

# Analysis of Aviation Fuel Thermal Oxidative Stability by Electrospray Ionization Mass Spectrometry (ESI–MS)

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**ABSTRACT:** In modern gas-turbine aircraft, aviation fuel is routinely used as a coolant to remove waste heat loads from, for example, lubrication and secondary engine systems, in addition to its conventional role as the energy source through combustion. The increase of the fuel temperature activates several liquid-phase reactions involving hydrocarbon molecules, dissolved oxygen, and indigenous heteroatomic (O, N, and S) polar compounds. The result of such reactions is the formation of gums and solid deposits within the fuel lines, which are of concern for the maintenance of gas-turbine engines. In the present paper, the thermal oxidative stability of commercial aviation fuel was investigated by the positive electrospray ionization mass spectrometry (ESI–MS) technique. Several classes of polar species, with different levels of alkylation, were detected in the unstressed jet fuel. The majority of these compounds were characterized by a molecular mass within the range of 90–250 Da. Thermally stressed jet fuel, under different experimental conditions, showed the presence of a broad molecular mass band of polar compounds in the range of 250–400 Da. This class of soluble high-molecular-mass compounds was not detectable when the dissolved oxygen was removed from the fuel by nitrogen sparging. Consistent with previous findings in the literature, we postulate that aggregation processes of these species, through polymerization or clustering reactions, could be responsible for the formation and precipitation of insoluble compounds, which ultimately lead to the formation of the oxidative deposits.

## INTRODUCTION

Aviation fuel thermal oxidative stability has been the subject of numerous studies for many years. In addition to its conventional use as a propellant, in fact, aviation fuel is also used as heat sink to remove waste heat loads from gas-turbine engine systems and various avionic components. With the introduction of more advanced gas-turbine engines with improved efficiency, even larger and more powerful avionics systems can require significantly more cooling. However, the use of aviation fuel as a coolant for this purpose is problematic because, as the fuel temperature increases, several liquid-phase chemical reactions involving hydrocarbon molecules, dissolved oxygen, and impurities take place. These reactions cause carbon deposits to build up within the fuel, constrict the fuel flow, potentially cause an engine shutdown, and decrease the effectiveness of surfaces to act as a heat exchanger.<sup>1–3</sup>

Dependent upon the temperature experienced by the liquid fuel during the heating process, two different mechanisms have been shown to be responsible for the fuel thermal degradation process and the formation of deposits. At lower temperatures, typically between 150 and 300 °C, hydrocarbon fuels react with dissolved oxygen contained within the fuel to form free-radical species. The air-saturated jet fuel typically contains about 70 ppmv of dissolved oxygen.<sup>1</sup> As shown by Heneghan and Zabar-nick first<sup>4</sup> and later by Beaver and co-workers,<sup>5,6</sup> the free-radical species, formed as a result of the fuel oxidation reactions, then react with naturally occurring heteroatomic molecules (nitrogen-, sulfur-, and oxygen-containing compounds) to form oxygenated species accountable as precursors for the formation of gums and deposits. This mechanism is usually referred to as fuel autoxidation or thermal oxidative instability and characterizes the fuel stability behavior in the autoxidation regime.<sup>1,2,4–6</sup>

At higher fuel temperatures, generally above 400 °C, the fuel instability mechanism is characterized by the breakdown of the hydrocarbon chemical bonds by pyrolytic cracking reactions, which converts long paraffinic chains into smaller alkanes and alkenes that further develop into aromatic compounds and solid deposits.<sup>3,7</sup> This condition is usually referred as fuel pyrolysis or simply fuel thermal instability and characterizes fuel stability behavior in the pyrolytic regime.<sup>1,3,7</sup>

The aim of the present study is to investigate the deposition mechanism in the thermal oxidative stability regime of commercial aviation jet fuel, Jet A-1, by electrospray ionization mass spectrometry (ESI–MS). The high selectivity of the ESI to the polar species may add further knowledge, understanding, and details to the mechanisms associated with the thermal oxidative stability of middle-distillate fuels. The formation of gums and solid deposits within the fuel lines is a very complex topic, which involves bulk liquid-phase reactions, nucleation of particles through polymerization or clustering reactions, solubility, transport phenomena, and surface reaction.<sup>1–10</sup> Possible variations in the main chemical composition of the aviation fuel, because of different oil sources or distillation processes, as well as variations in the chemical composition and concentration of naturally occurring heteroatomic species or impurities, further contribute to the complexity of the fuel stability phenomenon. Temperature, line pressure, amount of dissolved oxygen, and tube material are all important parameters affecting the solid deposition rate.<sup>1,2</sup> The difficulty in describing the oxidative deposit formation in middle distillates is due to the elusive nature of the underlying

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physics and chemistry, and the scarcity of numerical modeling efforts, as compared to a large body of experimental studies available in the literature, is a testament to this difficulty.

A relatively recent fundamental step toward enhancing the understanding of aviation fuel autoxidation was provided by Heneghan and Zabarnick.<sup>4</sup> When several jet fuels and jet fuel surrogates were thermally stressed, the authors noted an inverse relationship between the ease for the fuel to oxidize, i.e., fuel oxidation (on the basis of the rate of dissolved oxygen consumption), and the formation of deposits, i.e., fuel deposition tendency. It was argued that the observed results were consistent with the widely accepted idea that fuel oxidizes through a free-radical chain mechanism and deposit formation strongly depends upon the presence and reactivity of indigenous antioxidants in the fuel.<sup>4</sup> Such species are likely to be heteroatomic hydrocarbon molecules, which contain weak O–H, N–H, and S–H bonds, and are, therefore, particularly prone to hydrogen atom abstraction by peroxy radicals.<sup>4–6</sup> The main pathway for the oxidation mechanism of antioxidant species and subsequent deposit formation, as proposed and described by Heneghan and Zabarnick,<sup>4</sup> can be represented by the following three reactions:



where  $A\bullet$  is the corresponding radical of the general heteroatomic (antioxidant) molecule. In other words, the products of reaction R3 (dimerization reaction of  $AO\bullet_2$ ) are postulated to be responsible for the formation of the oxidative deposits.

