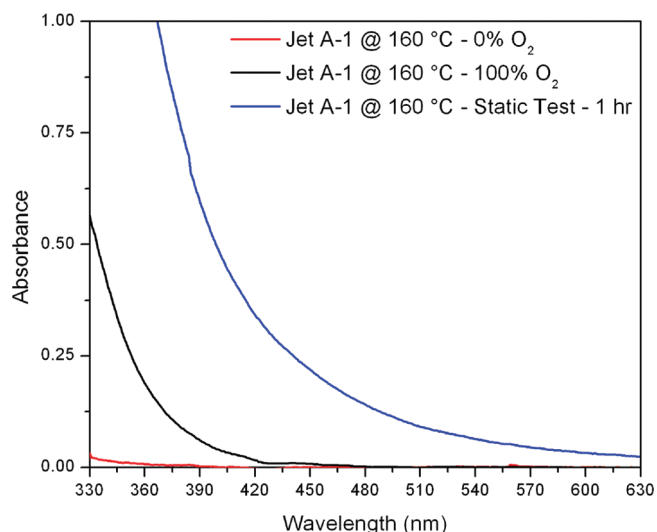


Figure 3. Comparison of the absorbance spectra of thermally stressed Jet A-1 at 160 °C in flow and static test conditions.

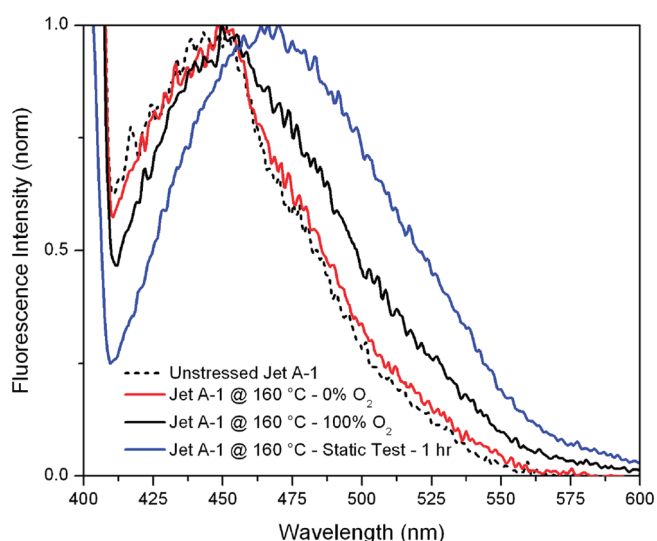


Figure 4. Normalized fluorescence spectra of thermally stressed Jet A-1 at 160 °C in flow and static test conditions. Excitation wavelength for all of the spectra was at 400 nm.

used, with the centers fixed at 440, 470, and 510 nm, respectively (Figure 6). The maximum values of the three functions are shown in Figure 7 for different fuel samples taken at the same conditions as the ones reported in Figure 4. For example, the intensity of the fluorescence band centered at 510 nm was higher for the two stressed Jet A-1 measurements with dissolved oxygen than the sample that was deoxygenated. Moreover, the spectrum relative to the deoxygenated Jet A-1 sample showed almost the same emission intensity for the bands at 440, 470, and 510 nm as the unstressed fuel sample, as shown in Figure 7.

It is well-known that longer emission or absorption wavelengths are achievable only by resonance effects because of the

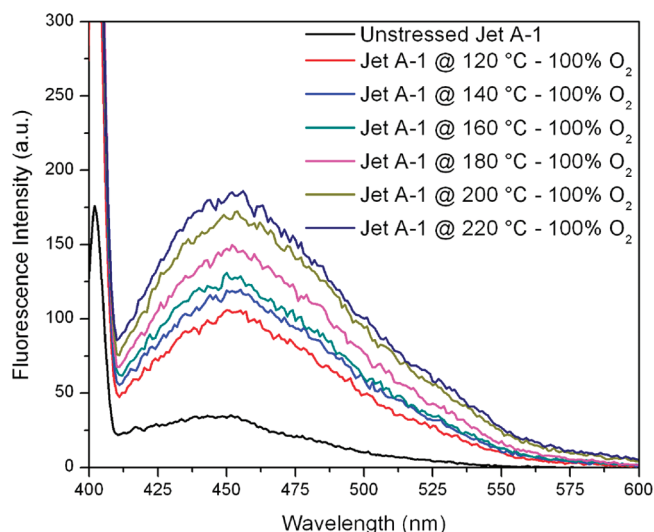


Figure 5. Fluorescence spectra of unstressed Jet A-1 and thermally stressed Jet A-1 at different temperatures in flow test conditions.

