

Three-Dimensional Fluorescence Spectra of Thermally Stressed Commercial Jet A-1 Aviation Fuel in the Autoxidative Regime

Mario Commodo,* Ivo Fabris, Owen Wong, Clinton P. T. Groth, and Ömer L. Gülder

Institute for Aerospace Studies, University of Toronto, 4925 Dufferin Street, Toronto, Ontario M3H 5T6, Canada

ABSTRACT: In this study, the thermal oxidative stability of a kerosene-type Jet A-1 commercial aviation fuel has been investigated using a three-dimensional (3D) excitation/emission matrix fluorescence (EEMF) method. The fuel was thermally stressed in flow test conditions over a range of temperatures in the autoxidative regime. To determine the effect of dissolved oxygen on aviation fuel thermal stability, the measurements were conducted for both air-saturated and fully deoxygenated fuel samples. The increase in the fuel temperature results in a large red shift of the fluorescence signals for the air-saturated fuel; however, fully deoxygenated fuel showed no difference in the fluorescence spectra with respect to neat fuel. The observed increase in the emission wavelengths of the collected spectra may be attributed to the formation of high-molecular-mass compounds within the liquid fuel. These species are formed as a consequence of the chemical reactions activated during the thermal stressing process. The use of 3D fluorescence spectra for aviation fuel analysis is shown to be a fast, suitable, and easily implementable tool for establishing and verifying fuel quality. Also, the level of fuel thermal degradation may be ascertained using this method, which should be of great interest for a better thermal management control of turbine engines.

■ INTRODUCTION

The use of onboard aviation fuel as a coolant to remove waste heat loads produced by turbine engines and avionic components is of great interest for the aircraft industry. However, kerosene-type aviation fuels, as well as other middle distillates, have the tendency to degrade at high temperatures and form solid deposits. Such phenomena are generally referred to as the thermal stability of the fuel, which is one of the specifications required for commercial aviation fuel and one of the most critical fuel properties.

Currently, aviation fuel thermal stability, for fuel certification, is determined using the Jet Fuel Thermal Oxidation Tester (JFTOT), American Society for Testing and Materials (ASTM) D3241 Standard.¹ It is worth noting, that the JFTOT, being a simple pass/fail verification procedure, does not offer a quantitative assessment of the amount of gums and solid deposits formed within the fuel lines.

The main problem concerning the fuel instability at elevated temperatures is the formation of solid deposits and gums within the fuel lines, thus constricting the fuel flow and increasing pressure drops. Moreover, if the fuel restriction is left unchecked, it decreases the effectiveness of the surfaces to act as heat exchangers and ultimately causes engine shutdown.^{2–4}

Dependent upon the temperature experienced by the liquid fuel during the heat transfer, two different mechanisms were shown to be responsible for the fuel thermal degradation process and the formation of deposits. At high fuel temperatures, generally above 400 °C, the fuel instability mechanism is characterized by the breakdown of the hydrocarbon chemical bonds by pyrolytic thermal cracking reactions. These reactions convert long paraffinic chains into smaller alkanes and alkenes that further develop, via cyclization and dehydrogenation reactions, into aromatic compounds and solid deposits.^{4–6} This condition is usually referred to as the pyrolytic regime.^{2–6} The accepted overall reaction mechanism from paraffins in jet

fuels can be summarized as follows: long-chain paraffins → alkenes → cycloalkenes/cycloalkanes → alkylbenzenes → polycyclic aromatic hydrocarbons (PAHs) → solids.⁶ Furthermore, it has been demonstrated that the thermal stability of pure hydrocarbons decreases in the order of tetralin > decalin > ethylcyclohexane > *n*-butylcyclohexane > *n*-decane > *n*-tetradecane.⁶ More recently, by assuming first-order kinetics, Widegren and Bruno⁷ found that Jet A (which is very similar to Jet A-1) has a thermal stability similar to that of C₁₀–C₁₄ *n*-alkanes.

At lower temperatures, typically between 150 and 350 °C, hydrocarbon fuels react with dissolved oxygen to form free-radical species. Air-saturated jet fuel typically contains about 70 ppm by volume of dissolved oxygen.¹ These free-radical species, formed as a result of the fuel oxidation reactions, then may react with naturally occurring heteroatomic molecules (nitrogen-, sulfur-, and oxygen-containing compounds) to form species that are precursors for the formation of gums and oxidative deposits. This mechanism is usually referred to as the autoxidation regime or aviation fuel thermal oxidative instability.^{2,8–12}

In the present study, a commercial Jet A-1 aviation fuel was thermally stressed within the autoxidation regime in flow test conditions in a range of temperatures from 120 to 200 °C. Furthermore, to address the dissolved oxygen dependence upon fuel thermal oxidative stability, Jet A-1 was stressed in both air-saturated and fully deoxygenated conditions, namely, 100 and 0% O₂, respectively. The analysis of both conditions is of interest in establishing the potential chemical and physical pathways responsible for the fuel oxidative degradation process.

