

## Evaluation of Organometallic Fuel Additives for Soot Suppression

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**Abstract:** In this work, we investigate the utility of the smoke lamp for evaluating the soot-reducing potential of additives, by comparing it to a more complex liquid-fed laminar diffusion flame. The additives, ferrocene (bis(cyclopentadienyl) iron- $\text{Fe}(\text{C}_5\text{H}_5)_2$ ), ruthenocene (bis(cyclopentadienyl)ruthenium- $\text{Ru}(\text{C}_5\text{H}_5)_2$ ), iron naphthenate (a 12% iron salt of naphthenic acid, which is a mixture of fatty carboxylic acids, some of which may include a cyclopentane ring), and MMT (Methylcyclopentadienyl manganese tricarbonyl- $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ ) are

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evaluated at various concentrations in the jet fuel JP-8. Although the smoke lamp is a simple, inexpensive, and widely-available test for evaluating the sooting potential of liquid fuels, it does not provide an effective measure of soot suppression by metal-containing additives. The drop-tube reactor more accurately captures the physical conditions and processes—droplet vaporization, ignition, and rich vs. lean operation—typically found in more complex systems. We find in the smoke lamp that ferrocene, and to a lesser degree ruthenocene, are effective soot suppressors when used in JP-8, and that their effectiveness increases with increasing concentration. In the smoke lamp, MMT and iron naphthenate have minimal effect. On the other hand, in the drop-tube reactor, all four additives are quite effective, especially at fuel lean conditions, where soot suppression reaches 90–95%. Under fuel-rich conditions, where in some cases the additives elevate the yield of soot aerosol slightly, we find a significant increase in the production of the soluble organic fraction of the aerosol, i.e., tar. In order to understand why the smoke lamp sometimes fails to indicate a soot suppressing potential (i.e., from MMT and iron naphthenate), soot samples were collected from a wick lamp burning ferrocene and iron naphthenate additives in JP-8. These samples, as well as several from the drop-tube reactor, were analyzed by X-Ray Fluorescence (XRF) in order to determine their metal content, and we find that the soot aerosol produced by the wick lamp using ferrocene-containing fuel had roughly 30 times the iron content of the soot aerosol produced by the wick lamp using iron-naphthenate-containing fuel. This difference in metal content is not found in samples produced in the drop-tube reactor. We conclude that the poor performance of iron naphthenate in the smoke lamp is likely the result poor vaporization of the additive from the wick, a consequence of its high molecular weight (average 465).

**Keywords:** Laminar diffusion flames; Soot and particulates

## INTRODUCTION

Reduction of particulate emission from combustion sources is motivated by concerns about the impact of soot particles on human health. Prompted by the strong correlations between the concentrations of particles with sizes under 2.5 micron (PM<sub>2.5</sub>) and cardiovascular and respiratory illness (Dockery et al., 1993), the U.S. Environmental Protection Agency has recently promulgated ambient air quality standards for PM<sub>2.5</sub>. Combustion sources are the primary contributor to fine particle emissions, particularly ultra fines (EPA, 1998; Watson and Chow, 1999; Oberdörster, 2001). In the past, major efforts have focused on mitigating the particulate emission from combustion sources such as coal-burning furnaces and diesel engines, with a focus on combustor design and exhaust treatment rather than on fuel chemistry/combustor interactions. However, a significant and economical impact can be achieved through the use of fuel additives.

The use of fuel additives is a cost-effective approach that has the potential of reducing PM<sub>2.5</sub> emissions. Howard and Kausch (1980)

provide an excellent review of the earlier literature on fuel additives for soot reduction with applications spanning oil-fired boilers, gas turbines, and diesel engines. The review focuses primarily on metal containing additives, identifying ferrocene (bis(cyclopentadienyl)iron- $\text{Fe}(\text{C}_5\text{H}_5)_2$ ) and MMT (Methyl-cyclopentadienyl manganese tricarbonyl- $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ ) as effective in a variety of practical combustion systems. However, they observe contradictory results for many additives designed to reduce soot, demonstrating that the temperature-oxidation history under which the additives act is critical to their effectiveness.