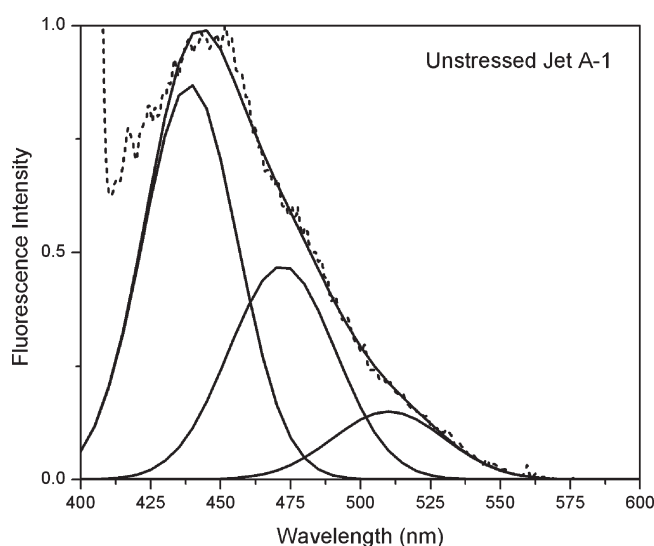


Figure 6. Deconvolution of the fluorescence spectra of unstressed Jet A-1.

formation of higher molecular-mass compounds because of conjugation effects.¹² Commercial Jet A-1 is a kerosene-type fuel, with its aromatics content limited to < 25 vol % by ASTM D1319. Also, most of the aromatics in the jet fuel are composed of mono-ring alkyl benzenes, which account for almost 13 vol % of the fuel.¹⁴ Over the range of stressed fuel temperatures from 120 to 220 °C investigated in this study, it is reasonable to consider that the rate of pyrolytic reactions for the hydrocarbon fuel molecules are negligible, and therefore, larger condensed aromatics cannot be formed within the fuel.³ This was also observed in the lack of differences in absorption and emission spectra between the unstressed Jet A-1 and the thermally stressed fuel sample in deoxygenated conditions. According to recent literature,² a polymerization process involving hydrocarbon fuel molecules, dissolved oxygen, phenols, and other heteroatomic molecules is the main mechanism responsible for gums and solid deposition caused by thermal oxidative instability. The formation of clusters of high-molecular-mass oxygenated compounds in the jet fuel, with higher polarity and lower solubility,² is in agreement with the

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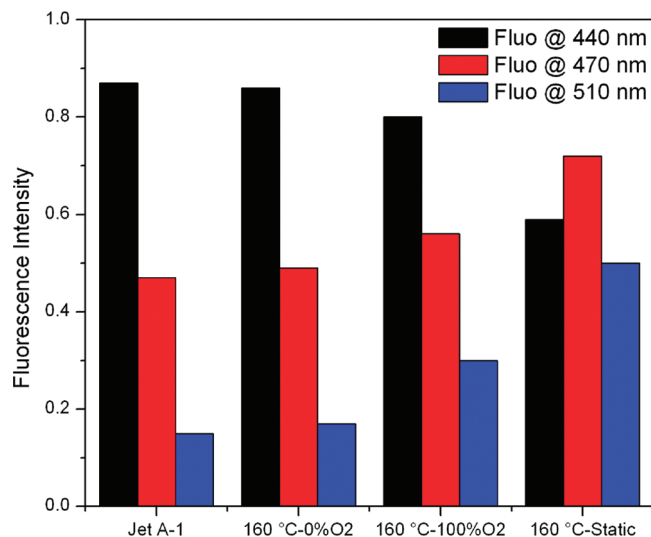


Figure 7. Fluorescence intensities of the three Gaussian functions used for the deconvolution method.

optical data in terms of both the presence of visible absorption and the red shift in the fluorescence emission spectra of air-saturated stressed fuel. These high-molecular-mass polymeric structures have higher polarity and lower solubility, which is why they can be considered as deposit precursors. They also

have a higher degree of conjugation that caused the observed optical red shifts.

Conclusions

UV–vis absorption and fluorescence spectroscopies were used to investigate the thermal oxidative stability of commercial aviation fuel Jet A-1. Experiments were performed in both flow and static conditions, with fuel containing air-saturated levels of dissolved oxygen and deoxygenated fuel. Both techniques were able to follow the fuel degradation process because of the autoxidation reactions. Therefore, UV–vis light absorption and fluorescence emission spectroscopies were shown to be valid tools for fast and reliable investigation of the thermal oxidative stability of aviation jet fuels. Moreover, the result of an increase in the absorption and emission wavelengths were also consistent with the view that high-molecular-mass oxygenated compounds are formed in fuel as a consequence of polymerization reactions activated by the increased temperatures and are strongly dependent upon the amount of oxygen dissolved in the fuel. Further work in this field, with different types of fuel samples, may promote additional insight into the autoxidative deposition mechanism of the aviation jet fuel.

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