Although the importance of heteroatom-containing species, such as phenols, on the thermal oxidative deposit mechanism for middle distillate fuels has long been known in the literature, as shown in Hazlett's review monograph,<sup>1</sup> the merit of Heneghan and Zabarnick's work<sup>4</sup> was to include such species as part of the fuel autoxidation mechanism. In this regard, the experimental results, recently proposed by Balster et al.,<sup>11</sup> for example, further confirm the importance of indigenous polar heteroatomic species in the thermal oxidative stability of aviation fuels. Their results, in fact, indicate a correlation between the total amount of polar species (primarily composed of phenols and various other oxygenated polar species but also nitrogen-containing polar species, even at lower concentrations, such as anilines, indoles, carbazoles, quinolines, and pyridines) and the amount of surface deposits produced. It is also well-known that surface fouling resulting from thermal oxidative stress of aviation fuel can be drastically reduced using highly refined fuels. For example, hydrotreated fuels, which have lower concentrations of heteroatomic species, typically have high thermal oxidative stability.<sup>1</sup>

Although there is an overall consensus regarding the gross features of fuel autoxidation chemistry, very little information is currently available about the nucleation process, which most likely occurs through polymerization or clustering reactions of oxygenated heteroatomic hydrocarbon species that form insoluble compounds and, in turn, may act as precursors of the deposits. Clearly, to understand better the chemical mechanism leading to the deposit formation, more information is needed on the chemical structure and molecular mass of the products of reaction R3, as postulated in Heneghan and Zabarnick's work.<sup>4</sup> For this purpose, further insight into the chemistry involved in aviation

**Table 1. Physical Properties of Jet A-1 Used in the Present Study<sup>a</sup>**

analysis	method	result
kinematic viscosity at 0 °F (cSt)	ASTM D445	3.795
kinematic viscosity at –20 °F (cSt)	ASTM D445	5.334
freezing point (°F)	ASTM D2386	–64
density at 15 °C (kg/m <sup>3</sup> )	ASTM D4052	806.7
estimated net heat of combustion (BTU/lb)	ASTM D4529	18555
sulfur X-ray (wt %)	ASTM D4294	0.0591
boiling range (°C)	ASTM D86	
initial boiling point		150.8
10% recovered		169.7
20% recovered		176.6
50% recovered		199.4
90% recovered		242.5
end point		270.2
residue (vol %)		1.2
loss (vol %)		0.4

<sup>a</sup> Fuel was sourced and analyzed by Shell Canada.

fuel thermal oxidative deposit formation is provided by Beaver and co-workers.<sup>5,6</sup> The authors proposed a sequence of reactions involving indigenous heteroatomic species, i.e., phenols, indoles, and carbazoles, activated by the presence of hydroperoxide radicals,<sup>4</sup> which ultimately lead to the formation of compounds with higher molecular mass, named soluble macromolecular oxidatively reactive species (SMORS). The formation of SMORS and their potential relevance in the deposit mechanism of middle distillates was first reported by Hardy and Wechter,<sup>12,13</sup> who analyzed concentrated extracts of SMORS species, separated from the fuel by methanol (MeOH) extraction.<sup>5,6,12,13</sup> Their analysis, by size-exclusion chromatography (SEC), found that the highest molecular-weight fraction of SMORS was between 600 and 900 Da, with an average empirical formula, estimated by elemental analysis, of  $C_{21}H_{20}O_2N$ .<sup>12,13</sup> These compounds were isolated via precipitation by adding a straight alkane solvent (from hexane to dodecane) to the SMORS sample, and this material was referred to as an extraction-induced precipitate (EIP). The presence of minor amounts of lower molecular-mass peaks, in the mass spectra, was also observed. As suggested by the authors, these species may correspond to fragments of the EIP, which dissociate during dissolution in methanol.<sup>13</sup>

In this study, the methanol extract of thermally stressed commercial Jet A-1, in air-saturated dissolved oxygen and deoxygenated conditions, was investigated by positive ESI–MS. The aim of the study was to analyze the evolution of the molecular-mass distribution of soluble polar components in thermally stressed aviation fuel to identify the formation of possible precursors of gums and solid deposits. Preliminary results will be presented and discussed along with some comments on the possible pathways for oxidative deposit formation based on our results and those in the literature.

## EXPERIMENTAL SECTION

**Sample Preparation.** Commercial aviation Jet A-1 fuel, provided by Shell Canada, was thermally stressed at a constant temperature of 160 °C, under static (no-flow) test conditions. Several key physical properties of the Jet A-1 fuel sample are listed in Table 1. For each test,

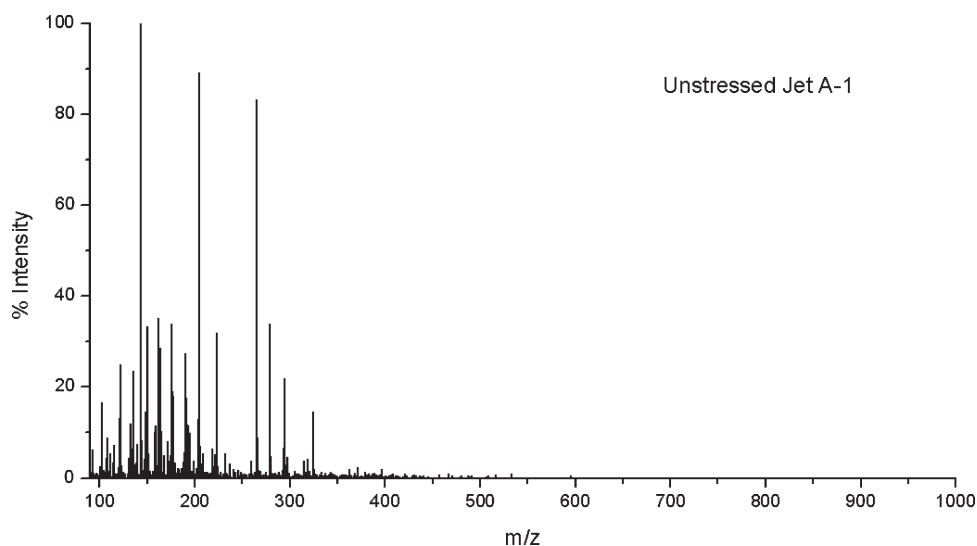


Figure 1. Positive ESI mass spectrum profile in the  $m/z$  90–1000 range for unstressed neat Jet A-1 fuel.