Received: January 9, 2012

Revised: March 9, 2012

Published: March 20, 2012

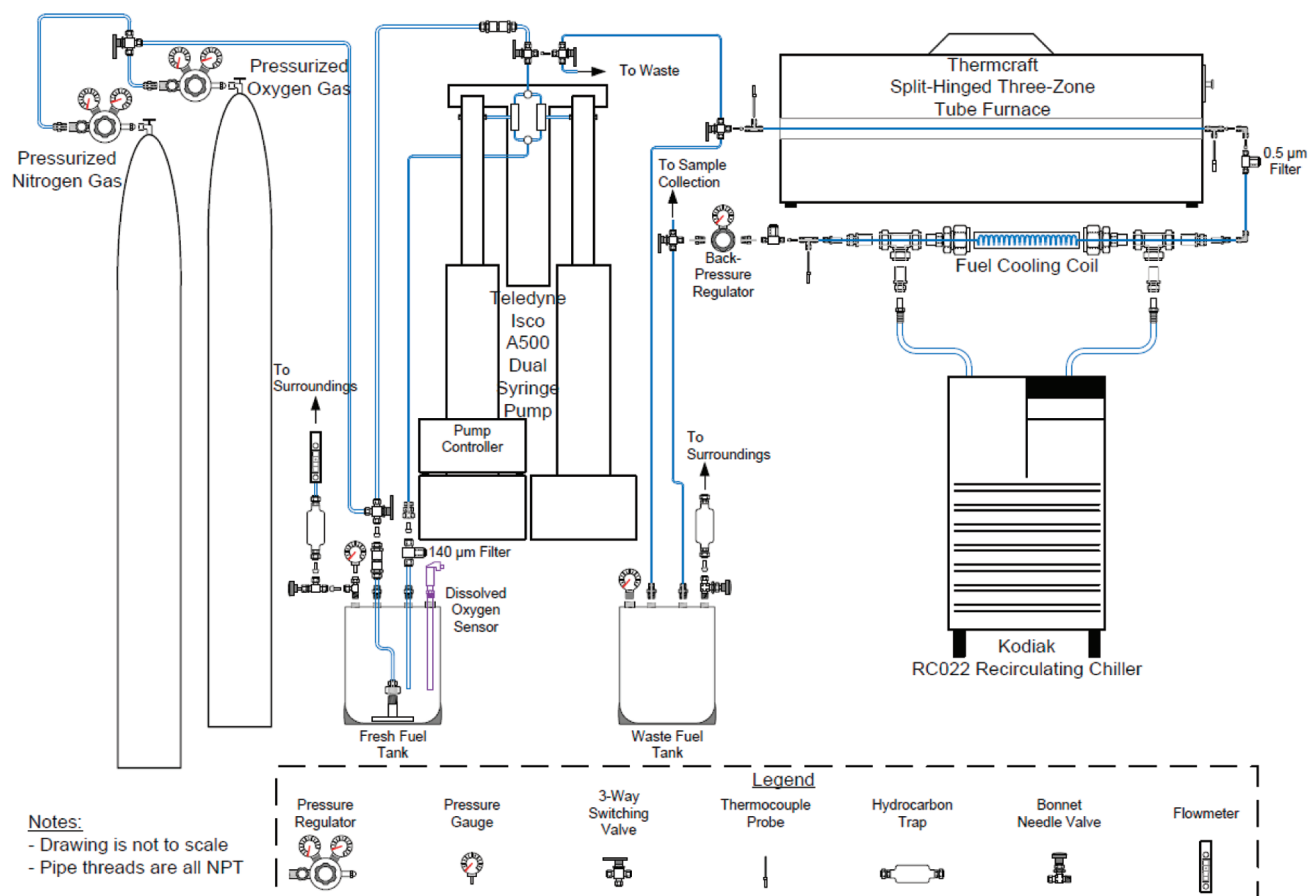


Figure 1. Detailed layout of the dynamic flow setup. Jet A-1 started in the fresh fuel tank that doubled as the gas-sparging vessel and was pushed through the furnace, cooling coil, and back-pressure regulator by the syringe pump. The three-way switching valves only allow for flow between the bottom port and only one of the side ports at any given time.

Thermally stressed aviation fuel was then investigated by ultraviolet–visible (UV–vis) fluorescence measurements. In particular, three-dimensional (3D) fluorescence plots of the Jet A-1 fuel samples, obtained by scanning the excitation wavelength and keeping the spectral range of emission wavelengths constant, were used as the experimental method to investigate the level of fuel degradation under different stressing conditions.

