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Insight into the Mechanisms of Middle Distillate Fuel Oxidative Degradation. Part 2: On the Relationship between Jet Fuel Thermal Oxidative Deposit, Soluble Macromolecular Oxidatively Reactive Species, and Smoke Point

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We present data that suggest that jet fuel smoke point and the formation of thermal oxidative deposit are linked by formation of a common intermediate, high molecular weight soluble macromolecular oxidatively reactive species (SMORS). Hardy and Wechter (*Energy Fuels* **1994**, *8*, 782−787) have previously observed that with diesel fuels containing unhydrotreated light cycle oil (LCO), the highest molecular weight fraction of SMORS can be conveniently quantified as an extraction-induced precipitate (EIP). These authors have also shown that for fresh diesel fuel, oxidatively stressed fuel EIP mass correlates well with results of accelerated storage stability determined by ASTM 5304. Consistent with this, data are presented that suggest EIP mass, from jet fuels oxidatively stressed in tubing bombs, correlates with mean thermal oxidative deposition in a flowing reactor. In addition, data are presented that suggest that for a polar compound doped oxidatively stressed jet fuel, EIP mass correlates with the total concentration of polar compounds doped into the fuel. Thus, for the first time the concentration of select polar aromatics has been directly linked with the formation of a deposit precursor (*Energy Fuels* **1994**, *8*, 782−787) and smoke point.

Introduction

A fundamental breakthrough in understanding the mechanisms of oxidative deposit formation in middle distillates was provided by Hardy and Wechter[1] in the early 1990s. It was suggested that the mechanism of diesel oxidative deposit formation, upon ambient storage, involves autoxidation of material typically present in high concentration in unhydrotreated catalytically cracked LCO blending stocks; subsequent coupling reactions involving these oxidized precursors then ensue. It was proposed that repeated oxidation and coupling cycles increase deposit precursor molecular weight until precipitation occurs at greater than 900 Da. Hardy and Wechter[1] have described this material as a soluble macromolecular oxidatively reactive species (SMORS). We have previously[2] proposed the reaction shown below, in abbreviated form here, to conceptualize SMORS formation (i.e., the SMORS hypothesis).

Scheme 1 depicts the autoxidation of indigenous fuel phenol to form a quinone; subsequent coupling of the quinone with electron-rich aromatic compounds, such as the carbazole derivative shown above, yields a low molecular weight SMORS. A more detailed discussion of the chemistry of the SMORS

Scheme 1
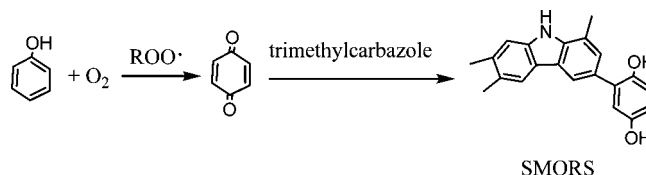
hypothesis is presented in the previous Article in this issue.[3] However, it is important to note the SMORS hypothesis is meant to be generic and applies to many other compounds in addition to those shown above. Any fuel phenol in principle can form ortho and/or para quinones upon oxidation. Most jet fuels contain phenols[4] whose concentration is known to determine both the rate of oxygen consumption and the extent of thermal oxidative deposit formation.[5] When phenols are oxidized into quinones, a powerful electrophilic species is generated, which can functionalize any electron-rich aromatics in the fuel by electrophilic aromatic substitution. Electron-rich aromatic compounds in jet[4] or diesel fuels[6] include, but are not limited to, indoles, carbazoles, pyrroles, anisoles (i.e., methoxybenzenes), and biphenyl anisoles. It is also possible that sulfur-containing compounds such as thiophene derivatives and/or nucleophilic thiols can also react with electrophilic quinones to promote

(1) Hardy, D. R.; Wechter, M. A. *Energy Fuels* **1994**, *8*, 782–787, and references within. .

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

(3) Sobkowiak, M.; Griffith, J. M.; Wang, B.; Beaver, B. *Energy Fuels*, **2009**, *23*, 2041−2046.

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

(5) Heneghan, S. P.; Zabarnick, S. *Fuel* **1994**, *73*, 35–43.

