INVESTIGATION OF FUEL ADDITIVE EFFECTS ON Sooting FLAMES

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INVESTIGATION OF FUEL ADDITIVE EFFECTS ON SOOTING FLAMES

PROBLEM/OVERVIEW

Soot is a combustion product which increases plume visibility and, hence, aircraft vulnerability, and may cause reduced engine durability due to increased heat transfer to critical engine components. Indeed, this problem may be aggravated further in the near future with the inception of alternative fuels use, e.g. shale or coal derived, since the latter tend to soot more heavily than conventional fuels. At present, there is an insufficient fundamental understanding of the mechanisms governing soot formation and its control, which hinders the design and development of advanced engines. In the past, fuel additive use has been shown, qualitatively, to be effective in reducing soot. Additives have been used successfully with both laboratory-scale flames and practical combustors, and a wide range of gaseous, liquid and solid substances have been tested (Ref. 1). Additive use offers a simple and practical alternative to radical engine redesign to achieve soot suppression. The present difficulty is that the mechanisms responsible for the soot abating action of additives are very poorly understood, which hampers more effective additive selection and evaluation as well as more widespread additive utilization.

TECHNICAL OBJECTIVES

The objective of this research program is to initiate a comprehension of additive mechanisms and, thereby, develop specific analytical criteria for future additive selection. The specific objectives of the program are as follows:

1) For well-defined gaseous and liquid-fueled flames, measure the effect of additives selected from Ba, Ce, Fe, K and Mn inorganic and/or organic compounds on soot particulate size, concentration and volume fraction. Make these measurements with spatial precision throughout the zone of soot formation.

2) Determine the importance of parameters such as flame temperature and fuel type on the soot altering properties of the additives selected.

3) In the seeded flame, identify the atomic, molecular or ionic states of additive derived species present. Throughout the flame zone, make absolute concentration measurements of one or more of the latter species, as appropriate. In addition, measure the concentrations of those flame species, e.g. the hydroxyl radical, which may be related to soot formation or oxidation and are perturbed by additive presence.
4) Use the above to identify the principal chemical or other processes responsible for fuel additive alteration of particulate properties resulting in soot abatement.

SCIENTIFIC APPROACH

In large part, past additive experiments have been intrusive in nature and/or restricted to postflame soot analysis. Although useful for comparing and cataloguing the effectiveness of various additives, such experiments offer little hope of clarifying soot suppressing mechanisms. To this end, it is necessary, as a very minimum, to measure the concentrations of soot, additive and additive derived species throughout the flame zone with spatial precision.

To achieve the program's objectives, an approach has been adopted which is a significant departure from that of earlier more qualitative and restrictive experiments, and offers more hope of clarifying the chemistry of additive soot suppression. In this approach, techniques for concentration and temperature measurement either presently in use or projected for use in the near term are in-situ and spatially precise. Specifically, the techniques include Mie scattering (Ref. 2), laser-induced fluorescence (Refs. 3,4), and laser-excited coherent anti-Stokes Raman scattering (CARS) (Ref. 5). These are appropriate, in the preceding order given, to measure soot particulate size and concentration, additive and unseeded flame species concentrations, and temperature. It is anticipated that measurements of this type, coupled with appropriate attention to the possible roles of fuel type and flame temperature, will aid significantly in seeking to clarify additive mechanisms.

Emphasis in this program is being given to Ba, Ce, Fe, K and Mn additives since the latter metals are known, qualitatively, to be effective soot suppressants. Measurements are being carried out for gaseous and liquid fuels to which are added, respectively, inorganic and organic compounds of the preceding metals.

CURRENT STATUS

Apparatus

The apparatus being used currently to make additive measurements is shown schematically in Fig. 1. With it there is the capability of making all the particulate, additive and additive related species measurements mentioned earlier. The apparatus in Fig. 1 is not immediately adaptable to flame temperature measurements via CARS. This is, however, not a significant difficulty since other facilities are available at UTRC which have been dedicated productively to temperature measurements via CARS for quite some time.

In Fig. 1, the 2x Nd:YAG laser operates pulsed and at a 532 nm wavelength. The laser functions both as a source for particulate light scat-
tering measurements at $\lambda_1 = 532$ nm, and also to excite a narrow linewidth tunable dye laser to operate at $\lambda_2 > 532$ nm. This dual function is achieved very simply by using a beam splitter, BS, to direct a fraction of the VAG laser output to the dye laser, while the remaining output bypasses the dye laser and goes directly to the flame above the burner, B. With the aid, then, of ordinary and dichroic mirrors, M, and D, respectively, as well as a lens L, focused collinear radiations impinge on the flame. The radiations at $\lambda_1 = 532$ nm and $\lambda_2 > 532$ nm are used for particulate light scattering and atomic/molecular laser-induced fluorescence measurements, respectively. For the particulate measurements, there are photomultipliers, PMT, located at 20 and 160$^\circ$ with respect to the incident laser beam direction. The PMTs are complemented by: apertures, A, to define the scattering angle as well as the sizes of the optical sample volume and viewing solid angle; polarization and narrow band optical filters, P, and F, respectively. Detection at 20 and 160$^\circ$ is used to measure particulate size, concentration and volume fraction (Refs. 6,7).

There is a third PMT in line with the laser axis and available for optical extinction measurements. It is frequently interchanged with an optical multichannel analyzer (OMA), subsequent to some modification of intervening optics, in order to make additive species optical emission measurements. The spectrometer in Fig. 1 along with the closely associated lenses, L, and prism, DP, are used principally to measure spectrally resolved laser-induced fluorescence intensities.