This paper is the third of a series of recent studies^{10,11} based on research performed by our group aimed at investigating the thermal oxidative stability of commercial aviation fuels. In our first study,¹⁰ the spectroscopic behavior of thermally stressed jet fuel by UV–vis light absorption and fluorescence techniques was analyzed. The fluorescence spectra of unstressed and thermally stressed Jet A-1 samples were excited at 400 nm and collected in the spectral range between 400 and 600 nm (Figures 5 and 6 in ref 10). The study showed that both techniques were able to detect and measure the fuel thermal oxidative degradation process.¹⁰ In particular, the results showed an increase in the light absorption and emission fluorescence wavelengths, i.e., red shifts, as a function of the fuel temperature and dissolved oxygen content.¹⁰ We pointed out that the observed red shift in the light absorption and fluorescence spectra of the stressed fuel samples compared to the neat one is likely due to the formation of high-molecular-mass compounds in the bulk liquid fuel as a result of the thermally activated autoxidation reactions.^{9–14}

More recently, we adopted electrospray ionization–mass spectrometry (ESI–MS), a well-established analytical technique able to screen a large number of polar compounds, in the low- and high-molecular-mass regions, to investigate the formation of soluble deposit precursors formed as a result of the autoxidative reactions and the presence of naturally occurring heteroatom molecules.¹¹

Our earlier experimental studies are in agreement with the literature and show that the oxidative deposit mechanism most likely includes the formation of soluble precursors consisting of high-molecular-mass heteroatom species with masses typically ranging between 250 and 400 Da. These soluble precursors undergo polymerization or clustering reactions, leading to the formation of insoluble species, because of the higher polarity, with a molecular mass in the range of 600–900 Da. The observed red shift,¹⁰ in the emission fluorescence spectra of the stressed fuel sample, may be attributable to the formation of this class of compounds.

In the present paper, we explore the entire red-shift phenomena, in terms of excitation/emission spectral regions, using 3D excitation/emission matrix fluorescence (EEMF) plots. The implementation of this method is aimed at better understanding the fluorescence characteristic of a commercial jet fuel as a function of the stressing temperature and dissolved oxygen content. The 3D EEMF approach, in fact, ensures that every possible excitation/emission combination will be analyzed by the spectrophotometer. Furthermore, this methodology may have the potential to lead to the development of a

fluorescence-based testing methodology for aviation fuel thermal stability verification.

EXPERIMENTAL SECTION

Jet A-1 Sample Preparation. The aviation fuel used in the present study was a commercial, kerosene-type Jet A-1, purchased from Shell Canada. The Jet A-1 was thermally stressed in flow conditions, from 120 to 200 °C, within a horizontal, split-hinged, three-zone Thermcraft tube furnace with a heated length of 91 cm. The temperature refers to the fuel temperature as measured right after the furnace exit. A detailed layout of the fuel thermal stability tester facility is shown in Figure 1. The fuel was introduced in the heating section via a Teledyne ISCO A500 dual-syringe pump with an air valve actuation package operated in continuous flow mode at a gauge pressure of 600 psi (4.14 MPa). 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 $1/8$ in. (3.18 mm) outer diameter and 0.069 in. (1.75 mm) inner diameter. After heating in the tube furnace, the fuel was immediately cooled to quench the chemical reactions, to prevent damage to the valves and the analytical equipment, and to allow the fuel to be sampled. Thus, a thermal bath heat exchanger was built around the pipe, and cooling water was continuously supplied from a Lytron Kodiak recirculating chiller. The fuel flow rate was fixed for all of the experiments at 1 mL/min corresponding to a thermally stressing residence time of 132 s. The current fuel thermal testing facility is similar to the facilities described by Roan and Boehman¹⁵ and Bruno and Windom¹⁶ and was designed to produce sufficient quantities of thermally stressed complex fluid and to allow for a full range of thermophysical property measurements.