(6) Bauserman, J. W.; Mushrush, G. W.; Hardy, D. R. *Ind. Eng. Chem. Res.* **2008**, *47*, 2867–75.

Table 1. Select Characteristics of JP-8 Jet Fuels

characteristic	4877[a]	4177[b]	4177[c]	4177[d]	4751[e]	2827[f]	2827[g]
thermal stability @ 260 °C; change in pressure, mm Hg;	0	1	4	4	0	0	2
thermal deposit rating, visual	<1	fail (peacock)	2	2	1	<1	1
existent gum (mg/100 mL)	0.4	0.6	1.2	1.8	<1	<1	2
particulate matter (mg/L)	0.3	not reported	0.3	0.9	0.7	0.3	0.7
filtration time (min)	5	not reported	6	5	4	4	26
aromatics (% vol)	19.2	16.9	17.0	16.3	19.6	19.2	17.4
smoke point (mm)	25.0	22.0	22.0	22.0	22.0	25.0	26.0
total sulfur (mass %)	0.01	0.13	0.14	0.14	427 (ppm)	0.06	0.08
hydrogen content (% mass)	13.5	13.7	13.7	13.7	13.8	13.8	13.8
API gravity	46.1	42.2	42.4	42.4	44.5	45.2	43.8

[a] Laboratory Test Report, POSF-4877, 3/7/2007, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [b] Laboratory Test Report, POSF-4177, 4/27/2006, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [c] Laboratory Test Report, POSF-4177, 2/17/2004, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [d] Laboratory Test Report, POSF-4177, 7/11/2002, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [e] Laboratory Test Report, POSF-4751, 2/14/2008, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [f] Laboratory Test Report, POSF-2827, 8/02/2007, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB. [g] Laboratory Test Report, POSF-2827, 8/17/2000, Department 13 SA-ALC/AFTLA, Wright-Patterson AFB.

deposit formation. However, this aspect of the SMORS hypothesis has not yet been explored.

The initial investigations by Hardy and Wechter[1] found that SMORS have interesting physical and chemical characteristics. The first interesting characteristic is their solubility. SMORS are more polar, because of oxygen incorporation, than the material they are derived from. Thus, SMORS can be isolated from an oxidatively stressed fuel matrix by a simple extraction procedure with methanol. GC/MS analysis of the methanol extract reveals numerous monomeric polar species in low concentration; these include phenalene, phenalenone, and indoles. Evaporation of the methanol yields SMORS as a liquid material. The second interesting chemical characteristic of SMORS is a propensity to form higher molecular weight material. A family of higher molecular weight SMORS, typically in the 600−900 Da range according to Hardy and Wechter,[1] can be isolated by simply adding a hydrocarbon solvent to the SMORS sample to precipitate a dark colored solid material. This material is referred to as an extraction induced precipitate (EIP). Wechter and Hardy[7] have also suggested that the storage stability of fresh diesel fuel can be predicted by determining fuel EIP mass after accelerated aging. In addition, it is likely that the combustion characteristics of the EIP (i.e., high molecular weight SMORS) are different from those of the fuel monomers from which it is derived. Thus, the SMORS hypothesis suggests the interesting possibility of a relationship between fuel thermal oxidative stability and soot formation upon combustion.

In this Article, the SMORS hypothesis is tested in jet fuels to ascertain whether it can describe the thermal oxidative deposit formation process. In addition, the relationship between SMORS and jet fuel smoke point is explored.

Experimental Section

The jet fuels used in this study were provided by the fuels group at Wright-Patterson AFB. These fuels were designate by USAF as POSF-3658, 2827, 4177, 4751, 4877, and 4820 (an isoparaffinic Fischer−Tropsch (FT) jet fuel). Select laboratory characteristics for some of these fuels are reported in Table 1. In some experiments, fuels were doped with polar compounds purchased from Aldrich Chemical Co. These compounds were used as received. When a liter of jet fuel was doped with 100 ppm total polars, 46.6 mg of phenol, 41.7 μL of 3-methylphenol, 3.2 mg of indole, 2.8 mg of 2-methylindole, and 2.8 mg of carbazole were added.