In applications involving liquid fuels, additives may suppress particulate emissions via four methods of action: 1) inhibit particle formation chemistry; 2) promote fuel atomization, which enhances vaporization and premixing; 3) increase ignition delay (flame lift-off distance), which allows more time for vaporization and premixing before the flame is established; and 4) catalytically enhance oxidation of carbon particles. It is this last effect that is presumed to be responsible for the effectiveness of the additives identified by Howard and Kausch (1980).

A commonly used tool for the evaluation of the sooting character of a liquid fuel (with or without additives) is the smoke lamp. In this device, the wick of a standardized lamp is raised until the flame begins to emit smoke; the height of the flame at this point is reported as the smoke point. In fact, this method has been adopted as the ASTM D 1322-97 standard—Standard Test Method for Smoke Point of Kerosene and Aviation Turbine Fuels. However, the question has been raised as to whether the smoke lamp is appropriate when the application has a more complex flame structure. For example, Himes et al. (1984) have shown that one can make fuel mixtures where the sooting tendency in the smoke lamp and in a simplified gas turbine combustor are quite different. Considering that the smoke lamp is unable to take advantage of two modes of additive action—atomization effects and ignition delay effects, its utility for evaluating additive effectiveness is questionable.

In this work, we investigate the utility of the smoke lamp for the evaluating the soot-reducing potential of additives, by comparing it to a more complex liquid-fed laminar diffusion flame. The latter experiment more accurately reproduces the physical conditions and processes of the flames in practical liquid-fueled systems, including the direct introduction of the liquid fuel (with or without additives) into the combustion environment, the ability to operate in both rich and lean conditions, and the potential impact of atomization and ignition delay. Our system, a laminar flowfield with a monodisperse droplet stream along its axis, is not identical to the turbulent reacting flows that are characteristic of practical combustors. However, the system is more well-defined and can be modeled relatively easily, in order to evaluate the validity of kinetic parameters for use in CFD simulations.

For the present purposes, we confine our study to organometallic additives that are believed to be oxidation catalysts, so that the smoke lamp is not *a priori* disadvantaged. We focus first on the effects of ferrocene, because it is well characterized and understood, especially in simple laboratory flame studies. After the recognition by Howard and Kausch (1980), and to a limited degree by Himes et al. (1984), of the effectiveness of ferrocene as a soot-suppressing additive, fundamental studies utilizing a premixed flat flame were undertaken by Ritrievi et al. (1987) and Feitleberg et al. (1993). Ritrievi et al. (1987) determined that, despite its previously-identified soot-reducing effect in practical systems, it in fact increases particle inception and yield in rich premixed flames. Feitleberg et al. (1993) found that in rich premixed flames, ferrocene produces a significant increase in yields of both insoluble particles and soluble organic material (tar), but no significant change in C<sub>1</sub>-C<sub>4</sub> chemistry, compared to undoped flames.

Additional fundamental studies of ferrocene turned to coannular diffusion flames. Bonczyk (1991) determined that in a diffusion flame, ferrocene catalyzes soot particle burnout, and suggests that it is based on the presence of solid iron oxide particles around which the soot nucleates. Zhang and Megaridis (1996) found that, as in rich premixed flames, ferrocene enhances particle inception in diffusion flames, and that iron particles are indeed incorporated within the carbon particle aggregates. Kasper and Siegmann (1998) confirm these findings, showing that in a diffusion flame doped with ferrocene, iron oxide particles nucleate before soot particles, and serve as nucleation points for the soot particles. They also confirm that the iron oxide acts as a catalyst to promote soot burnout at the flame tip. Hirawasa et al. (2004) return to a rich premixed flame, and show that the addition of ferrocene has little effect on C<sub>5</sub> or PAH chemistry, further confirming the role of iron particles as sites for soot nucleation.