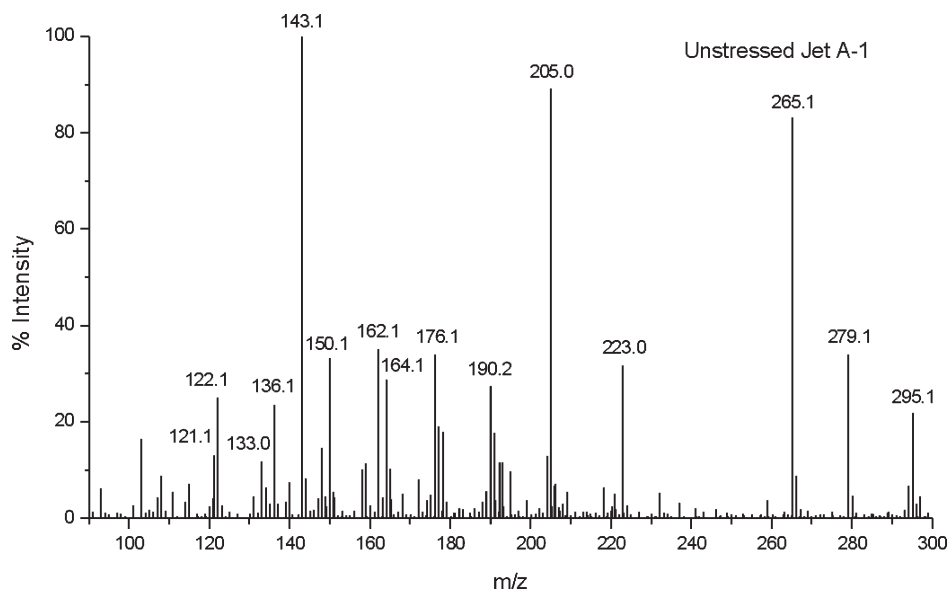


Figure 2. Expanded positive ESI mass spectrum profile in the  $m/z$  100–300 range for unstressed neat Jet A-1 fuel.

30 mL of jet fuel sample was used to partially fill a  $1/4$  in. outer diameter, 0.18 in. inner diameter, 316 stainless-steel tube. The tube reactor, partially loaded with Jet A-1, was then pressurized with oxygen to ensure that the autoxidation reaction rate was not oxygen-limited. The tube was then heated, over a 2 h period, with a horizontal, split-hinged, Thermcraft furnace, with a heated length of 91 cm.

Further, to evaluate the dependence of the oxidative deposit mechanism on dissolved oxygen, the fuel was also thermally stressed in deoxygenated conditions, achieved by sparging Jet A-1 with nitrogen for several minutes (5–7 min were typically sufficient to fully deoxygenate the jet fuel). Nitrogen sparging has been demonstrated in previous studies as an effective procedure to decrease the formation of carbon deposits.<sup>14</sup> Further details of the fuel thermal stability test facility at the Institute for Aerospace Studies, University of Toronto, have been previously reported in the literature.<sup>15</sup>

The polar component extraction procedure followed that reported first by Hardy and Wechter<sup>12,13</sup> and then by Beaver and co-workers

after.<sup>5,6</sup> Thermally stressed fuel samples were mixed with methanol (5:2 fuel/methanol ratio) in a separatory funnel. The methanol layer was then separated from the fuel and analyzed by positive ESI–MS.

**ESI–MS of Hydrocarbon-Based Fuels.** Since its first application in the mid-1980s by Fenn et al.,<sup>16</sup> ESI–MS has rapidly become one of the most versatile and powerful analytical methods for the analysis of both low- and high-molecular-mass polymers, biomolecules, and inorganic and organometallic complexes.<sup>17</sup> However, despite the very large range of applications in which ESI–MS has been successfully used, it is only a relatively new and emerging technique for the analysis of hydrocarbon liquid fuels.<sup>16,18–30</sup> Crude oils and their refined products, such as gasoline, kerosene, and diesel, are in fact known to be largely composed of nonpolar hydrocarbon molecules, while ESI is traditionally considered a technique that is most suitable for molecules that have polar functionalities.<sup>16–21</sup> The first experiments with ESI–MS were carried out on a range of petroleum products, including crude oil, jet fuel, and gasoline by Zhan and Fenn.<sup>18</sup> Their results clearly showed that