Table 2. Volume of SMORS and EIP Mass Isolated from Fuels with and without Tubing Bomb Thermal Oxidative Stress[a]

expt. no.	jet fuel POSF	thermal oxidative stress	SMORS (mL/100 mL fuel) ± standard deviation	EIP (mg/100 mL fuel) ± standard deviation
1	4177	no	4.9 ± 0.1	0.41 ± 0.01
2	4751	no	4.9[b]	0.1[b]
3	4877	no	5.0 ± 0.1	0.0
4	2827	no	5.6 ± 0.1	0.0
5	4177	yes	5.1[b]	6.63 ± 2.99
6	4751	yes	5.0 ± 0.0	7.86 ± 0.81
7	4877	yes	6.1 ± 0.1	2.5 ± 0.85
8	2827	yes	5.1 ± 0.0	3.37 ± 0.66

[a] Tubing bomb stress was for 2 h at 250 °C and 150 psi air. [b] Only one determination.

PSU Flowing Reactor. A description of this reactor and the experimental protocol used is found in part 1 of this series.[3]

Tubing Bomb Study. [8] A 30 mL fuel sample is loaded into tubing bomb reactors and charged with an oxygen (or air) pressure of 150 psi. The tubing bomb is then submerged into a fluidized sand bath, preheated to a selected temperature, and stressed for varying time lengths. After the stress was complete, the bombs are withdrawn from the sand bath, quenched in cold water, carefully opened, and then the fuel was filtered with a grade 691 VWR glass microfiber filter. Particle retention size for these filters is 1.5 μm.

SMORS Isolation. The stressed filtered fuel sample is placed into a separatory funnel and extracted with methanol (5:2 fuel to methanol ratio). The methanol layer is separated from the fuel and followed by concentrated with a rotary evaporator. After being cooled, the volume of the resulting liquid (SMORS) is measured with a graduated cylinder.

EIP Mass Determination. Thirteen milliliters of hexane is added to the SMORS sample followed by filtration of insoluble material with a preweighed grade 691 VWR glass microfiber filter. Particle retention size for these filters is 1.5 μm. The samples were dried for 1 h at 100 °C prior to mass determination.

Smoke Point Determination. Smoke point measurements at PSU were implemented according to ASTM method D 1322 in the summer/fall of 2007.

Results and Discussion

In Table 2, experiments 1−4, is reported SMORS volumes and EIP mass for four unstressed jet fuels. Fuels 4177, 4751, and 4877 are younger than fuel 2827, which is at least 14 years old. Interestingly, the fuels all have similar volumes of SMORS and minimal EIP mass. That minimal EIP mass was isolated from the three "fresh" unstressed fuels suggests that long periods

(7) Wechter, M. A.; Hardy, D. R. In *Proceedings of the 5th International Conference on Stability Handling Liquid Fuels*; Giles, H. N., Ed.; Rotterdam: The Netherlands, 1995; pp 919−28.

(8) Song, C.; Eser, S.; Schobert, H. H.; Hatcher, P. G. *Energy Fuels* **1993**, *7*, 234–243.
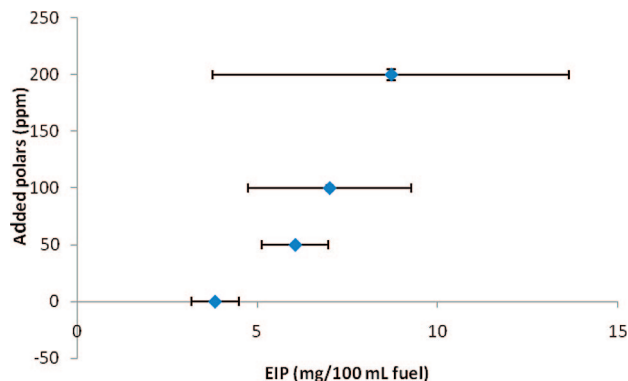
Figure 1. Correlation between the total concentration of polar compounds doped into POSF-2827 and EIP mass produced by tubing bomb stress for 2 h at 250 °C under 150 psi air. Each point is the average of two experiments with the standard deviation indicated on the plot.

of ambient storage are required to generate high molecular weight SMORS. Hardy and Wechter[1] have found that diesel fuels containing unhydrotreated LCO blending stocks require at least 6 months of ambient storage to generate EIP mass. It is likely that jet fuels contain lower concentrations of polar aromatic deposit precursors as compared to the LCO-doped diesel fuels examined by Hardy and Wechter.[1] Thus, the observed "better" storage stability observed is understandable. However, the absence of EIP mass in the old fuel (2827) suggests that years of ambient storage could have significantly depleted the concentration of high molecular weight deposit precursors, which is observed as a lack of EIP mass.

