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# Insight into the Mechanisms of Middle Distillate Fuel Oxidative Degradation. Part 1: On the Role of Phenol, Indole, and Carbazole Derivatives in the Thermal Oxidative Stability of Fischer–Tropsch/Petroleum Jet Fuel Blends

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The U.S. Air Force (USAF) has committed to use 1/1 volumetric blends of conventional jet fuels with Fischer–Tropsch (FT) derived fuels by 2016. Previous work by Balster et al. (Balster, L. M.; Zabarnick, S.; Striebich, R. C.; Shafer, L. M.; West, Z. *Energy Fuels* **2006**, *20*, 2564–2571) examined the relationship between thermal oxidative deposit and the concentration of various polar compounds present in 20 petroleum jet fuels. The thermal oxidative stability of FT blends, derived from four conventional jet fuels selected from the study of Balster et al. (Balster, L. M.; Zabarnick, S.; Striebich, R. C.; Shafer, L. M.; West, Z. *Energy Fuels* **2006**, *20*, 2564–2571), was examined with the Penn State University (PSU) flow reactor. Excellent linear correlations were found between fuel thermal oxidative deposit and indigenous fuel phenol, indole, and carbazole concentrations. This data is consistent with a mechanism previously proposed for the thermal oxidative degradation of both jet and diesel fuels (Beaver, B.; Gao, L.; Burgess-Clifford, C.; Sobkowiak, M. *Energy Fuels* **2005**, *19*, 1574–1579).

## Introduction

The U.S. Air Force (USAF) has been working toward use of jet fuel that is a 1/1 volumetric blend of synthetic fuel and petroleum-derived JP-8. The synthetic fuel component is likely to be a coal/biomass derived Fischer–Tropsch jet fuel. This ambitious plan is predicated upon ultimately addressing environmental, economic and national security concerns.

Currently, the U.S. imports approximately 60% of its crude oil from foreign sources. This situation is problematic both from the perspective of national energy security and balance of trade. To address these concerns, the U.S. Department of Defense is attempting to use its leverage as the world's largest single user of transportation fuels to stimulate the development of a coal-derived fuel industry. The long-term goal of this initiative is to provide both leadership and the initial economic incentive necessary to replace a significant portion of foreign crude oil imports with synthetic fuels derived from domestic coal/biomass. A significant U.S.-based coal/biomass transportation fuel industry, when fully implemented, may also lower future crude oil prices by decreasing global crude oil demand.

The proposed future USAF jet fuel blend will be environmentally superior to current JP-8 fuel that is derived totally from petroleum. Corporan et al.<sup>3</sup> have shown that combustion of FT/JP-8 blends result in reductions in particle mass, particle number,

and engine smoke number in both T63 turboshaft and atmospheric swirl-stabilized research combustors. The soot reductions varied directly with the concentration of the FT component in the jet fuel. These results suggest that FT/JP-8 blends can reduce particulate emissions in both legacy and modern combustion systems. Finally, FT/JP-8 blends are expected to have lower sulfur emissions owing to the low sulfur content of FT fuels, which may be helpful in the global struggle to mitigate acid rain.

To address concerns over future carbon emissions the USAF may require the Fischer–Tropsch portion of the fuel to be produced by facilities employing CO<sub>2</sub> capture and sequestration. In addition, it may be required that ~20% of the carbon content of the Fischer–Tropsch portion of the fuel be derived from biomass. If this policy is implemented the use of a 1/1 volumetric blend of FT/JP-8 would likely decrease the future carbon footprint of the USAF.

The effect upon the thermal oxidative stability of blending Fischer–Tropsch jet fuel into petroleum-derived jet fuels seems to be stress time/temperature dependent. It is generally accepted that dilution of the petroleum jet fuels' indigenous polar compounds with nonpolar FT hydrocarbons will improve thermal stability under *mild* oxidative stress conditions. Consistent with this expectation is the fact that South Africa has been using 1/1 FT/Jet A-1 blends for civil aviation for many years with no apparent adverse effects. Also consistent with this observation Balster, Balster, and Jones<sup>4</sup> reported in 1996 that 1/1 blends of a Jet A fuel, POSF 2827, with a paraffinic/cycloparaffinic solvent (Exxsol D-80) increases the thermal oxidative stability in a single-pass tubular heat exchanger operated isothermally at 185 °C for stress durations of less than