The aviation fuel was thermally stressed at two distinct conditions: (a) air-saturated fuel, 100% O₂, corresponding to about 70 ppmv of dissolved O₂, and (b) fully deoxygenated fuel, 0% O₂, achieved by a nitrogen-sparging procedure.^{10,15}

Fluorescence Measurements. Three-dimensional excitation/emission fluorescence spectra were obtained using a Perkin-Elmer model LS-50B luminescence spectrophotometer. The emission spectra were collected in the range of 300–600 nm, with a scan speed of 240 nm/min and a resolution of 0.5 nm ($\Delta\lambda_{em} = 0.5$ nm). Excitation and emission slit widths were both fixed at 5 nm. Excitation was increased from 330 to 520 nm by intervals of 10 nm ($\Delta\lambda_{ex} = 10$ nm). Thus, a maximum of 20 independent spectra were collected for each sample of fuel. All of the fluorescence spectra were corrected for self-absorption. Furthermore, the light scattering signals relative to each of the detected spectra were subtracted to have a clear representation of the fluorescence regions in the 3D plots. In this regard, following the procedure illustrated by Patra and Mishra,¹⁷ a “deconvolution” method based on a Gaussian fitting procedure was implemented to subtract the Rayleigh scattering at the excitation wavelength to each of the collected emission spectra. An example of the emission fluorescence spectra, before and after the scattering signal subtraction, is shown in Figure 2.

RESULTS AND DISCUSSION

The formation of gums and solid deposits within the fuel is a very complex process that includes liquid-phase chemical kinetics, polymerization and/or clustering reactions to form high-molecular-mass compounds, solubility, and mass-transfer phenomena.^{2–15,18} Many years of research in this field have led to the conclusion that fuel oxidation is the result of a free-radical mechanism, which involves fuel hydrocarbon molecules, dissolved molecular 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

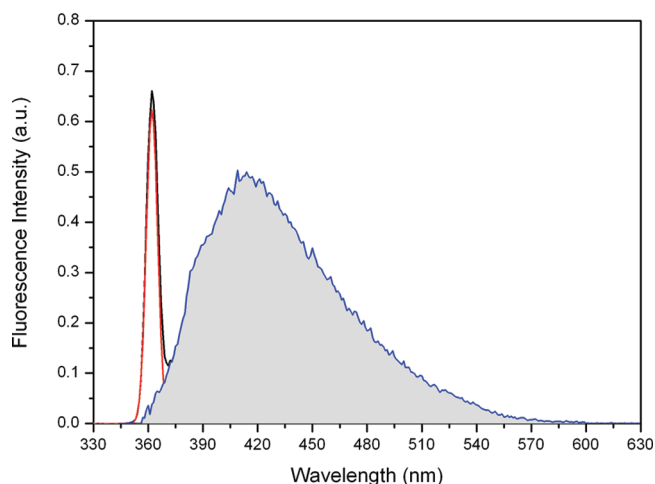


Figure 2. Typical fluorescence spectrum of thermally stressed Jet A-1 (black line). The Gaussian-type light scattering contribution is shown by the red curve. The scattering-subtracted emission spectrum is shown by the blue curve.

rate, and, if present at high concentrations, promote and increase the amount of gums and solid deposits.^{8,11} This is the reason because surface fouling, resulting from thermal oxidative stress of aviation fuel, can be drastically reduced using highly refined fuels.^{2,8} For instance, hydrotreated fuels, which have lower concentrations of heteroatomic species, typically have high thermal oxidative stability.² 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 gums and solid deposits).

Typical fluorescence spectra of a thermally stressed fuel sample at 140 °C with 100% dissolved oxygen are shown in Figure 3a, while a cross-section of the relative contour plot is shown in Figure 3b. The emission fluorescence spectra were collected starting at the excitation wavelength of 330 nm because of the light absorption properties of the Jet A-1 fuel used. The absorption spectra of neat unstressed Jet A-1 and thermally stressed Jet A-1 samples, with and without dissolved oxygen, are reported in our previous work.⁸ UV–vis absorption spectra of liquid hydrocarbon fuels are characterized by a structureless line profile with increasing absorption at shorter wavelengths. The broad, increasing absorption profile, shown by any petroleum sample or refined product, corresponds to the absorption edge of electronic excitation.^{17,18} The 330 nm wavelength corresponds to the optical absorption edge of the commercial Jet A-1 used in the present work, and its value is very consistent to what was previously reported by Patra and Mishra for kerosene hydrocarbon fuel (see Table 1 in ref 17). This optical property is related to the concentration and chemical identity of the constituent aromatic hydrocarbons in the fuel.^{19,20} It is also known that the presence of larger aromatics, i.e., higher number of condensed aromatic rings, in the fuel and, in general, in any liquid matrix, leads to a shift of the electronic absorption edge to longer wavelengths.¹⁷ Now, it is worth noting that refined products of crude oil, such as kerosene, diesel, and gasoline, are complex mixtures of hundreds of hydrocarbons with greatly varying compositions depending upon the crude source, refining process, and distillation procedure. However, the Jet A-1 aviation fuel is a kerosene-type fuel, and its aromatics content is limited to less than 25% by volume specified by ASTM D1319 standard.