In addition to ferrocene and the aforementioned MMT, two additives that can be considered variations on ferrocene are investigated here: ruthenocene (bis(cyclopentadienyl)ruthenium-Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>), a ruthenium based ferrocene-like compound; and iron naphthenate (a 12% iron salt of naphthenic acid, which is a mixture of fatty carboxylic acids, some of which may include a cyclopentane ring). Ruthenocene is of interest because its structure is the same as ferrocene, with a ruthenium atom in place of iron, therefore separating the effect of chemical structure from the identity of the metal. Iron naphthenate is of interest because it allows the incorporation of the iron into the fuel in a chemically different way.

In order to evaluate potential artifacts that might result from the use of the existing standard for the measurement of smoke point in aviation turbine fuels, these additives are evaluated, at various concentrations, in the jet fuel JP-8, using both a smoke lamp and a drop-tube reactor

supporting a liquid-fed laminar diffusion flame. The smoke lamp experiments are interpreted in the usual way, by measuring the flame height at which smoke is observed. In the drop-tube experiments, we measure soot aerosol yield by mass, normalized by fuel fed. Selected soot samples are also analyzed by X-Ray Fluorescence (XRF), in order to determine the metal content of soots produced from fuels containing different additives.

## EXPERIMENTAL

For this study, four metal-containing organic compounds are added to JP-8, a military aviation fuel similar to Jet-A, composed of 99% kerosene. The additives evaluated are ferrocene, ruthenocene, MMT, and iron naphthenate (80% in mineral spirits). Fuel-additive mixtures are prepared with metal-atom concentrations of 100, 300, 500 and 1000 ppm by weight for all solutions. Because the method of action of these additives is believed to be catalyzed oxidation by the metal atoms, we submit that the concentration of the metal atoms in the fuel mixture is the most appropriate normalization for the comparison and characterization of the effectiveness of these additives. However, in practical terms, one must keep in mind the total quantity of additive that will be used, and how it may affect other fuel properties, e.g., viscosity, in potentially adverse ways. Actual fuel blending is accomplished overnight on a magnetic stirrer.

### Evaluation by Smoke Lamp

The effectiveness of these additives in suppressing the soot emission from jet fuel is evaluated in two ways. Smoke lamp experiments are performed according to the ASTM D 1322-97 standard (Standard Test Method for Smoke Point of Kerosene and Aviation Turbine Fuels). The sample is burned in a closed wick lamp that is calibrated against pure hydrocarbon blends of known smoke point. The wick is raised continuously until smoke appears at the tip of the flame. The maximum flame height is determined where the smoke has not appeared yet. The measurement is repeated three times and the average value is reported. This test method provides a standard indication of the relative smoke producing properties of kerosene and aviation turbine fuels in a diffusion flame. Fuels with low smoke producing tendency have high smoke point values. Usually the more aromatic fuels tend to produce more soot. The apparatus is calibrated according to the standard using the following blends of known smoke point values: (a) 60% isooctane (2,2,4-trimethylpentane) + 40% toluene; (b) 100% isooctane. For our apparatus and location, a correction factor  $f = 0.98$  is obtained and applied to the observed smoke point

in all subsequent experiments. Measurements were repeatable on average to  $\pm 0.5$  mm.

### Evaluation by Drop-Tube Reactor

In addition to the evaluation of fuel additives by smoke lamp, we also employ a drop-tube reactor, where the fuel is injected directly into a hot, oxidizing environment and burned in a laminar diffusion flame. This system is meant to more accurately capture the physical conditions and processes of the flames in practical liquid-fueled systems, including the direct introduction of the liquid fuel (with or without additives) into the combustion environment, the ability to operate in both rich and lean conditions, and the potential for atomization and ignition delay to have an impact. The drop tube reactor, first utilized by Hanson (1982) and Rah (1984), consists of a fuel feed system, furnace, and sample collection system, as depicted in Figure 1 and described next.