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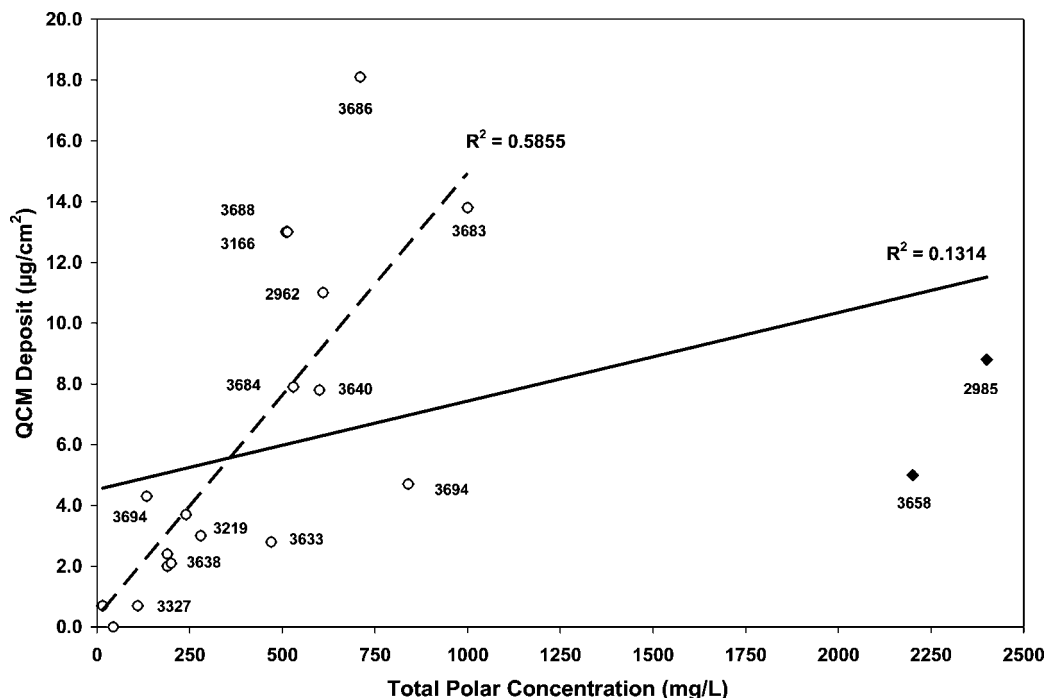
<sup>‡</sup> The Pennsylvania State University.

(1) Balster, L. M.; Zabarnick, S.; Striebich, R. C.; Shafer, L. M.; West, Z. *Energy Fuels* **2006**, *20*, 2564–2571.

(2) Beaver, B.; Gao, L.; Burgess-Clifford, C.; Sobkowiak, M. *Energy Fuels* **2005**, *19*, 1574–79.

(3) Corporan, E.; DeWitt, M.; Belovich, V.; Pawlik, R.; Lynch, A.; Gord, J.; Meyer, T. *Energy Fuels* **2007**, *21*, 2615–2626.

(4) Balster, L.; Balster, W.; Jones, E. G. *Energy Fuels* **1996**, *10*, 1176–1180.



**Figure 1.** Work of Balster et al. reporting the relationship between jet fuel total polar concentration vs QCM deposit for (a) 20 fuels, with a solid line curve fit and (b) 18 fuels with outliers POSF-2985 and 3658 excluded with the curve fit indicated by a dashed line (data from ref 1).

18 min (of a possible 24 min of stress). However, at longer term stress durations, 18–24 min, blending resulted in decreased thermal oxidative stability. In 2003 Hemighaus and O'Rear<sup>5</sup> reported that volumetric blends of four different commercial Jet A's with an isoparaaffinic FT jet fuel resulted in a decrease in the jet fuel thermal oxidation tester (JFTOT) breakpoints. In two cases FT addition of less than 10% volume to stable Jet A's caused failure in the JFTOT specification. A nonoptimized commercial additive package containing a dispersant was found to limit the decline in the JFTOT breakpoint. Interestingly, these investigators found that using a normal paraaffinic hydrocarbon, rather than an isoparaaffinic blending stream, did not cause a decline in JFTOT break points. Also in 2003, Bauldreay et al.<sup>6</sup> reported both enhancement and decline in thermal oxidative stability, based upon a carbon burn off JFTOT technique, with 15% and 25% blends of paraaffins into various Jet A's. The paraaffinic material was derived from the Shell Middle Distillate Synthesis.

It has been suspected for decades that indigenous fuel polar aromatic compounds are involved in both ambient (i.e., storage stability) and thermal oxidative deposit formation in both jet<sup>7–13</sup>

and diesel fuels.<sup>14–19</sup> Reconciling the above FT blending studies with the proposed mechanisms of formation of jet fuel thermal oxidative deposits is hampered by a lack of knowledge of the composition and concentration of the polar compounds in the fuel blends utilized. In Figure 1 is presented previous work by Balster et al.<sup>1</sup> summarizing the correlation for a suite of 20 petroleum-derived jet fuels between thermal oxidative stability and fuel total polar concentration. These fuels were selected to span the range of thermal oxidative stability encountered due to different crude sources and refinery conditions. Thermal oxidative stability was estimated by the quartz crystal microbalance (QCM) technique, while the fuel total polar concentration was determined by an HPLC method. In addition, an SPE-HPLC-GC-MS technique was used to qualitatively identify and estimate the concentrations of the various polar compounds. The fuels in Figure 1 can be grouped into three different classes based upon their QCM deposit levels:  $<1 \mu\text{g}/\text{cm}^2$  low depositors,  $2\text{--}9 \mu\text{g}/\text{cm}^2$  intermediate depositors, and  $>9 \mu\text{g}/\text{cm}^2$  heavy depositors. Balster et al.<sup>1</sup> have drawn two different trend lines shown in Figure 1. A poor correlation ( $R^2 = 0.131$ ) is obtained for the plot for all 20 fuels (solid line). However, the dashed line has a reasonable linear correlation ( $R^2 = 0.586$ ) with 18 fuels. This line assumes that fuels 2985 and 3658 are outliers owing to their extreme polarity.