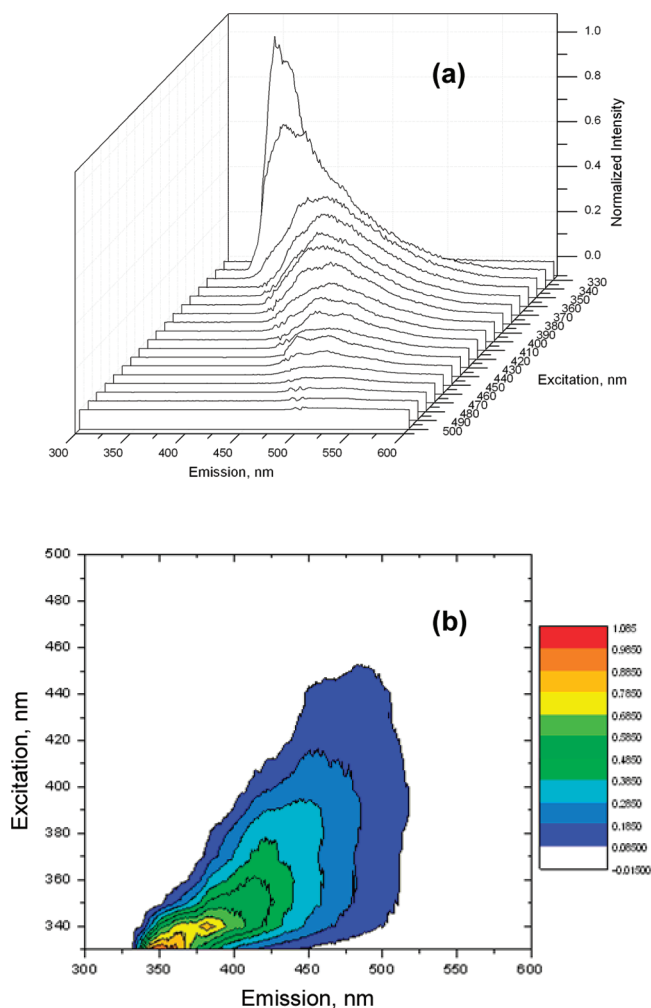


Figure 3. (a) Three-dimensional fluorescence plot of a thermally stressed Jet A-1 fuel sample at 140 °C in air-saturated condition. (b) Relative contour plot diagram.

Moreover, most of the aromatics in the jet fuel are composed of mono-ring alkyl benzenes that account for almost 13% by volume of the fuel.²¹ This is consistent with the optical absorption edge of our Jet A-1, because the presence of larger PAHs, i.e., two, three, or four condensed aromatic rings, would lead to a shift of the absorption edge at a longer wavelength in the visible region of the spectrum.

The effect of an increasing fuel temperature on the fluorescence properties of the fuel is reported in Figure 4. A large red shift of the fluorescence spectra for the thermally stressed fuel sample is observable when compared to the spectra of neat unstressed fuel. As a general rule, in a contour plot of a 3D fluorescence spectra, smaller aromatic compounds with fewer conjugated rings are located in the lower left area of the diagram, while the higher molecular-mass aromatics are located in the upper right area of the diagram.^{22,23} As shown in Figure 4, the aviation fuel used in the present study has a maximum fluorescence excitation (λ_{ex}) and emission (λ_{em}) at wavelengths of 330 nm (limited by the light absorption properties of Jet A-1) and 350 nm, respectively, which may correspond to an aromatic mixture containing mainly one or two condensed aromatic rings.²⁴

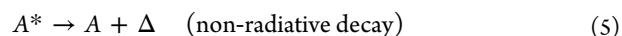
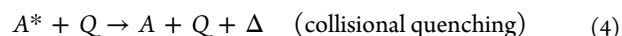
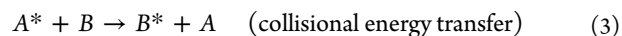
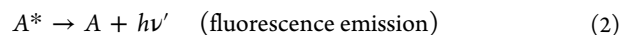
Over the range of stressed fuel temperatures from 120 to 200 °C investigated in this study, it is reasonable to consider that

the rate of pyrolytic reactions for the hydrocarbon fuel molecules are negligible, and therefore, larger condensed aromatics cannot be formed within the fuel.^{2–9} This is further confirmed by our fluorescence measurements performed in the absence of dissolved oxygen in the fuel samples (refer to Figure 5).

Even at temperatures as high as 200 °C, the resulting 3D fluorescence counter plot shows nearly no difference compared to the unstressed aviation fuel. It is worth noting that, at the same temperature, 200 °C, the air-saturated fuel sample showed a very large red shift compared to the neat Jet A-1 sample, as evidenced by comparing the relative contour plots in Figures 4 and 5.