**Table 2. Main Polar Compound Classes Detected by ESI–MS in the Unstressed Jet A-1 Fuel**

[M + H] <sup>+</sup>	CH <sub>2</sub> number	relative intensity (%)
Unknown		
107.1		30.6
121.1		100
135.1		21.8
Alkylated Pyridines or Anilines		
108.1	C <sub>2</sub>	25.8
122.1	C <sub>3</sub>	77.8
136.1	C <sub>4</sub>	71.5
150.1	C <sub>5</sub>	100
164.1	C <sub>6</sub>	85.8
178.2	C <sub>7</sub>	54.6
192.2	C <sub>8</sub>	35.6
206.2	C <sub>9</sub>	21
Unknown		
134.1		17.7
148.1		41.4
162.1		100
176.1		96.5
190.2		77.1
204.2		35
218.2		18.4
232.2		14.5
Alkylated Quinolines		
144.1	C <sub>1</sub>	78
158.1	C <sub>2</sub>	100
172.1	C <sub>3</sub>	79.1
186.1	C <sub>4</sub>	16.9
Alkylated Carbazoles		
168.2	C <sub>0</sub>	100
182.2	C <sub>1</sub>	42.4
196.2	C <sub>2</sub>	16.5

petroleum products contain a sufficiently high amount of polar compounds, such that they may be ionized by ESI to provide spectra substantial compositional information. Furthermore, the high mass resolving power and mass accuracy provided by the use of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICT MS) coupled to the ESI method, for example, allowed Marshall and co-authors<sup>22</sup> to identify about 500 different polar constituents of unprocessed diesel fuel over a mass range from 200 to 452 Da. Other typical applications in which ESI–MS has been used span from the analysis of asphaltenes,<sup>23,24</sup> petroleum resins,<sup>25</sup> identification and analysis of trace components and additives,<sup>26–28</sup> and fuel mixing contamination.<sup>29,30</sup> The use of ESI–MS for petrochemical analysis was also reviewed in recent papers by Qian et al.<sup>19</sup> and Marshall and Rodgers.<sup>20</sup>

**ESI–MS: Instrument Parameters.** The ESI–MS experiments were conducted using an AB/SCIEX QStar XL quadrupole time-of-flight mass spectrometer with an Ionics HSID interface and equipped with an electrospray source operated in positive-ion mode. The electrospray (ES) drying gas was nitrogen. Samples were introduced using a syringe pump with a flow rate of 100  $\mu\text{L}/\text{min}$ , using as a solvent 50:50 MeOH/H<sub>2</sub>O + 0.05% formic acid (HCOOH) and a loop injection of 5  $\mu\text{L}/\text{min}$ . The methanol extract fuel samples were further diluted with

MeOH (1:100 dilution ratio). The mass spectra were all collected in the mass/charge ( $m/z$ ) 90–1000 range and corrected for peaks observed analyzing pure methanol as a blank.

It may be argued that the pre-extraction procedure to separate polar compounds from the fuel is unnecessary because the ESI method is itself already highly selective for these species. The pre-spray methanol extraction procedure serves to concentrate the products of the fuel thermal oxidative stability process, to have a higher signal/noise ratio in ESI–MS spectra. Also, this procedure was followed to minimize effects because of such a complex matrix and to preserve consistency with other previous work.<sup>5,6,12,13</sup>

## RESULTS AND DISCUSSION

As previously described in the Introduction, the formation of gums and solid deposits, occurring as a consequence of the fuel thermal oxidative degradation process, is likely the result of a free-radical mechanism, which involves hydrocarbon fuel molecules, dissolved oxygen, and indigenous heteroatomic (N, O, and S) compounds. The result of such reaction pathways, therefore, is the formation of higher molecular-mass species with higher polarity (presence of O, N, and eventually S atoms) and lower solubility in the fuel.<sup>5,6</sup> The reduction of the solubility (the jet fuel is mostly nonpolar) is the driving force for the precipitation of this material and their contribution to surface deposit formation. Therefore, on the basis of its ability to selectively ionize and characterize basic and acid polar compounds over a relatively large range of molecular mass in a very complex matrix, such as crude oil and its refined products, ESI–MS appears to be a promising technique for the analysis of aviation fuel thermal oxidative stability. Specifically, the following characteristics of ESI make it a particularly suitable ionization system for the purpose of the present study:<sup>18–30</sup> (i) the application of ESI is highly selective to the polar species; (ii) sample volatility is irrelevant, which makes ESI able to measure species with molecular mass as high as 100 MDa; and (iii) the extreme softness of the ionization method occurring through ESI implies little or no mass fragmentation problems.

The ESI mass spectra for the unstressed Jet A-1 over the entire  $m/z$  range, from 90 to 1000, adopted in this study is showed in Figure 1. Most of the peaks were concentrated in the spectral region below  $m/z$  300; a similar mass profile for aviation fuel was showed by Eide et al.<sup>28</sup> In ESI applications, the degree of charging (the formation of singly or multiply charged ions) typically tends to increase with an increasing molecular mass. For molecules with molecular weights below 500 Da, ESI is usually characterized by protonated singly charged ions.<sup>17</sup> Therefore, all of the species in the present study are considered as singly charged, as further evidenced by the  $m/z$  1 spacing between each peak and its corresponding <sup>13</sup>C isotope peak.<sup>17</sup> Thus, in jet fuel spectra, the mass/charge ratio unit,  $m/z$ , can also denote the mass unit, Da.

A mass scale expansion from  $m/z$  90 to 300 is shown in Figure 2. Several periodic peaks with a relative difference corresponding to 14 mass units are clearly distinguishable in the spectra. These peaks are typically attributed to the different numbers of the CH<sub>2</sub> group on alkyl chains for the same class of compounds, i.e., same homologue series.<sup>22</sup> Another series of incremental peaks, with a lower intensity, differing approximately by 2 mass units (i.e., the mass of two hydrogens) is also observable in Figure 2. The latter is consistent with a difference in saturation between compounds of neighboring  $m/z$  values, i.e., the presence of double bonds within the alkyl chains. Similar