The data presented in Figure 1 provides an opportunity to experimentally test a detailed mechanism we proposed in 2005 for formation of thermal oxidative deposit in jet fuels (and diesel fuels).<sup>2</sup> This mechanism is depicted in abbreviated form in Scheme 1. Structure 3 in Scheme 1 is proposed to be a jet fuel thermal oxidative deposit precursor. This structure is based upon earlier work by Hardy and Wechter<sup>17</sup> that reported an average empirical formula of  $\text{C}_{21}\text{H}_{20}\text{O}_2\text{N}$  for oxidative deposit precursors

(5) Hemighaus, G.; O'Rear, D. J. *8th International Conference on Stability Handling Liquid Fuels*, Steamboat Springs, CO, 2003; International Association for the Stability and handling of Liquid Fuels (I.A.S.H.); pp 1126–1137.

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(7) Hazlett, R. N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; American Society for Testing and Materials: Philadelphia, 1991.

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(12) Kuprowicz, N. J.; Zabarnick, S.; West, Z. J.; Ervin, J. S. *Energy Fuels* **2007**, *21*, 530–544.

(13) Zabarnick, S.; Phelps, D. K. *Energy Fuels* **2006**, *20*, 488–497.

(14) Beaver, B. D. *Fuel Sci. Technol. Int.* **1991**, *9* (10), 1287–1335.

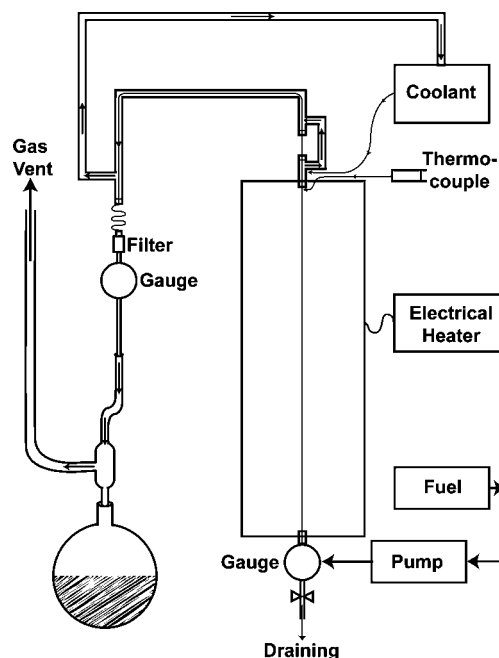
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(16) Zuhdan, A.; Batts, B. D. *Energy Fuels* **1992**, *6*, 681–690.

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(18) Pande, S. G.; Hardy, D. R. *Energy Fuels* **1997**, *11*, 530–544.

(19) Pande, S. G.; Hardy, D. R. *Energy Fuels* **1995**, *9*, 177–182.



**Figure 2.** Diagram of the Penn State University (PSU) flow reactor.

isolated from five diesel fuel blends containing unhydrotreated LCO that were at least 6 months old. In addition, structure **3** is consistent with pyrolysis/field ionization mass spectroscopy analysis which indicated the presence of indole/carbazole structures in the diesel fuel deposit precursors.

In Scheme 1, step 1 is proposed to be rate limiting and have a first-order dependency in both phenol and peroxy radical concentration.<sup>20</sup> Deposit formation is initiated by conversion of indigenous fuel phenols into quinones and hydroquinones as shown in steps 1–4. These steps are consistent with the inverse relationship between the rate of fuel oxygen consumption and thermal oxidative deposit formation first noted by Hardy et al.<sup>8</sup> and independently by Heneghan et al.<sup>9</sup> Thus, the initial rate of oxygen consumption (and deposit formation) is determined by the relative rate of initiation of peroxy radical formation (not shown) and the indigenous phenol concentration. This mechanism is also consistent with the suggestion of Heneghan and Zabarnick<sup>11</sup> that step 3 is the primary pathway toward oxidative deposit formation. Owing to the inherent reactivity of quinones as good electrophiles and carbazoles (and indoles) as good nucleophiles, step 5 is expected to be rapid. The detailed mechanism of step 5 is proposed to be electrophilic aromatic substitution (EAS) to form compound **1**.