The very large red shift in the fluorescence emission observed in Figure 4 may be attributed to the formation within the thermally stressed fuel samples of high-molecular-mass compounds with increasing conjugation resulting from the autoxidation mechanism. These compounds are likely to be related to the autoxidation instability phenomenon responsible for gums and solid deposit formation in the low-temperature regime, i.e., no hydrocarbon pyrolysis reactions. However, it is worth noting that also the formation of small oxidative products, such as aldehydes and ketones, may interfere in the fluorescence emission processes via intramolecular energy transfer.²⁵ Future work, perhaps involving pre-separation chromatographic methods, followed by spectroscopic analysis would probably clarify this point.

Another interesting aspect is the observed increase in the fluorescence quantum yield as a function of the fuel stressing temperature, as depicted in Figure 6. The fluorescence quantum yield is the ratio of the number of the photons emitted to the number absorbed. It is strictly related to the emissive rate of the fluorophore and its rate of radiationless decay, such as vibrational relaxation, internal conversion, or collisional energy transfer/quenching.²⁶ Non-radiative processes, in fact, reduce the fraction of excited molecules that actually emit fluorescence. On the other hand, for a specific multifluorophoric sample at a given excitation wavelength, the fluorescence spectrum and its area incorporate the effects of the energy transfer, self-absorption, and quenching.^{23–27} Some of these processes were also illustrated by Downare and Mullins,²⁷ as follows:



where A is the fluorophore, h is Planck's constant, ν is the frequency of the light, B is an acceptor fluorophore, Q is a generic quencher species, and Δ is the heat, while an asterisk (*) represents the relative excited electronic state.

Now, in the hypothesis of neglecting both the presence of collisional energy transfer (reaction 3) and collisional quenching (reaction 4), fluorescence emission as well as the fluorescence quantum yield can only be interfered by the presence of radiationless phenomena because of vibrational relaxation and/or internal conversion of the fluorophore species. Note that the above hypothesis is supported by the fact that the deposit mechanism in the autoxidative regime only