*Feed System.* The liquid fuel feed system consists of an orifice droplet generator at the end of a water-cooled probe. Jet fuel is fed into a cavity that has a thin plate with a  $50\ \mu\text{m}$  orifice in the bottom. The incoming fuel is pressurized to 35 kPa, which forces the fuel through the orifice. Uniformly sized droplets (verified by inertial separation) of  $160\ \mu\text{m}$  diameter are generated at the orifice by liquid-column breakup, and then drop through the reaction zone. Mass flow controllers control the gas supply for the system. Reaction gas is fed into the top of the system. The gas flows downwards through the reactor around the feed probe, where it is preheated. Oxygen and nitrogen (alternatively helium) are individually controlled and mixed prior to entering the system. By varying the oxygen concentration, experiments may be performed under a variety of rich or lean conditions.

*Furnace.* The furnace, manufactured by Astro Industries, Inc, has an electrically heated reaction chamber consisting of a 5 cm diameter, 112 cm long quartz tube running through the center of the furnace and a graphite heating element surrounding the quartz tube. The softening temperature of the quartz tube, approximately  $1300^\circ\text{C}$ , limits the upper temperature of the furnace. The cavity between the quartz tube and the furnace shell is continuously purged with helium. A type-K thermocouple in this cavity near the exterior of the quartz tube is used to provide feedback to the heating controller, which is tied in with the OPTO-22 control system for the laboratory. Optical access is provided by two quartz windows, 1-cm wide by 30 cm long, located on opposite sides of the furnace

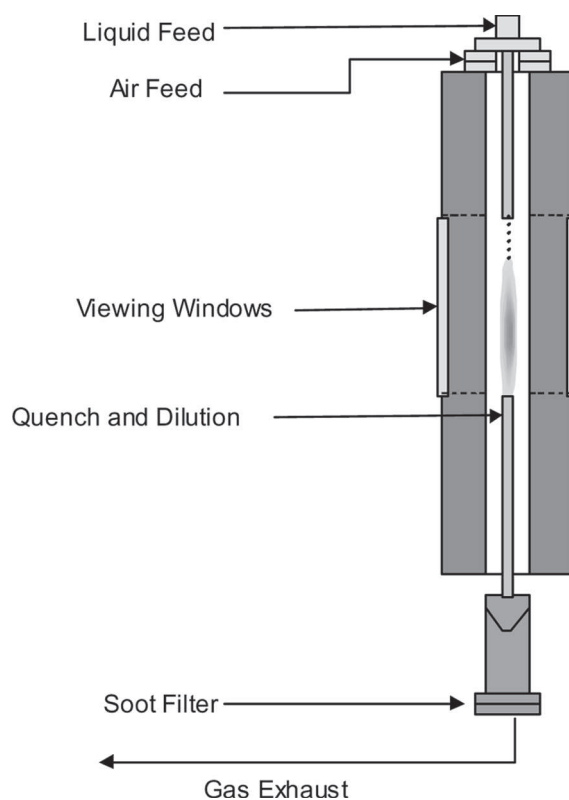


Figure 1. Schematic of the drop-tube furnace.

and symmetrically centered around the hot zone. The feed probe is positioned with the injector just below the top of the windows, allowing observation of fuel droplets as they are generated. Pressure in the reaction zone is controlled by a valve in the sampling/exhaust system, and is monitored and maintained at laboratory ambient pressure (0.84 kPa).

*Sample Collection System.* The sample collection system consists of a water-cooled probe and a sample filter. The sampling end of the probe extends upwards into the reactor, and the depth of insertion can be adjusted to vary the residence time of the experiment. Helium is injected radially through a sintered metal tube that makes up the innermost wall of the probe, and through additional holes at the tip of the probe to enhance quenching of the sample as it enters the probe. The soluble organic (tar) and particle phases of the soot aerosol are collected on a single 0.2  $\mu\text{m}$  Teflon filter (Millipore FGLP09050). For the purposes of evaluating JP-8 soot yield, the tar and particle phases are lumped together in

a single gravimetric measurement of the material on the filter. However, in some cases these phases may be separated by ultrasonic agitation in Dichloromethane (DCM) followed by filtration through a second 0.2  $\mu\text{m}$  Teflon filter, aided by vacuum. The material remaining on the second filter is deemed the insoluble particle phase, while the soluble material is deemed the tar phase. Several methods of post-filtration treatment for moisture removal were examined, including oven drying at 100°C and use of a desiccant chamber, but these methods did not significantly affect the final mass on the filter, indicating that moisture absorption is not significant.