It is important to note that compared to indigenous fuel phenols and carbazoles/indoles, compound **1** has increased molecular weight, polarity, and reactivity with radical species. The reason for the enhanced reactivity of compound **1** with radical species (particularly peroxy radicals and/or possibly molecular oxygen) is due to the weaker O–H bond compared to phenol. Abstraction of a hydrogen atom from compound **1** will form the highly delocalized resonance hybrid shown in Scheme 2. It is the stability of this species which increases the reactivity of the O–H bond in **1** relative to phenol. This species is also expected to rapidly form quinone **2** in Scheme 1 by loss of a second hydrogen atom. Although quinone **2** can react with

any nucleophilic species in solution, step 7 is shown with reaction of unoxidized compound **1** to form compound **3**. It is expected that compound **3** would still be fuel soluble but would be more reactive with peroxy radicals (and possible O<sub>2</sub>) than compound **1** owing to additional enhanced resonance effects. Thus, it is expected that compound **3** would rapidly oxidize to a quinone (faster than compound **1** or unreacted indigenous phenols) and couple with other fuel nucleophilic species by electrophilic aromatic substitution to form higher molecular weight deposit precursors. Thermal oxidative deposit precursor deposition occurs when precursor mass and polarity accedes the ability of the fuel to solubilize (typically in the mass range of 600–900 Da).<sup>17</sup>

The significance of the mechanism proposed in Scheme 1 is that it provides a logical rationalization for the growth in thermal oxidative deposit precursor molecular weight. The chemical origin of this phenomenon is formation of progressively weaker O–H bonds due to enhanced resonance stabilization of the resulting radical species upon hydrogen atom abstraction. Second, since the rate-limiting step in Scheme 1 is proposed to be step 1, this mechanism predicts that the rate of thermal oxidative deposit formation will linearly increase with fuel phenol concentration.<sup>21</sup>

There are two goals in the present work: first, to clarify the effect upon thermal oxidative stability, under high-temperature flow conditions, of blending equal volumes of a Fischer–Tropsch-derived isoparaffinic jet fuel with a variety of jet fuels of known polarity; second, to test the mechanism proposed in Scheme 1, that fuel concentration of indigenous phenol derivatives is linearly related to the mass of thermal oxidative deposit formation.

## Experimental Section

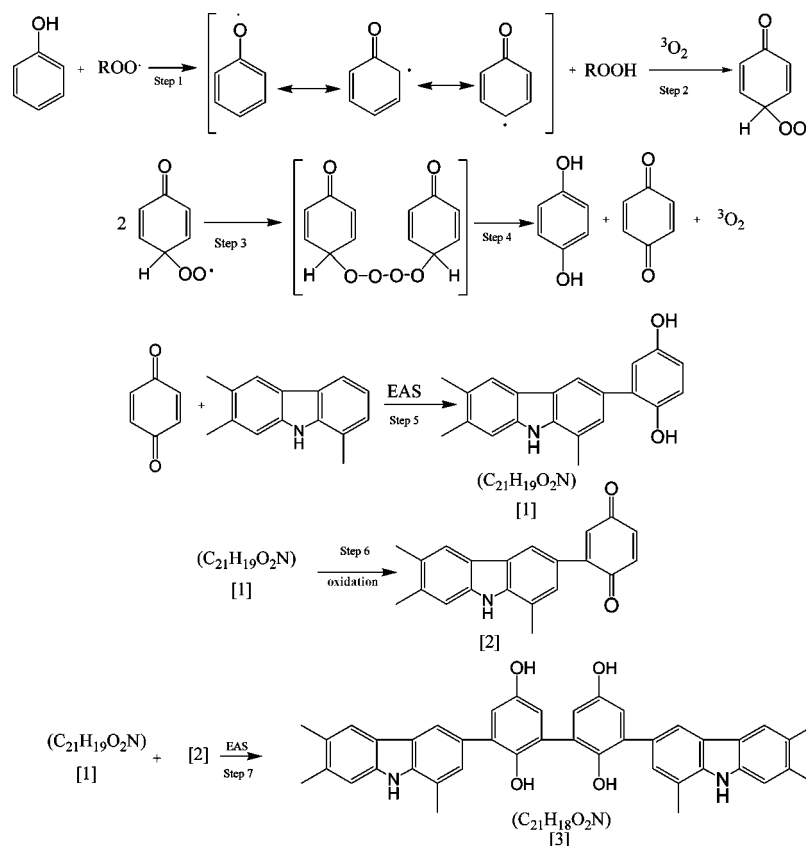
**Materials.** The fuels tested were JP-8 (POSF-3804), Jet A (POSF-3602), Jet A (POSF-3658), Jet A (POSF-3683), and an isoparaffinic Fischer–Tropsch jet fuel (POSF-4820), which were supplied by the U.S. Air Force. Stainless steel 316 tubing was purchased from Alltech Associates, Inc. A thermocouple probe with the lead wire attached and a stripped end was purchased from Omega Engineering, Inc.

**Penn State University (PSU) Flow Reactor Studies.** Reactions were carried out in a vertically mounted single-tube flow reactor (Figure 2). The length of tubing in the reactor furnace was 36.2 in. (90 cm) with an outer diameter (o.d.) of 0.0625 in. and an inner diameter (i.d.) of 0.04 in. A liquid hourly space velocity (LHSV) of 182 h<sup>-1</sup> was used. The fuel was saturated with air at atmospheric pressure and then pumped with the back pressure maintained at 500 psig with a 2.23 mL/min flow rate and in the laminar flow regime. The reactor temperature calibration profile was obtained using multiple runs, with decahydronaphthalene (Aldrich) as the fuel, with a thermocouple probe placed into the bulk fuel, using a 1/16 in. stainless steel tee (Restek Corp.) at different tube positions.<sup>2</sup> The standard conditions have a thermocouple placed at the top of the reactor, just before the exit from the furnace, to measure the bulk fuel exit temperature. The reactor was heated in such way to keep the exit temperature constant at 550 °C and held at this temperature for 6 h.