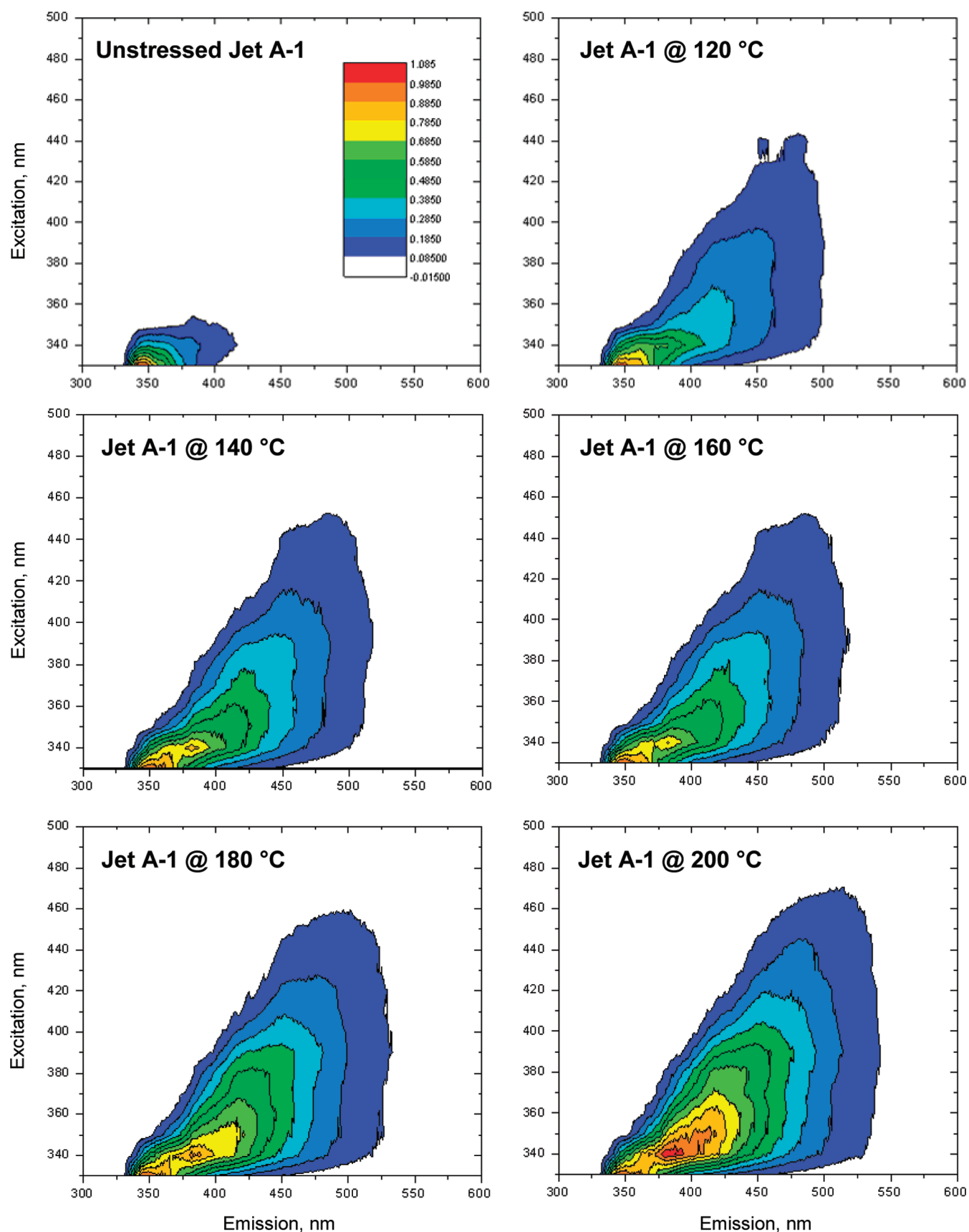


Figure 4. Three-dimensional fluorescence plots of stressed Jet A-1 at various temperatures, in air-saturated conditions.

involves a very small portion of the fuel. In other words, the main fuel composition can be assumed constant whether the

aviation fuel is thermally stressed or not. This was further confirmed by some preliminary measurement that we

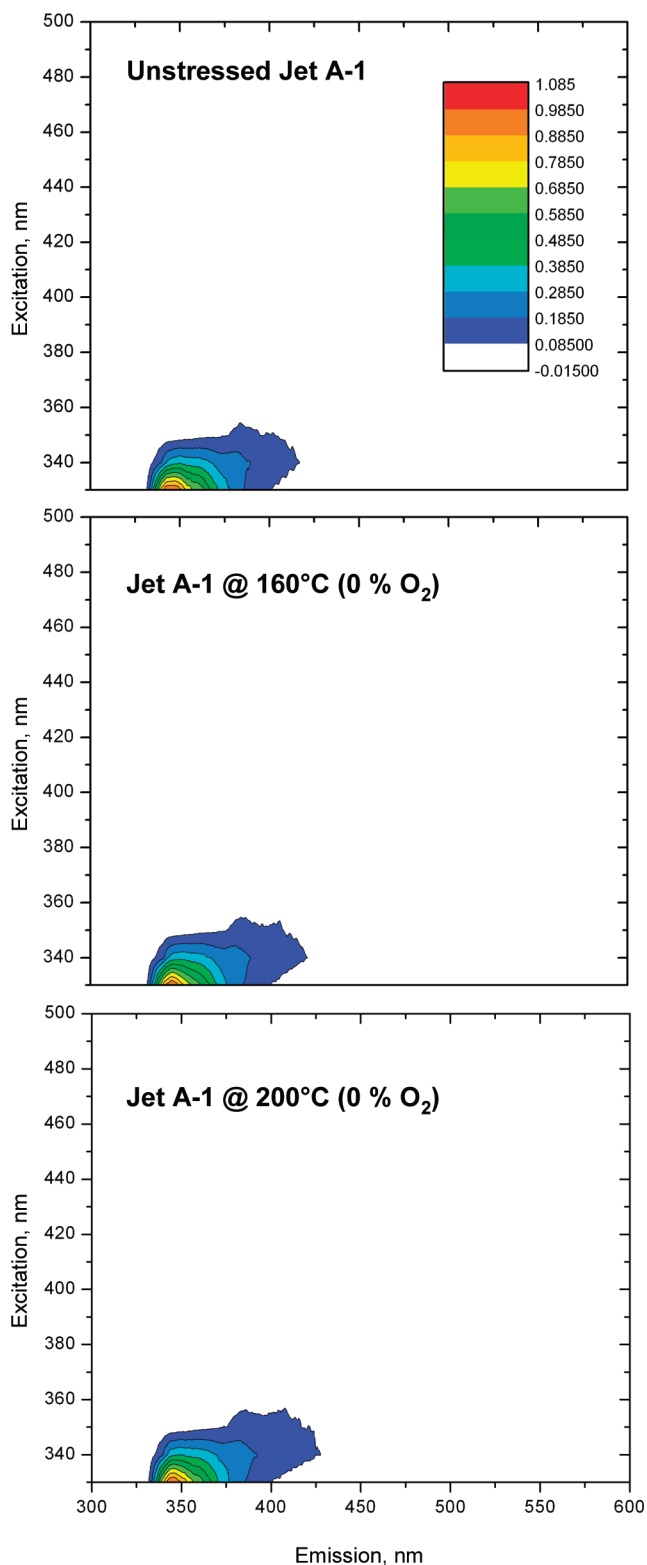


Figure 5. Three-dimensional fluorescence plots of both unstressed Jet A-1 and stressed Jet A-1 at two different temperatures, in fully deoxygenated conditions.