#### Evaluation by X-ray Fluorescence

XRF is used to determine the metal content of selected soot aerosols produced by the smoke lamp and the drop-tube furnace. However, the smoke lamp has a relatively small wick and fuel reservoir, requiring long sampling times and frequent fuel replenishment. As an alternative, a larger wick lamp (Shor International "Simplicity Burner") is used to generate larger quantities of soot from a wick-based flame. It is not expected that the increase in scale affects vaporization behavior or combustion chemistry, as the lamp is otherwise functionally identical to the smoke lamp. Solutions of ferrocene and iron naphthenate, each 500 ppm iron in JP-8, are burned individually in the lamp, with the wick raised enough to produce a visible emission of soot. A 7.5 cm diameter chimney is placed over the lamp to stabilize the flame and direct the soot upward. A Teflon filter, the same variety used in the drop-tube furnace experiments, is placed in a filter holder approximately 30 cm above the flame, and a vacuum pump is used to pull the soot onto the filter. Samples are collected for 30 minutes, yielding 0.1–0.5 g soot aerosol. The filters are then placed in glass sample jars and are retained for later analysis.

Soot samples collected from both the wick lamp and the drop-tube furnace are analyzed by XRF. The energy-dispersive XRF measurements are performed with a Spectro X-lab 2000 instrument that is equipped with a Bragg-polarized excitation source. Because the plane-polarized photons may not scatter into the plane of polarization, the amount of Compton and coherent scattered radiation seen by a detector when using a Bragg-polarized source in a Cartesian geometry is greatly reduced. The full-width-half-maximum energy resolution of the detector used in these measurements is 135 eV for the 5.90 keV Mn  $K_{\alpha}$  X-ray. The XRF measurements are made using a combination of three excitation targets with a Pd anode; molybdenum for Cr–Y and Hf–Th (35 kV, 4.4 mA), aluminum oxide for Zr–Nd (52 kV, 5.7 mA), and highly oriented pyrolytic graphite for Na–V (15 kV, 13 mA).

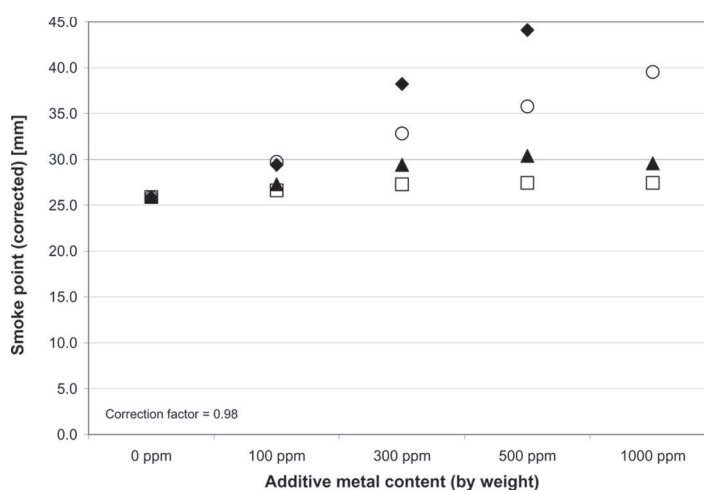


The areal concentrations in the thin samples are determined using the Lucas-Tooth, Price method. The method is calibrated using over sixty thin-film standards from MicroMatter, Inc. (Seattle, WA). For the thick-target XRF analysis, the samples were prepared for XRF analysis by mixing approximately 2 grams of finely ground sample with approximately 0.5 grams of X-ray Mix (Chemplex) in a virgin polycarbonate vial for 15 minutes on a mixer mill. The resulting mixture was then pressed into a 32-mm diameter pellet. The concentrations were determined using a combination of the Compton and fundamental parameters models. The thick-target XRF method was calibrated with over 70 pressed-pellets of standard reference materials.