**Characterization of Carbon Deposition.** Upon completion of the reaction the reactor tubing was washed three times with pentane to remove any residual fuel followed by removal from the reactor.

(20) This assumption may be overly simplistic. Nonetheless, an inhibited peroxy-chain mechanism is known to have a linear relationship between the rate of autooxidation and antioxidant concentration, see: Tudos, F.; Fodor, Z.; Iring, M. In *Oxidation Inhibition in Organic Materials*; Pospisil, J., Klemchuk, P. P., Eds.; CRC Press: Boca Raton, 1990; Vol. 2, p 234.

(21) In this paper it is assumed that the mass of thermal oxidative deposition by both the QCM method and the PSU flow reactor roughly correlates with the rate of thermal oxidative deposit formation. The origin of this assumption is that each method determines the total oxidative deposition mass in a fixed amount of time under fixed conditions. Thus, differences in fuel composition should be of primary importance in determining both the rate and the total mass of thermal oxidative deposition.

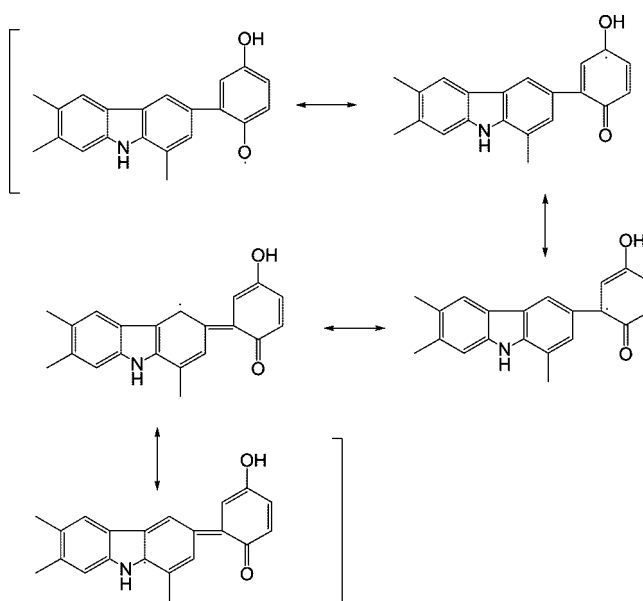
**Scheme 1. Mechanistic Hypothesis Used To Rationalize the Chemistry of Jet Fuel Thermal Oxidative Deposit Formation (previously published in ref 2)**

Afterward, the reaction tubing was cut into 2-cm pieces, washed again with pentane, and dried in a vacuum oven at 100 °C overnight. Upon completion of the drying, the total carbon deposition on each piece was determined using a LECO model RC 412 multiphase carbon analyzer.

## Results and Discussion

From the suite of 20 fuels presented in Figure 1 four fuels were selected for additional study. Three intermediate depositors (POSF 3602, 3804, and outlier 3658) and a heavy depositor fuel POSF 3683. The fuel types, refinery process information, and polar species distributions for these fuels as reported by Balster et al.<sup>1</sup> are compiled in Table 1. Particularly interesting is outlier fuel POSF 3658 since this fuel has an unusually high concentration of indoles and carbazoles. Since POSF 3658 is only an intermediate depositor with the QCM technique and the mechanism proposed in Scheme 1 predicts this fuel to be a heavy depositor, this fuel was of particular interest.

The neat fuels were stressed for 6 h at a flow rate of 2.23 mL/min in the Penn State flow reactor using 316 stainless steel tubing with a fuel exit temperature of 550 °C. Previous work has shown these conditions involve complete oxygen consumption.<sup>22</sup> Previous work has also shown that fuel temperatures above 600 °C are required to initiate pyrolytic deposition.<sup>23,24</sup> In Figure 3 tube carbon deposit is plotted versus the distance along the stainless steel tube for three separate runs with POSF 3804. Excellent reproducibility is noted, and all subsequent flow

**Scheme 2. Structure of the Resonance Hybrid of Oxidized Compound 1 from Scheme 1<sup>a</sup>**

<sup>a</sup> Only select structures are shown. Extensive resonance delocalization in oxidized **1** (i.e., a very stable radical) is expected to make the OH bond in compound **1** weak and very reactive with peroxy radicals and possibly even reactive with molecular oxygen.

reactor data is for individual runs. In Figure 4 is plotted flow reactor mean carbon deposits versus fuel total polar concentration for all four neat fuels plus their respective 1/1 volume blends with a Fischer–Tropsch jet fuel. Excellent correlations ( $R^2 = 0.996$ , dashed line) are found between flow reactor mean carbon deposits and total polar concentration for three fuels and their

(22) Ervin, J. S.; Ward, T. A.; Williams, T. F.; Bento, J. *Energy Fuels* **2003**, *17*, 577–86.