That thermal stressing significantly increases fuel EIP mass (Table 2, experiments 5–8) and at times changes the SMORS volumes is consistent with the SMORS hypothesis: oxidative stress transforms reactive fuel monomeric polar compounds into low molecular weight SMORS followed by conversion into higher molecular weight SMORS, which can be isolated as EIP. That thermal stressing all of the fuels results in a narrow, but at times statistically significant, difference in EIP mass for all four fuels suggests that EIP mass may be limited by both fuel solubility and the concentration of deposit precursors. Finally, Table 2 suggests that there is no relationship between SMORS volume and EIP mass.

Figures 1–3 contain data additionally testing the SMORS hypothesis. In Figure 1 are results from adding fresh polar deposit precursors to the old jet fuel (2827) followed by tubing bomb stress and fuel EIP mass determination; three different concentrations of a mixture of polar compounds were doped into the fuel, 50, 100, and 200 ppm total polars. The polar dopants were a mixture of commercially available phenol, 3-methylphenol, indole, 2-methylindole, and carbazole. To our knowledge, these are the first data directly linking specific polar aromatic compounds to EIP formation, the proposed deposit precursor.[1] The reason for the large error spread in EIP mass for the experiment with 200 ppm of polars doped into the fuel is unknown.[9] In Figure 2 is a comparison of mean thermal

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(9) It is possible that the scatter in the EIP values in the case of addition of the 200 ppm of total polar dopant is a result of not sufficiently controlling the evaporation of methanol (and other fuel components) during the SMORS isolation step. A preliminary examination of a jet fuel-derived SMORS sample by ^{1}H NMR is consistent with a high concentration of paraffinic material being present. This observation suggests the possibility of the paraffin concentration of the SMORS sample becoming significantly altered during rotary evaporation if these conditions are not carefully monitored. Such a scenario could affect EIP yield in the subsequent paraffin-induced precipitation step (see Experimental Section).
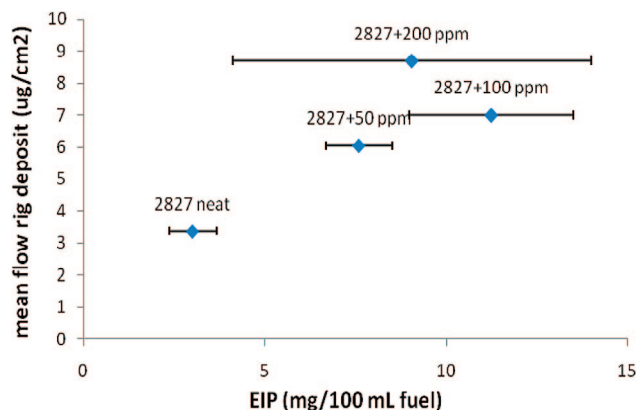

Figure 2. Correlation between mean tube thermal oxidative deposit, determined with the PSU flowing reactor at 350 °C, and EIP mass produced by tubing bomb stress for 2 h at 250 °C under 150 psi air. The neat jet fuel (2827) was doped with three different concentrations of polar aromatic compounds to yield total polar concentrations of 50, 100, and 200 ppm. Each point is the result of only a single flow rig experiment and the average of two EIP determinations.
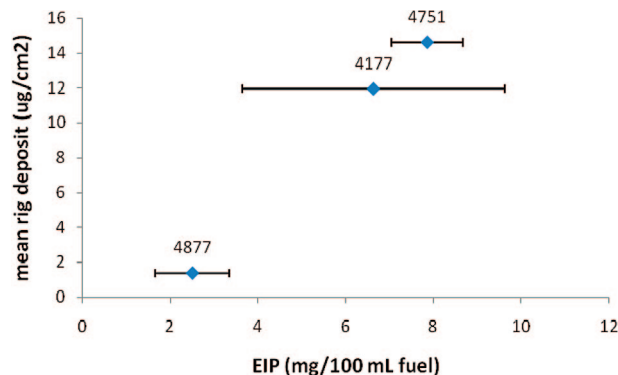