## RESULTS AND DISCUSSION

### Smoke Lamp

Figure 2 shows the results from a series of tests, using the smoke lamp, of these additives in JP-8 at several concentrations. For ferrocene we observe a generally linear trend of increasing smoke point (decreasing sooting tendency) with increasing concentration, in agreement with the previous studies of ferrocene. The smoke point of the 1000 ppm Fe in JP-8 solution is over the limit of the apparatus and was therefore not measured. Ruthenocene increases the smoke point substantially at all



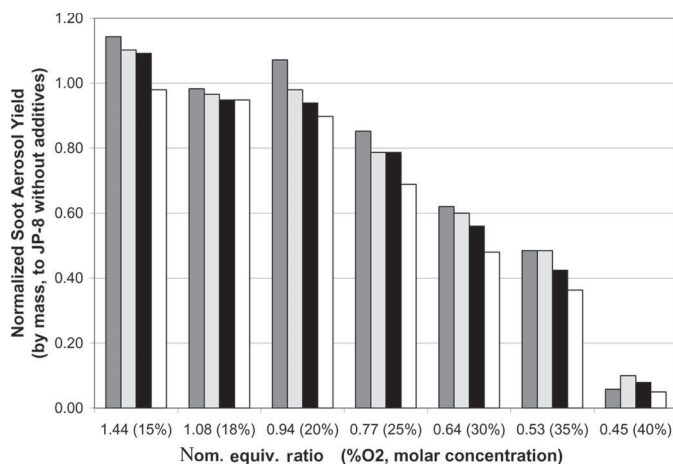
**Figure 2.** Effect of additives in JP-8 on the smoke point.  $\blacklozenge$  Ferrocene,  $\circ$  Ruthenocene,  $\blacktriangle$  MMT,  $\square$  Iron Naphthenate. Data from Palotas et al. (2003).

concentrations, although to a lesser extent than ferrocene. MMT and iron naphthenate have small but detectable effects. (The symbol size in the figure corresponds to the average repeatability of these measurements.) The fact that MMT and iron naphthenate affect the smoke point to a much lesser extent, although they are reported in the literature as effective additives, indicates that their effectiveness is not captured by the smoke lamp. The fact that iron introduced as a naphthenate does not raise the smoke point to a similar degree as in ferrocene emphasizes the importance of the additive's chemical or physical properties. Similarly, the fact that the other proven additive, MMT, is also substantially less effective than ferrocene in the smoke lamp, indicates that the smoke lamp does not reproduce the combustion conditions that allow the additive to function effectively. The closest match to ferrocene is achieved by ruthenocene, suggesting that the similar structures or similar physical properties are responsible for these compounds' effectiveness in the smoke lamp.

The results from the smoke lamp can be considered somewhat anomalous. In particular, the poor performance of MMT is surprising given its effectiveness in more complex combustion configurations. It is also surprising that the results for the iron-containing additives are so divergent. In attempting to explain inconsistent results for additives in different combustion configurations, Howard and Kausch (1980) identify temperature-oxidation history as an important factor. In our study, we believe that the smoke lamp's use of a wick, an atypical fuel delivery method compared to most practical combustors, may inhibit the vaporization of some additives. To investigate this issue further, we perform two additional studies: evaluation of soot yields from flames fed by a simplified atomizer, and investigation of the metal content in the soot produced from a wick lamp using different additives.