(23) Sobkowiak, M.; Burgess-Clifford, C.; Beaver, B. D. *Energy Fuels* **2007**, *21*, 982–986.

(24) Beaver, B. D.; Sobkowiak, M.; Burgess-Clifford, C.; Wei, Y.; Fedek, M. *Energy Fuels* **2007**, *21*, 987–991.

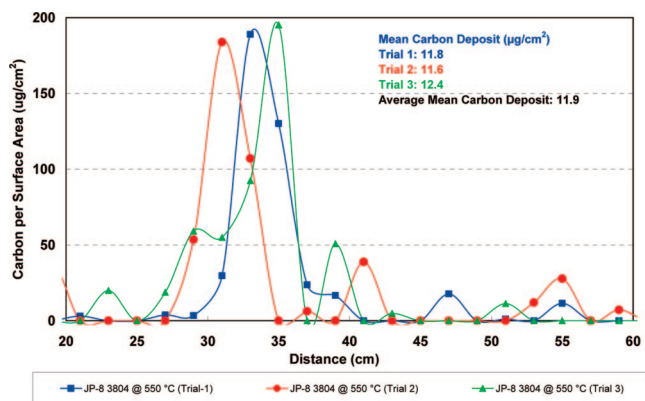


**Table 1. Polar Species Concentration and Refinery Conditions for Jet Fuels Examined (data from ref 1)**

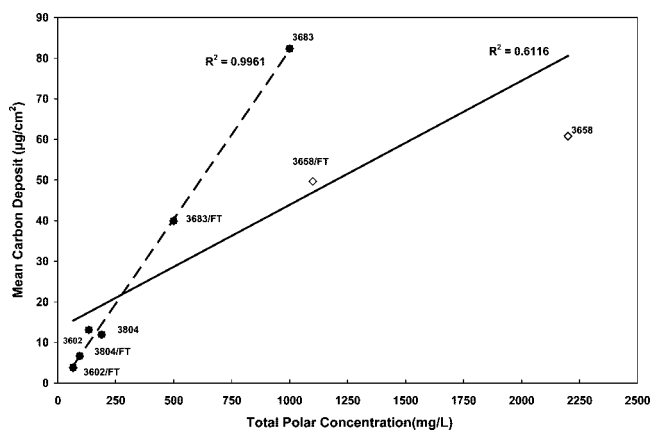
POSF number/ fuel type	refinery process	% phenols	% other oxygenates	% indoles and carbazoles	% pyridines and quinolines	QCM deposits $\mu\text{g}/\text{cm}^2$	total polars (mg/L)
3804/JP-8	unknown	78.9	5.7	4.2	0.0	2.4	190
3602/Jet-A	hydrotreated	31.9	58.3	6.5	2.0	4.3	134
3658/Jet-A	hydrocracked	43.3	1.5	47.0	1.7	5.0	2200
3683/Jet-A	hydrotreated-thermally cracked	71.4	21.3	6.1	0.8	13.8	1000

FT blends if fuel 3658 and its FT blend are treated as outliers. However, even with fuel 3658 and its FT blend included the correlation is still reasonably good with an  $R^2$  value of 0.612 (solid line). Our results suggest blending 50% FT fuel into three petroleum-derived jet fuels resulted in approximately a 50% decrease in mean carbon deposits. However, fuel 3658 results in only a  $\sim 20\%$  decrease in thermal oxidative deposit with FT blending.

The origin of the outlier status of 3658 and its FT blend (and 2985 in Figure 1) is not clear. However, we suggest that such behavior is related to the high concentration of indoles and carbazoles in these fuels. The 18 fuels in the linear region of Figure 1 have total indole and carbazole concentrations ranging from 0–85 ppm, while fuel 2985 has 283 ppm and fuel 3658 has 1034 ppm.<sup>1</sup> It is conceivable that with high concentrations of indigenous indole and/or carbazole derivatives these compounds are more reactive than phenols with peroxy radicals.



**Figure 3.** Reproducibility of the PSU flow reactor for three separate 6 h runs with fuel POSF-3804. Fuel temperature at furnace exit is maintained at 550 °C, while the flow rate is 2.23 mL/min at 500 psig of back pressure.