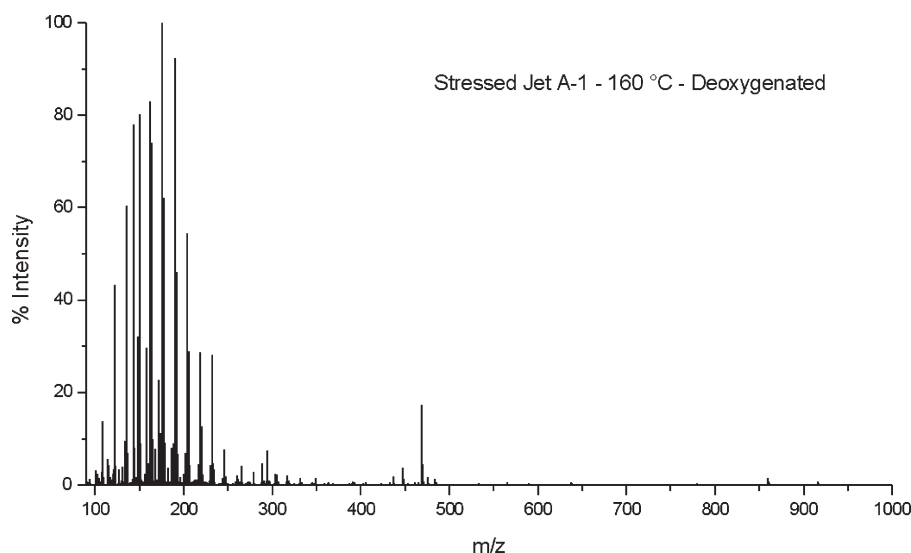


Figure 3. Positive ESI mass spectrum profile in the  $m/z$  90–1000 range for thermally stressed Jet A-1 fuel in fully deoxygenated conditions.

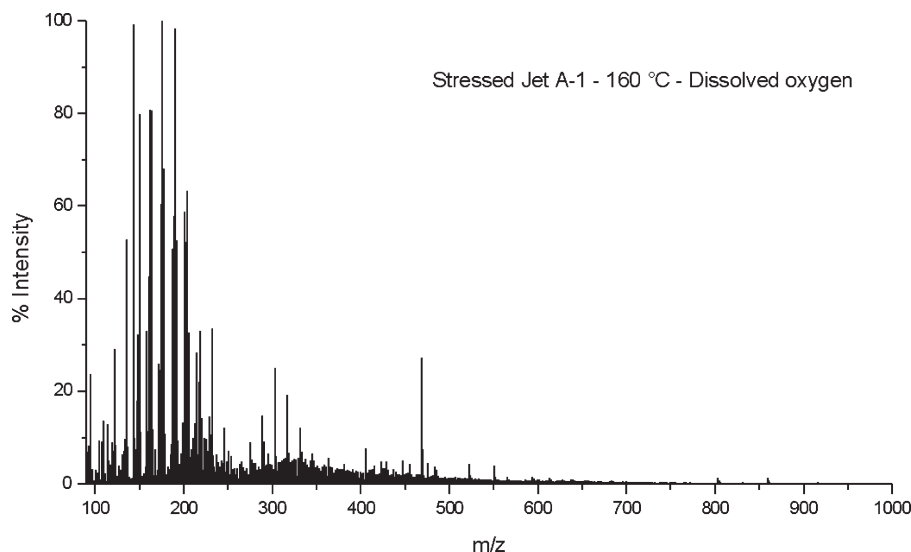


Figure 4. Positive ESI mass spectrum profile in the  $m/z$  90–1000 range for thermally stressed Jet A-1 fuel in air-saturated dissolved oxygen conditions.

peak distribution patterns were reported in the literature for crude oils,<sup>16</sup> diesel fuel,<sup>21,22</sup> and petroleum resins.<sup>25</sup>

On the basis of their specific molecular mass, we attempted to identify some of the homologue series shown in the spectra in Figures 1 and 2. The series are reported in Table 2, together with the relative intensities for each class of compounds and the calculated number of methylene ( $\text{CH}_2$ ) groups. The species listed in Table 2 were also previously detected by Balster et al.,<sup>11</sup> for a large number of aviation fuel types. They used silica gel solid-phase extraction (SPE) followed by high-performance liquid chromatography (HPLC) to separate and concentrate the polar species for subsequent analysis via gas chromatography–mass spectrometry (GC–MS). Similar classes of polar compounds were also measured in aviation and diesel fuel by Link et al.,<sup>31</sup> using liquid–liquid extraction combined with HPLC analysis. Speculation about the relative concentration of the homologue species based on the relative intensity of the  $m/z$

peaks may not be worthwhile because different polar compounds have typically different propensity to ionize.<sup>22</sup> As expected, all of the main homologue series showed in Figures 1 and 2, except for the ones at  $m/z$  107.1, 121.1, and 135.1, are characterized by peaks at even values of the  $m/z$  ratio. This is because naturally occurring heteroatomic polar compounds in aviation fuels typically contain at most only one nitrogen atom.<sup>11</sup> In MS, in fact, by following the nitrogen rule,<sup>32</sup> an even-electron ion, which corresponds to an odd mass compound, typically contains an odd number of nitrogen atoms. As a consequence, the  $m/z$  108.1, 122.1, 136.1, 150.1, 164.1, 178.2, 192.2, 206.2, and 220.2 sequence could match with either alkylated pyridines or anilines. Both of them, in fact, are generally present in aviation fuels.<sup>11</sup> The  $m/z$  144.1, 158.1, 172.1, and 186.1 sequence may be attributable to  $\text{C}_1$ – $\text{C}_4$  alkylated quinolines, while the  $m/z$  168.2, 182.2, and 196.2 sequence may be attributable to  $\text{C}_0$ – $\text{C}_2$  alkylated carbazoles (carbazole and mono- and dimethyl carbazole).