### Drop-Tube Furnace

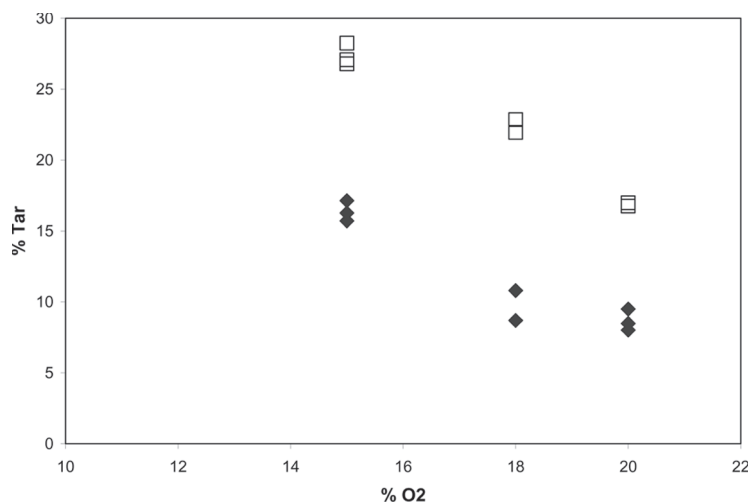
Figure 3 shows the results from the drop-tube furnace. Results are shown for a variety of oxygen concentrations, from 15% to 40% in  $N_2$ , and the corresponding nominal equivalence ratio (NER) based on the ratio of fuel and oxygen flowrates. The soot yields presented in Figure 3 are reported as a fraction of the yield from JP-8 alone at the same temperature and oxygen concentration. In this experimental configuration, we find that all four additives have a significant soot reduction effect, particularly under conditions where significant excess oxygen is available. Ferrocene is still generally the best performer, followed closely by ruthenocene, MMT, and iron naphthenate, in that order. At the highest oxygen concentration (40%: NER = 0.45), the performance of iron



**Figure 3.** Soot suppression in the drop-tube reactor (1100 C, 300 ppm metal additives). Dk Gray–Iron Naphthenate; Lt Gray–MMT; Black–Ruthenocene; White–Ferrocene.

naphthenate improves relative to the other additives, and is near that of ferrocene.

It is also important to note that under conditions where there is insufficient oxygen for soot burnout, the mass of material collected is essentially unchanged compared to untreated JP-8. Because ferrocene has previously been found to enhance particle inception (Zhang and Megaridis, 1996), we must consider whether this is also happening in our experiments. If the total aerosol yield is unchanged by the addition of an additive, and particle loading is increased, there must be a corresponding decrease in the tar phase of the aerosol. In order to examine this issue more closely, several samples are solvent extracted to determine the relative contribution of particles and tar to the overall aerosol yield. We find that the addition of ferrocene significantly increases the fraction of tar in the aerosol, as shown in Figure 4. In the range of 15–20% O<sub>2</sub>, the aerosols produced by JP-8 with ferrocene consistently have double the tar fraction found in those from JP-8 alone. In fact, we find that at 18% and 20% O<sub>2</sub>, the addition of ferrocene appears to double the yield of tar (per unit of fed fuel). On the other hand, at 15% and 18% O<sub>2</sub>, the addition of ferrocene decreases the yield of insoluble material (per unit fuel fed). These results would seem to contradict those of Hirasawa et al. (2004), who show that under (rich) premixed flame conditions, the addition of ferrocene appears to have virtually no effect on C<sub>5</sub> chemistry. They conclude that the enhanced soot formation (under rich conditions) is the result of particle nucleation induced by iron oxide



**Figure 4.** Tar fractions from low- $O_2$  samples. Solid—JP-8; Open—JP-8 with ferrocene (300 ppm iron).

nanoparticles. If this were the case in our system, we would not expect to see such significant and consistent increases in tar in the presence of ferrocene. Our finding on the other hand is in agreement with that of Feitleberg et al. (1993).