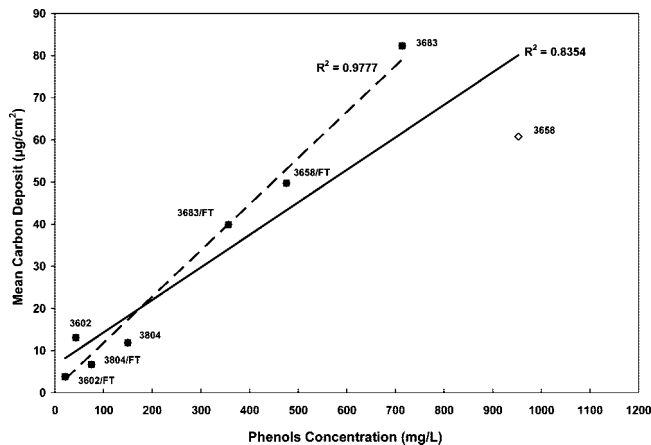
**Figure 4.** Relationship between jet fuel total polar concentration and mean carbon deposit from the PSU flow reactor. The solid line curve fit is for all eight fuels (four neat fuels plus their respective 1/1 blends with a Fischer–Tropsch jet fuel). The dashed line is for six fuels (three neat fuel plus their respective 1/1 FT blends) with outliers neat POSF-3658 and its 1/1 Fischer–Tropsch blend excluded. The fuel total polar concentrations for the neat fuels were taken from ref 1.

If such were the case then the structure of the oxidized indole/carbazole deposit precursors would be very different than deposit precursors **1–3** shown in Scheme 1. This proposed difference in the structure (and presumably solubility) of the deposit precursors may explain the outlier status of 3658 and 2985. In addition, the extreme polarity of these outliers may limit thermal oxidative deposit by a dispersant effect.

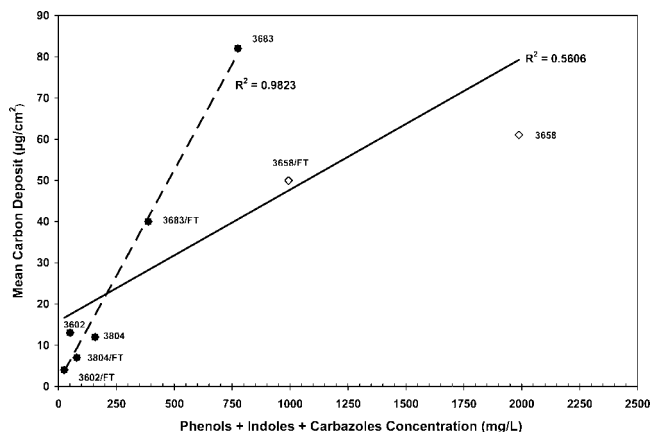
A good correlation ( $R^2 = 0.835$ , solid line) is obtained in Figure 5 for all fuels and blends with a plot of flow reactor mean deposit versus fuel phenol concentration. If neat fuel 3658 is treated as an outlier the correlation is excellent ( $R^2 = 0.978$ , dashed line). It is interesting to note that, comparing Figures 4 and 5, the FT blend of fuel 3658 has “moved” into the linear region of the deposit curve. This fact suggests that there is a complex relationship between fuel polarity and the mechanistic details of thermal oxidative deposit formation.

Figure 6 reveals that a plot of flow reactor mean carbon deposits versus fuel concentration of phenols, indoles, and carbazoles has a reasonable linear correlation ( $R^2 = 0.561$ , solid line) for all four fuels plus their respective FT blends. When outlier fuel 3658 and its FT blend are excluded, the correlation improves to  $R^2 = 0.982$  (dashed line). Interestingly, Figure 7 reveals that the plot of flow reactor mean carbon deposits versus fuel indole and carbazole concentration has a poor correlation ( $R^2 = 0.265$ , solid line) for all four fuels plus their respective FT blends. However, if fuel 3658 and its FT blend is excluded, the correlation for the remaining six fuels is excellent,  $R^2 = 0.998$  (dashed line). We suggest the observed disparity between the correlation coefficients, with and without the outliers, is suggestive of a change in the mechanism for thermal oxidative deposit formation at high indole and carbazole concentrations (i.e., >85 ppm), as previously suggested.

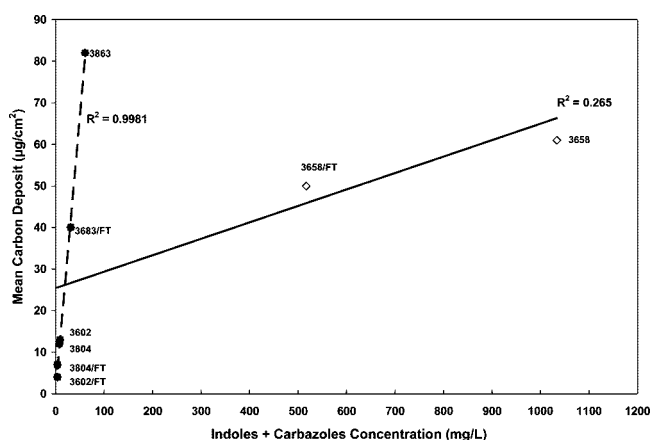
In Scheme 1, step 5 is proposed to be fast relative to rate-limiting step 1. Thus, step 5 cannot account for the observed linearity observed in Figure 7. However, a plot of fuel phenol



**Figure 5.** Relationship between the concentration of jet fuel phenols and mean carbon deposits from the PSU flow reactor. The solid line curve fit is for all eight fuels (four neat fuels plus their respective 1/1 blends with a Fischer–Tropsch jet fuel). The dashed line is for seven fuels (three neat fuel and their respective 1/1 FT blends plus the POSF-3658/FT blend) with outlier neat POSF-3658 excluded. The fuel polar species concentrations for the neat fuels were taken from ref 1.