performed using proton nuclear magnetic resonance (^1H NMR). Moreover, it is well-known that molecular oxygen behaves as a strong fluorescence quencher species. However, on the basis of the measurement reported in Figure 5, we observed a negligible influence of the dissolved O_2 in the fluorescence

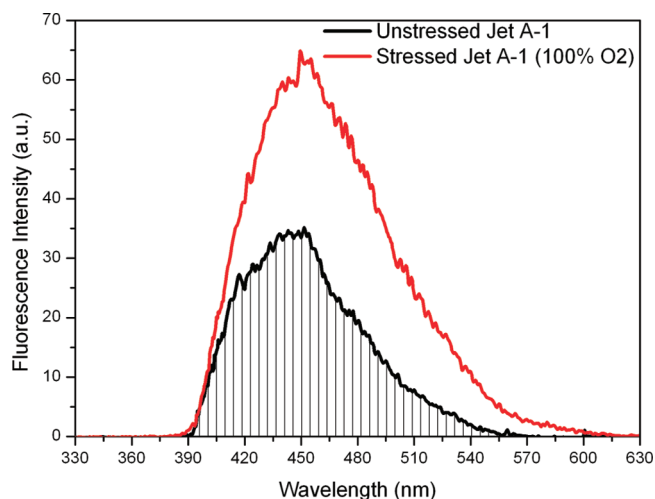


Figure 6. Fluorescence spectra excited at 400 nm (after scattering subtraction) of unstressed Jet A-1 and thermally stressed Jet A-1 samples at 160 °C. The area under the spectrum of unstressed jet fuel is cross-hatched.

spectra, perhaps because of the low concentration of oxygen. In fact, both the unstressed Jet A-1 (which was air-saturated with maximum dissolved O_2) and the two stressed fuel samples, at 160 and 200 °C (which were in fully deoxygenated conditions) showed similar fluorescence intensities.

The discussion above implies that the observed increase in the fluorescence intensity, i.e., the increase in the emission quantum yield, as a function of the fuel temperature, can be explained only by considering either an increase in the concentration of the fluorophore species or through the formation of higher molecular-mass compounds with higher rigidity and, therefore, lower propensity to dissipate energy via non-radiative processes.^{28,29} Also, it is possible that the presence of specific substituent groups and, in particular, electron-donating groups, such as $-\text{OH}$, may enhance the fluorescence efficiency, i.e., fluorescence quantum yield.²⁹ Unfortunately, our current results do not allow for further speculation on the chemistry of the instability phenomena of the aviation fuel at high temperatures. Perhaps the use of time-resolved fluorescence measurements in addition to the static fluorescence spectra performed in the current study would lead to further insight into the mechanism of oxidative deposit formation in aviation fuel. More work is certainly needed to clarify this topic.

CONCLUSION

In this work, the third in a series of studies performed to investigate the chemistry of the aviation fuel thermal stability, Jet A-1 aviation fuel was thermally stressed over a range of temperatures to cover the entire autoxidative regime. The jet fuel was stressed in both air-saturated and fully deoxygenated conditions to evaluate the dissolved oxygen dependence of the aviation fuel instability. The unstressed and thermally stressed fuel samples were then characterized by 3D fluorescence analysis. The increase in the fuel temperature results in a large red shift of the fluorescence spectra, which increases by increasing the fuel temperature. Such a red shift in the emission spectra was not observable if the dissolved oxygen was removed from the fuel. Our results imply that the autoxidation products, possible precursors of the oxidative deposits, are most likely to

be large polymers or clusters of heteroatom aromatic compounds. These compounds, as compared to the naturally occurring aromatic heteroatom species, have higher molecular masses, higher polarity, and lower solubility in the fuel, as well as a higher conjugation level and most likely higher structural rigidity, as confirmed by current measurements. Finally, from a practical point of view, the 3D fluorescence analysis seems to be a promising powerful method to evaluate the level of fuel thermal degradation (thermal stability) and, eventually, the level of fuel aging (storage stability).

AUTHOR INFORMATION

Corresponding Author

*Telephone: 416-667-7700. Fax: 416-667-7799. E-mail: mario.commodo@unina.it.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from Pratt and Whitney Canada. The authors also thank Dr. Patrizia Minutolo [Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche (CNR), Italy] for insightful discussion during the preparation of the manuscript.

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