### X-Ray Fluorescence

In order to resolve the question of the performance of the additives in the smoke lamp vs. the drop tube furnace, samples of soot from both, using ferrocene and iron naphthenate additives, were subject to analysis by XRF. In soot from the smoke lamp using ferrocene-doped fuel, we find an iron distribution of  $19150 \text{ ng/cm}^2$ , corresponding to 1.2% by mass of the total material collected. On the other hand, in the soot from the smoke lamp using iron-naphthenate-doped fuel, we observe an iron distribution of  $649 \text{ ng/cm}^2$ , corresponding to 0.008% by mass of the total material collected. In other words, the soot aerosol produced by the smoke lamp using ferrocene-containing fuel had roughly 30 times the iron content (and 1/5 the total mass) of the soot aerosol produced by the smoke lamp using iron-naphthenate-containing fuel.

For the XRF analysis of soot from the drop-tube furnace, JP-8 with additives at 500 ppm metal content was burned in 30% and 40%  $O_2$ , concentrations where these additives have a large effect on soot aerosol yield. At 30%  $O_2$  we find that the soot aerosols from the ferrocene-doped and iron-naphthenate-doped fuels have iron contents of 0.083% and

0.078%, respectively. The difference can be accounted for by the somewhat greater degree of oxidation when ferrocene is used. At 40% O<sub>2</sub>, the iron content of the soot from iron-naphthenate-doped fuel rises to 0.360%, a result that is consistent with the much lower overall soot yields at this condition; the carbonaceous material undergoes a much greater degree of oxidation than at 30% O<sub>2</sub>, leaving behind a residue that is significantly enhanced in iron concentration.

Given that in both the smoke lamp and the drop tube furnace, the presence of iron in the soot aerosol is directly related to the effectiveness of the additive, we can conclude that the poor performance of iron naphthenate in the smoke lamp is the result of an insufficient amount of iron making its way into the gas phase. This is probably the result of the relatively higher molecular weight (average molecular weight 465), and corresponding lower volatility, of iron naphthenate compared to both ferrocene and JP-8.

## CONCLUSIONS

The standardized test for measuring the sooting potential of liquid fuels, the smoke lamp, does not provide an effective measure of soot suppression by metal-containing additives; it suggests that MMT, a well known soot suppressant, is weakly effective. It also shows that a given concentration of iron in the fuel has widely different effects when added as either ferrocene or iron naphthenate. The differences in effectiveness of the metal-containing additives measured in a smoke lamp is attributed to the low volatility of the iron naphthenate (average molecular weight 465), which is reflected by the iron content of the soot collected from a wick lamp. The soot aerosol produced by the ferrocene-containing fuel has roughly 30 times the iron content of the soot aerosol produced by the iron-naphthenate-containing fuel (with additive concentrations selected to yield the same iron content).

The deficiencies of the smoke lamp are overcome when using a heated drop tube reactor into which the fuel with and without additive is injected in a monodisperse liquid stream. Such a system has the advantages as an additive screening tool of atomizing and vaporizing the totality of liquid fuel and additives, operating fuel rich and fuel lean, and providing measures of soot yield, ignition delay, and post combustion oxidation. The laminar flow and well-characterized droplet size also provide a laminar diffusion flame that has the potential of providing fundamental information through modeling.

Tests were conducted with jet-fuel mixtures with the four additives added in amounts yielding metal concentrations ranging from 100 to 1000 ppm. These additives only result in soot reduction when excess oxygen is available ( $NER < 1$ ), substantiating the hypothesis that they

are oxidative catalysts, effective only when there is sufficient oxygen for soot burnout to be a factor. In addition, when oxygen concentrations are low ( $NER > 1$ ), the additives in some cases produce slightly more soot aerosol than the neat fuel, consistent with data previously reported in the literature on rich premixed flames.

Evaluation of the particle-tar fractionation under these conditions has revealed that ferrocene increases the tar fraction significantly. For the purposes of evaluating fuel additives, therefore, it appears that more representative results can be obtained using direct injection of the liquid fuel-additive blend into a combustion environment and that the drop tube reactor provides a better screening tool for additives than the standard smoke lamp test.

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