**Figure 6.** Relationship between the concentration of jet fuel phenols, indoles, carbazoles, and mean carbon deposit from the PSU flow reactor. The solid line curve fit is for all eight fuels (four neat fuels plus their respective 1/1 blends with a Fischer–Tropsch jet fuel). The dashed line is for six fuels (three neat fuel and their respective 1/1 FT) with outlier neat POSF-3658 and its FT blend excluded. The fuel polar species concentrations for the neat fuels were taken from ref 1.



**Figure 7.** Relationship between the concentration of jet fuel indoles and carbazoles and mean carbon deposit from the PSU flow reactor. The solid line curve fit is for all eight fuels (four neat fuels plus their respective 1/1 blends with a Fischer–Tropsch jet fuel). The dashed line is for six fuels (three neat fuels and their respective 1/1 FT blends) with outlier neat POSF-3658 and its FT blend excluded. The fuel polar species concentrations for the neat fuels were taken from ref 1.

concentration versus fuel indole and carbazole concentration for the 18 fuels in the linear region of Figure 1 has a correlation coefficient of 0.86 (data not shown). This observation suggests that, at least for these fuels, phenol, indole/carbazole, and total polars concentration are linearly related.

This idea is further explored in Table 2 with data from Balster et al.<sup>1</sup> on correlation coefficients obtained from plots of fuel thermal oxidative deposition mass, determined by the QCM technique, versus relative concentrations of various polar species. In the second column of Table 2 it is evident that there are not any linear correlations observed when all 20 fuels are compared. However, Balster et al.<sup>1</sup> reported, in the third column of Table 2, that if a few fuels can be assumed to be outliers then reasonable linearity can be observed between thermal oxidative deposit mass and fuel concentration of total polars, phenols, and other oxygenates (other oxygenates are oxygen-containing compounds other than phenols). However, only a modest linear correlation is observed with indole and carbazole concentrations.

**Table 2. Correlation Coefficients for Plots of the Relative Amounts of Polar Species versus Thermal Oxidative Deposits by the Quart Crystal Microbalance Method (data is from ref 1)**

polars, total or subclass	$R^2$ (all 20 fuels)	$R^2$ (fuels excluded by Balster et al. <sup>1</sup> )	$R^2$ (if additional fuels are excluded)
total polars	0.13	0.59 (2985, 3658)	
phenols	0.21	0.60 (2985, 3658)	0.65 (2985, 3658, 3327, 3638, 3633, 3593)
other oxygenates	0.08	0.76 (2985, 3694)	
indoles	0.00	0.38 (2985, 3658)	
carbazoles	0.01	0.37 (3658)	
indoles and carbazoles	0.00		0.77 (2985, 3658, 3327, 3638, 3633, 3593)
pyridines	0.04		
anilines	0.00		
quinolines	0.02		

The fuels assumed to be outliers by Balster et al.<sup>1</sup> are based upon extreme concentrations (i.e., very polar outliers) for the various polar species examined.

The mechanism proposed in Scheme 1 suggests that in addition to the very polar outliers (2985, 3658) that fuels 3327, 3638, 3633, and 3593 should also be excluded. The latter four fuels do not contain phenol and/or indole and carbazole derivatives, the proposed deposit precursors. In addition, with the mechanism proposed in Scheme 1 indole and carbazole derivatives are mechanistically identical in their capacity to promote deposit formation. Both species can be classified as electron-rich aromatic compounds. Indeed, plotting total indole and carbazole derivative concentration versus oxidative deposit for the remaining 14 fuels improves linearity considerably ( $R^2 = 0.77$ ) as shown in the forth column of Table 2. A similar treatment with the phenol data also improves the linearity of the plot ( $R^2 = 0.65$ ).

The good linearity ( $R^2 = 0.76$ ) observed in the third column of Table 2 for the plot of thermal oxidative deposit versus the concentration of other oxygenates is at first glance inconsistent with the mechanism proposed in Scheme 1. However, as previously found with indole and carbazole derivatives, plotting fuel concentration of other oxygenates versus phenol concentration reveals a linear correlation ( $R^2 = 0.62$ ) for 19 of the fuels in Figure 2 (data not shown).

## Conclusions

With conventional jet fuels it has been shown that blending equal volumes of an isoparaffinic Fischer–Tropsch fuel improves thermal oxidative stability under 550 °C flow conditions (Figure 4). Also reported is data consistent with a linear relationship between fuel phenol concentration and thermal oxidative deposit formation (Figure 5). The origin of this relationship is suggested to be a first-order dependency in fuel phenol concentration proposed for the rate-limiting step for deposit formation (step 1, Scheme 1). Since fuel phenol concentration is found to linearly correlate with fuel total polars, indole and carbazole, and other oxygenate concentrations, the origin of the various linear relationships observed here is accounted for by Scheme 1.

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