Figure 3. Correlation between three different jet fuels for mean thermal oxidative deposit, determined with the PSU flowing reactor at 550 °C, and EIP mass produced by the same fuels with tubing bomb stress for 2 h at 250 °C under 150 psi air. Each point is the result of only a single flow rig experiment and the average of two EIP determinations.

oxidative deposit for polar compound doped 2827 jet fuel, determined in the PSU flowing reactor at 350 °C, and tubing bomb stressed fuel EIP mass. Figure 3 compares tubing bomb stressed fuel EIP mass and mean thermal oxidative deposit at 550 °C for the three "fresh" jet fuels. On balance, all of these data suggest there are correlations between the concentration of the doped fuel polar compounds, stressed fuel EIP mass, and mean jet fuel thermal oxidative deposition.

Wechter and Hardy[7] have reported similar correlations between EIP mass and oxidative deposit, determined by ASTM D 5304, for refinery fresh diesel fuels doped with unhydrotreated LCO. All of these observations are consistent with the hypothesis that the chemistry of thermal oxidative deposit formation, in both jet and diesel fuels, is similar.[2] In addition, D 5304 (i.e., deposit formation after 16 h at 90 °C and 100 psig oxygen overpressure) has been accepted as the method of choice for the U.S. Navy for estimating the long-term storage stability of diesel fuels.[10] Therefore, it is likely that the chemistry of oxidative fuel deposit formation over a wide temperature range, from ambient storage through 550 °C, is similar in both jet and diesel fuels. However, it is likely that the rate constants for the various mechanistic steps for deposit formation change with

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(10) Hardy, D. R.; Hazlett, R. N.; Beal, E. J.; Burnett, J. C. *Energy Fuels* **1989**, *3*, 20–24.
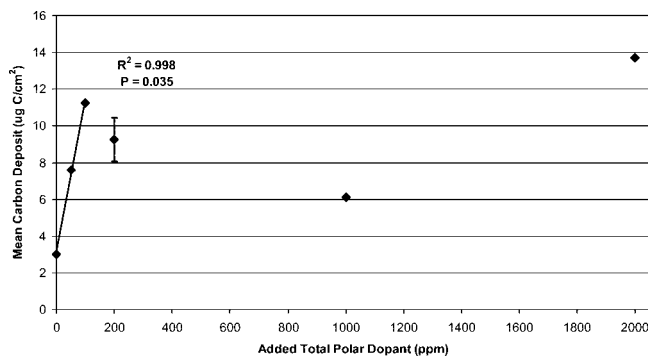
Figure 4. Comparison of mean tube thermal oxidative deposit and total polar compound dopant concentration in POSF-2827. Mean thermal oxidative deposit amounts were determined in the PSU flowing reactor @ 350 °C. Each point is a single run except for the 200 ppm polar doped run, which is the average of three separate runs.

temperature. This phenomenon may cause some unusual observations with respect to temperature and thermal oxidative deposition as found in the next Article in this issue.

An unusual observation is also noted in Figure 4 where mean flow reactor thermal oxidative deposits are plotted as a function of total polar dopant concentrations added to fuel 2827. All points in Figure 4 are for single runs except the 200 ppm case, which is reported as the mean of three runs. Figure 4 suggests that there is a change in the mechanism of deposit formation between 100 and 200 ppm added polars. With up to 100 ppm of added polars, thermal oxidative deposit is found to linearly correlate in a statistically significant manner. However, at concentrations of greater than 100 ppm, total polar dopants thermal oxidative deposit is not found to be linearly correlated. It is not clear whether this behavior is unique to fuel 2827 or if this is a general observation when the selected polar dopants are used in any fuel. It is important to note that in part 1 of this series[3] thermal oxidative deposit formation was approximately linear up to approximate 1000 ppm total indigenous polars. However, it is also important to note that the nature of the indigenous polars in the examined fuels was more diverse than the dopants used here, which were simple phenol and indole/carbazole derivatives.