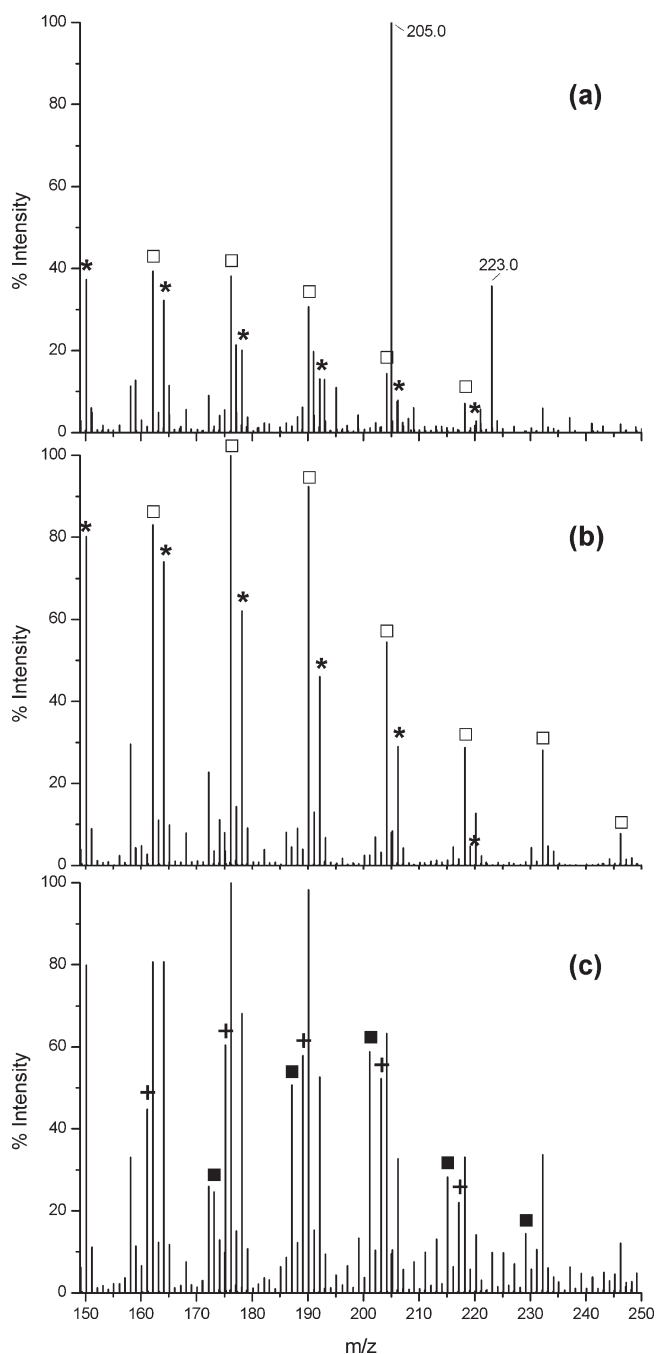
The relative intensity of the alkylated carbazoles series, as shown in Table 2, indicates a prevalence of non-alkylated carbazoles in the Jet A-1 fuel investigated in the present study. Furthermore, the general signal intensity of the measured  $m/z$  168.2, 182.2, and 196.2 series was typically very low compared to other homologue series. The lower intensity is likely due to lower ESI efficiency, characteristic of carbazole compared to pyridine homologues. Marshall et al.<sup>22</sup> pointed out that basic pyridine homologues are selectively ionized, while non-basic compounds, such as pyrrole, carbazole, and indole homologues, are typically not ionized by ES.<sup>22</sup> However, alkyl carbazoles were shown to be detectable by ESI–MS in a study aimed to analyze crude oil resins.<sup>25</sup>

Two other unknown series were also present in the mass spectra of the pristine Jet A-1 at  $m/z$  107.1, 121.1, and 135.1 and  $m/z$  134.1, 148.1, 162.1, 176.1, 190.2, 204.2, 218.2, and 232.2, respectively, as listed in Table 2. For the latter series, within the mass resolution of the our instrument, we found a reasonable chemical formula that the  $m/z$  134.1 peak could correspond to a  $C_9H_{12}N^+$  ion, the  $m/z$  148.1 peak could correspond to a  $C_{10}H_{14}N^+$  ion, the  $m/z$  162.1 peak could correspond to a  $C_{11}H_{16}N^+$  ion, etc., for all of the other peaks of the homologue series. Three other strong peaks are also distinguishable at  $m/z$  143.1, 205.0, and 265.1, as shown in Figure 2. We speculate that these last three, which do not belong to any of the measured homologue series, may be representative of a trace amount of additives, typically present in any commercial aviation fuel. The  $m/z$  143.1, for example, may be attributable to one molecule of di(ethylene glycol) monomethyl ether (DEGMME) with one  $Na^+$  ion attached, as shown by Zhan and Fenn.<sup>18</sup> DEGMME is used as a detergent in aviation fuel. The use of high mass-resolving power MS could certainly lead to a more accurate interpretation of the heteroatomic polar compounds and their chemical composition in aviation fuels.

The ESI–MS spectrum for the stressed Jet A-1 in the fully deoxygenated condition is reported in Figure 3. The mass spectrum does not show any significant difference compared to the one corresponding to the unstressed fuel sample of Figure 1. We repeated the entire procedure: fuel deoxygenation, thermal stress, and ESI–MS analysis, 3 times and always obtained very similar results. Some small differences in the relative intensities of the different homologues series were observed, but these were within experimental error.