There are at least two separate mechanistic possibilities that can account for the low levels of oxidative surface deposit observed with fuel 2827 doped with greater than 100 ppm total polars (Figure 4). The first possibility is that the fuel has sufficient indigenous dispersancy to slow deposit agglomerization, which minimizes surface deposit formation. Such a possibility can be experimentally tested because the dispersed polar deposit could likely be isolated from the oxidatively stressed fuel as EIP mass. To test this hypothesis, the EIP mass was determined after a flowing reactor oxidative stress of fuel 2827 with 2000 ppm of total polars dopant added. This experiment produced a mean tube deposit of 13.7 ug C/cm^2 (see Figure 4) with a post-stress EIP mass of only 1.8 mg/100 mL fuel (data not shown) as compared to a pre-stress value of zero (Table 2, experiment 4). This level of EIP mass is not consistent with the hypothesis of polar doped 2827 having a high level of dispersancy, which limits deposit agglomeration.

We have previously proposed that electron-rich aromatic molecules such as pyrroles,[11,12] indoles,[13] and carbazoles can be thermally promoted to react directly with molecular oxygen.[14−16] It is conceivable that such chemistry could ultimately lead to production of a high concentration of peroxyl radicals. Under such oxidative stress conditions, it is likely that paraffin peroxyl radical termination reactions could predominate

Table 3. Examination of the Correlation of Jet Fuel Smoke Point and the Rate of Thermal Oxidative Deposit Formation in the Presence or Absence of FT Blending for POSF-3658 with Tubing Bomb Stress @ 350 °C and 150 psi of Oxygen

expt. no.	FT addition	stress time (min)	m_{solids} (mg)	smoke point (mm)
1	no	0	0.0	17.5
2	no	2	12.5	17.5
3	no	5	42.1	17.7
4	no	10	35.2	17.3
5	yes	0	0.0	27.8
6	yes	2	12.0	28.8
7	yes	5	38.2	29.3
8	yes	10	38.3	28.8

with EIP and surface deposits being limited. Such termination reactions are expected to yield paraffin alcohols and carbonyl derivatives. However, much additional work is required to illuminate this possibility.

Next, the relationship between jet fuel thermal oxidative stability and soot formation was explored.[17] It is known from previous work that fuel 3658 contains a high concentration of polar aromatic compounds and that it has been stored for many years under ambient storage conditions.[4] We reasoned that this fuel should contain high molecular weight SMORS (i.e., a high EIP mass). Unfortunately, we did not have enough fuel to directly test this hypothesis. However, this hypothesis was confirmed in the following indirect manner. The smoke point was determined for all of the samples reported in Table 3. The fact that the unstressed fuel sample (Table 3, experiment 1) had a failing smoke point of 17.5 (military jet fuel specifications require a 19 minimum) is consistent with the following scenario. Fuel 3658 was received by USAF with a smoke point ≥19 many years ago and formed high molecular weight SMORS upon prolonged ambient storage. We also suggest that high molecular weight SMORS are the origin of the low smoke point for fuel 3658. The constant smoke point observed in Table 3 (experiments 1−4) while stressing fuel 3658 without FT blending is consistent with minimal change in fuel high molecular weight SMORS concentration during the experiment. Presumably, the fuel's indigenous polar compounds are oxidatively converted first into low molecular weight SMORS and then into higher molecular weight SMORS (i.e., EIP) at the same rate that EIP is converted into deposit.

In Table 4 is reported another study examining the hypothesis of a correlation between jet fuel concentration of high molecular weight SMORS and smoke point. It is evident that fuels 4177 and 4751 are the only unstressed fuels with EIP mass and thus likely contain high molecular weight SMORS formed upon ambient storage. Consistent with our hypothesis is that these two unstressed fuels have the lowest smoke point and thus the highest soot generating propensity in Table 4 (experiments 1−4). In a separate experiment, a high molecular weight SMORS sample was obtained in the following manner: after tubing bomb stress of 25 mL portions of all four fuels, the resulting SMORS were isolated and then combined to form a "composite" SMORS