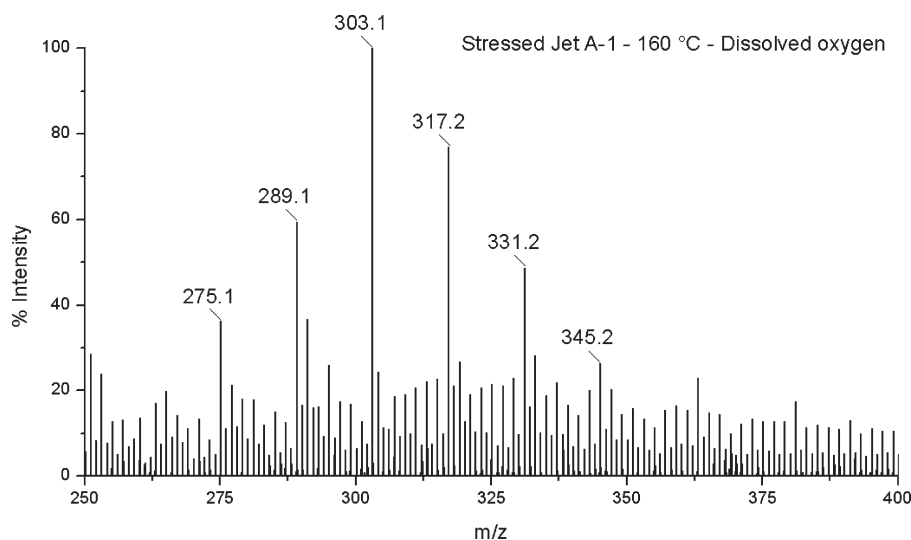
Slightly different but very interesting was the ESI–MS spectra result from the air-saturated thermally stressed Jet A-1 sample, shown in Figure 4. In this case, the mass spectra shows, in addition to the previously described peaks in the  $m/z$  100–250 range, the presence of compounds with higher molecular masses in the  $m/z$  250–400 range. The presence of an intense ion at  $m/z$  469.3 was also typically observed in the thermally stressed fuel samples whether the fuel was in deoxygenated or air-saturated conditions. This ion is most likely due to a contaminant collected during the thermal-stressing procedure. In the low-molecular-weight region,  $m/z$  100–250, two additional homologue series at  $m/z$  161.1, 175.1, 189.1, 203.1, and 217.2 and  $m/z$  173.1, 187.1, 201.1, 215.1, and 229.2, respectively, were observed in the air-saturated thermally stressed Jet A-1 compared to both the unstressed fuel sample and the fully deoxygenated thermally stressed fuel sample, as shown in Figure 5.

At this point, it is worth noting that the molecular mass of a possible SMORS molecule previously proposed by Beaver and co-authors<sup>5,6</sup> is 317 Da and has a molecular formula of



**Figure 5.** Expanded positive ESI mass spectrum profile in the  $m/z$  150–250 range of (a) unstressed neat Jet A-1 fuel, (b) thermally stressed Jet A-1 fuel in fully deoxygenated conditions, and (c) thermally stressed Jet A-1 fuel in air-saturated dissolved oxygen conditions. Symbols refer to the main homologue series: (\*)  $m/z$  150.1, 164.1, 178.2, 192.2, 206.2, and 220.2, (□)  $m/z$  162.1, 176.1, 190.2, 204.2, 218.2, and 232.2, (+)  $m/z$  161.1, 175.1, 189.1, 203.1, and 217.2, and (■)  $m/z$  173.1, 187.1, 201.1, 215.1, and 229.2.

$C_{21}H_{19}O_2N$  (see Scheme 1 in ref 6). The proposed compound results from a reaction mechanism involving phenols, hydroperoxide radicals (as a result of the autoxidation reactions), and carbazoles (specifically a 3-methyl carbazole).<sup>5,6</sup> It is likely that, if differently alkylated carbazole molecules participated in the proposed mechanism, the SMORS molecules would be

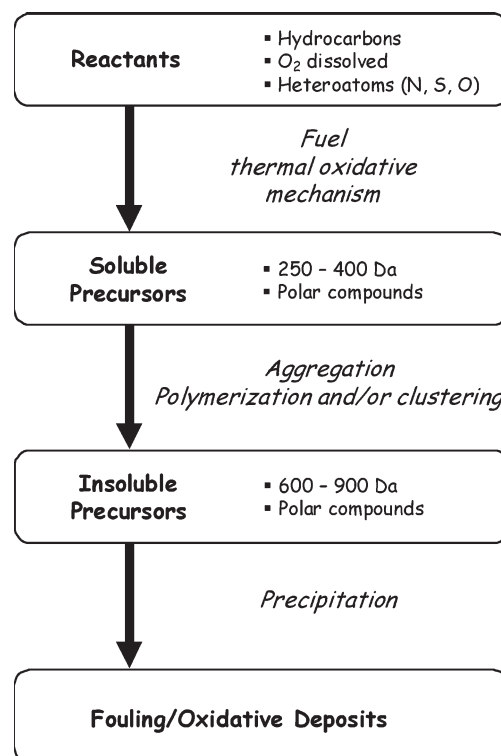


**Figure 6.** Expanded positive ESI mass spectrum profile in the  $m/z$  250–400 range for thermally stressed Jet A-1 fuel in air-saturated dissolved oxygen conditions.

represented by a homologous series with parent positive  $[M + H]^+$  ions peaks located, for example, at  $m/z$  290, 304, 318, and 332. However, in our experiments, the main homologous series in the  $m/z$  250–400 range was at  $m/z$  289.1, 303.1, 317.2, and 331.2, as shown in Figure 6. Again, it should be emphasized that the experiments were repeated 3 times and always yielded the same result. Furthermore, we also performed thermal oxidative tests at other temperatures, i.e., 180 and 200 °C, and the  $m/z$  289.1, 303.1, 317.2, 331.2 series was always present as the major homologue series in all of the mass spectra at these other temperatures.

Recalling the nitrogen rule,<sup>32</sup> because the measured series shows odd-electron ion peaks, the corresponding compounds cannot contain just one nitrogen atom or, more generally, any odd number of nitrogen atoms. Therefore, as a result of the measured mass spectra, this class of high-molecular-mass species (resulting from the thermal oxidative stress of the jet fuel) must have an even number of nitrogen atoms, in our case most likely either 0 or 2. Note, that the absence of a specific pattern of  $m/z$  peaks, corresponding to a specific class of compounds, does not necessarily mean they are absent in the analyte solution. Some of the fuel oxidative products may simply not be ionizable by ES. However, Porter et al.<sup>25</sup> in a study aimed to investigate polar resin fractions in crude oils and diesel by ESI tandem mass spectrometry (MS/MS) identified a major constituent to be alkylated carbazoles in the crude oil sample and quinoline compounds along with oxygen or sulfur heterocycles and alkyl carbazoles in a diesel sample. Interestingly, the ranges of dominant ions resulting from the mass spectra of the extracted resins closely resemble those found in our thermal oxidative stability experiments. It is clear that the comparison of our data to those relative to extracted resins as measured by Porter et al.<sup>25</sup> is only qualitative in terms of the spectral range of dominant ions. The assessment of possible chemical similitude between resins and oxidative products requires specifically designed comparative studies.

To obtain information about the chemical structure of the 250–400 Da species, we also performed some preliminary multiple-step MS/MS measurements. Unfortunately, the signal intensity of the parent ion species was too low to produce an acceptable signal/noise mass spectrum of the relative fragments.



**Figure 7.** Proposed liquid-phase thermal oxidative deposition mechanism for aviation fuel.

In this regard, it is suggested that the possibility of a pre-extraction procedure, capable of separating and/or concentrating the high-molecular-mass compounds, 250–400 Da, to the indigenous polars species, with molecular mass <250 Da, is a necessary step for a more accurate analysis of the chemical nature of the fuel thermal oxidative products.

The present experimental results would seem to partially disagree with the mechanistic model previously proposed as the major pathway for oxidative deposit formation in thermally stressed aviation fuels.<sup>5,6</sup> In particular, the presence of an odd ion

peak series in our mass spectra raises some doubts about the universality of the autoxidation mechanisms previously proposed in the literature.<sup>5,6</sup> Perhaps other reaction pathways are involved in the aviation fuel autoxidation mechanism, responsible for the formation of the oxidative deposits. On the other hand, although no dimers,  $[2M + H]^+$ , or trimers,  $[3M + H]^+$ , of the high-molecular species were shown by the ESI–MS spectra, our results seem to confirm that the deposit precursors are most likely oxygenated, eventually nitrogen-containing, compounds with a molecular mass ranging from 250 to 400 Da, as postulated by Beaver and co-authors.<sup>5,6</sup> In other words, although our measurements seem to confirm the thermal oxidative mechanism previously theorized by Beaver and co-authors,<sup>5,6</sup> such a chemistry may only be considered generic because a wider range of heteroatom compounds needs to be taken into account. Aggregation of these deposit precursor species may lead to the formation of insoluble macromolecules, with higher molecular mass and polarity, responsible for the formation of the deposits. Furthermore, it is worth noting that the molecular mass of the EIP found by Hardy and Wechter<sup>12,13</sup> by SEC analysis was in the 600–900 Da range, which corresponds to aggregates of two or three of the species that we measured by ESI–MS. Perhaps the use of a higher dilution ratio in the present measurements, as compared to those of previous studies,<sup>5,6,13,13</sup> avoided the occurrence of aggregation phenomena, and that would explain the absence in the mass spectra of species with molecular mass corresponding to dimers or trimers of the 250–400 Da compounds. In other words, the 250–400 Da species may be considered as the parent monomeric structures of higher molecular-mass (600–900 Da) and lower solubility compounds, which ultimately form the deposits via precipitation. Note that, although ESI is a soft ionization technique, weak covalent bonds may fragment during ionization. In other words, aggregates may be destroyed in the ionization process because of the strong change in the liquid-phase composition during the ESI. This was previously observed by Linsheid and co-workers<sup>33</sup> in a work aimed to investigate the molecular composition of fulvic acid by coupling SEC analysis to the ESI–FT-ICR MS technique.

Therefore, as results of this experimental investigation and on the basis of the previous literature in the field of thermal oxidative stability of middle distillates, a plausible mechanism leading to the formation and deposition of solid material is proposed and summarized in Figure 7.

## CONCLUSION

Preliminary experiments using ESI–MS were carried out to study the thermal oxidative stability of aviation jet fuel. Commercial Jet A-1 was thermally stressed in the static condition in a tube reactor in fully oxygenated and deoxygenated conditions. Deoxygenate fuel was obtained by means of a nitrogen sparging procedure. Polar compounds were then extracted by the liquid–liquid phase extraction procedure (5:2 fuel/methanol ratio) already proposed in the literature.<sup>5,6,12,13</sup> The methanol extracts were then analyzed by ESI–MS operated in positive-ion mode. The mass spectra of the unstressed Jet A-1 showed several homologous series corresponding to naturally occurring heteroatomic compounds, most likely containing nitrogen. When the mass spectra of the stressed fuel samples were compared to the unstressed sample, several important observations were made, which may be summarized as follows: (i) thermally stressed aviation jet fuel leads to the formation of soluble polar

heteroatomic compounds with molecular mass ranging between 250 and 400 Da; (ii) the absence of this class of species in the mass spectra of the fully deoxygenated thermally stressed fuel sample would seem to indicate that these compounds are the result of the fuel autoxidation mechanism and its interaction with naturally occurring polar species in the aviation fuels; (iii) the analysis of the mass spectra and the relative homologous series does not entirely support the universality of recently proposed deposition mechanisms in the literature; and (iv) aggregation of these soluble high-molecular-mass compounds (within the range of 250–400 Da) may be responsible for the formation of the deposits through the formation and precipitation of insoluble species.

The preliminary results of this study have therefore shown the capability of using the ESI–MS technique as a valid method for fuel thermal oxidative stability investigations. Further research, using mass spectrometers with higher resolving power, i.e., able to resolve overlapping peaks, and different types of aviation fuels, i.e., with different thermal stability propensity, would certainly promote a better understanding of the mechanism responsible for the thermal oxidative stability of aviation fuel and the formation of surface deposits. Furthermore, analyte concentration studies, which may also reveal the tendency of the detected high-molecular-mass compounds, in 250–400 Da, to form multimers, will be the subject of future studies.

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