(11) Beaver, B. D.; Treaster, E.; Kehlbesck, J. D.; Martin, G. S. *Energy Fuels* **1994**, *8*, 455–62.
(12) Beaver, B. D.; Teng, Y.; Guiriec, P.; Hapiot, P.; Neta, P. *J. Phys. Chem. A* **1998**, *102*, 6121–28.
(13) Beaver, B.; Gilmore, C.; Veloski, G.; Sharief, V. *Energy Fuels* **1991**, *5*, 274–80.
(14) Beaver, B. *Fuel Sci. Technol. Int.* **1991**, *9*, 1287–335.
(15) Beaver, B.; Gilmore, C. *Fuel Sci. Technol. Int.* **1991**, *9*, 811–23.
(16) Beaver, B. D.; Hazlett, R. N.; Cooney, J. V.; Watkins, J. M., Jr. *Fuel Sci. Technol. Int.* **1988**, *6*, 131–50.
(17) It is known that generally smoke point is an excellent indicator of a fuels sooting propensity. See: Yang, Y.; Boehman, A. L.; Santoro, R. J. *Combust. Flame* **2007**, *149*, 191–205.

Table 4. Effect of Pre- and Post-Stress SMORS[a] Concentration upon Jet Fuel Smoke Point

expt. no.	jet fuel POSF	pre-stress SMORS content (mL/100 mL fuel) ± standard deviation	EIP (mg/100 mL fuel) ± standard deviation	smoke point (mm)
1	4177	4.9 ± 0.1	0.41 ± 0.01	22.7
2	4751	4.9[b]	0.1[b]	24.0
3	4877	5.0 ± 0.1	0.0	25.2
4	2827	5.6 ± 0.1	0.0	24.5
5	4177	plus 3 mL post-stress SMORS	not determined	20.3
6	4751	plus 3 mL post-stress SMORS	not determined	21.6
7	4877	plus 3 mL post-stress SMORS	not determined	23.0
8	2827	plus 3 mL post-stress SMORS	not determined	21.6

[a] SMORS were isolated from fuel's stressed in tubing bombs at 130 °C for 3 h and 100 psi of air. [b] Only one determination.

sample. A 3 mL portion of the combined SMORS sample, a post-stress SMORS sample, was added to a 20 mL sample of each fuel followed by smoke point determination. Table 4 (experiments 5−8) very clearly shows an inverse relationship between smoke point and high molecular weight SMORS concentration (i.e., post-stress SMORS).

Conclusions

The major practical implication of this research is that there is likely a significant drop in jet fuel smoke point prior to combustion due to thermal oxidative degradation. This observation is consistent with the poor air quality, in terms of particulate matter (PM), generally observed at busy commercial airports. It is likely that inbound aircraft are the major source of air particulates because jet fuel thermal oxidative stress is greatest during landing.[18] Fortunately, Table 3 also contains data that suggest a possible future solution to this problem. When fuel 3658 is blended with a Fischer−Tropsch (FT) jet fuel to make a 1/1 volume blend, a significant increase in smoke point is observed (i.e., 10 mm, in experiments 5−8). This observation is consistent with dilution of high molecular weight SMORS by the FT blending component improving the fuel smoke point. Interestingly, comparing neat 3658 with its FT blend suggests that after 5 min of tubing bomb stress similar amounts of thermal oxidative deposit are generated (i.e., Table 3, experiment 3 vs 7). This is consistent with the FT blend being a poorer solvent for high molecular weight SMORS. In addition, the smoke point of the FT blend improves by ∼1.5 mm (experiment 5 vs 7). These observations suggest that the FT "diluted" fuel is losing high molecular weight SMORS faster than they are produced under the stress conditions. However, at 10 min of stress (i.e., experiment 8), the observed decline in the fuel's smoke point is consistent with the fuel's high molecular weight SMORS concentration increasing due to increasing thermal stress.

Finally, we have established that the SMORS concept developed by Hardy and Wechter[1] for estimating the storage stability of diesel fuels can also be applied to describe the thermal oxidative stability of jet fuels (Figures 1−3).

(18) Hazlett, R. N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; ASTM: Philadelphia, PA, 1991; p 9.