Gaseous Fuels

For gaseous fuels, particulate size, concentration and volume fraction have been measured, with and without additives present, in the laboratory-scale laminar ethylene/air diffusion flame shown in Fig. 2. The flame is sustained by a symmetric Wolfhard-Parker burner, and soot parameters have been determined throughout the flame zone for various salts of the previously referenced metals (Refs. 8,9). The particulate measurements have been supplemented by optical/spectroscopic emission measurements to identify the chemical states of additive derived flame species. Preliminary results have shown that dissimilar metals behave differently as additives and, hence, their discussion below is segregated.

Results are given in Figs. 3 and 4 for soot size and volume fraction respectively, at one point in the flame, for two different Ba compounds in varying concentration. The additive is contained in the emerging oxidant stream above the burner surface in the form of an atomized spray of water containing the salt at the molar concentrations given. The soot diameter is determined from the angular dissymmetry of laser light scattered at 20/160$^\circ$. Knowing the diameter, D, the concentration, N, is evaluated from the absolute scattered intensity at either 20 or 160$^\circ$. The volume fraction, $f_v$, in Fig. 4 is calculated from, $f_v = (\pi D^2/6)N$, and is normalized with respect to its value with water alone present, $f_v^*$. 

The diameter in Fig. 3 has a weak dependence on concentration. This contrasts with results of earlier alkali metal fuel additive work at UTRC
and with present results for a K compound described below. The sharp reduction in \((f_v/f_v^0)\) in Fig. 4 at higher molarities results principally from a decrease in \(N\) since, as pointed out, \(D\) remains relatively constant. As is evident in Figs. 3 and 4, the acetate and nitrite of Ba are equally effective as additives, thereby establishing the metal atom as the critical species. In fact, other Ba salts were evaluated with similar conclusions, and these data are summarized in Fig. 5. The slight differences in Fig. 5 between the different compounds for the parameters \(D\) and \((f_v/f_v^0)\) are within experimental error and, hence, the latter compounds are nearly identically effective. Also within experimental error, the diameters with and without additives present are not discernibly different at the given molar concentration.

In addition to particulate characterization at the measurement point appropriate to Figs. 3, 4 and 5, the additive derived species Ba, BaO and BaOH have been identified from their optical emission spectra as present at this point as well. Such identifications are essential to isolating the one or more additive related species responsible for soot suppression. In Fig. 6, observed spectra in the interval 5300 to 6100 Å (530 to 610 nm) are shown, from which it is possible unequivocally to identify the species Ba and BaO. The atomic line near 5900 Å (590 nm) results from the presence of Na as an impurity; the numbers in parentheses identify BaO vibration-to-vibration transitional bandheads. Other spectra have been observed in the interval of 7000 to 8000 Å (700 to 800 nm) and identified with BaOH emission.

Laser-induced fluorescence measurements of the preceding Ba species have not yet formally begun. This requires a significant change in the operating wavelength range of the dye laser, which although feasible has not yet been made. Instead, laser-induced fluorescence has been demonstrated for the monohydroxide of a metal very closely related to Ba, namely Sr, which has an excitation wavelength more accessible presently. Accordingly, it is anticipated and essentially confirmed that Ba measurements will indeed be possible.

There have been past speculations concerning the possible role of the hydroxyl radical, OH, in relation to Ba additive effectiveness. Alkaline earth metals, \(M\), are known to catalyze \(H\)-atom formation in flames through reactions of the type, \(M + 2H_2O \rightarrow M(OH)_2 + 2H\). In a flame, the \(H\) and OH are related through, \(H + H_2O \rightarrow H_2 + OH\). Accordingly, if one assumes that soot oxidation (burn-out) and, hence, abatement occurs through, \(C + OH + CO + (1/2)H_2\), then the synergistic roles of OH and \(M\) are evident. In view of the foregoing, some attention is and will be given in this program to OH. Low resolution emission spectra of OH observed for the referenced ethylene/air flame are shown in Fig. 7. Perturbation of the emission intensity in Fig. 7 has been observed for Ba salt additives; however, specific inferences regarding the synergism mentioned above are not possible until additional and more detailed data are acquired.
As pointed out, it is important to determine the effectiveness of an additive at various points in the flame. The spatial dependence of Ba additive effectiveness as a soot suppressant is given in Figs. 8 and 9. In Fig. 8, the measurement points are at the given heights above the burner lip and their locus lies along the flame periphery. The points in Fig. 9 are also at the given heights above the burner lip, but their locus is a vertical line passing through the center of the flame. The data in Figs. 8 and 9 demonstrate that Ba is most effective as a soot suppressant at points corresponding to relatively long residence times, and that for median positions, e.g. 23 and 28 mm, the effectiveness maximizes at the flame periphery in the vicinity of the main reaction zone.

Measurements have been made for K compounds as additives as well, where the flame studied, approach and specific measurements were nearly identical to those for Ba above. Results for a KNO₃ additive are given in Figs. 10 and 11. The data are for the flame edge at 18 mm height, and several aspects of these data are worthy of particular attention. First, K has a much more pronounced effect on size than does Ba. Second, at 18 mm measurement height, K is a strong soot suppressant whereas the Ba efficiency in Fig. 8 is clearly diminished from its peak at 38 mm. Finally, the K effectiveness occurs at molar concentrations which are very much smaller than those for Ba. Spatial data which have been gathered for K indicate a different behavior than for Ba, with, e.g., K effectiveness remaining relatively undiminished along the flame periphery in the direction of the burner lip. Based on the latter observation, the K mechanism of soot suppression appears to differ from that for Ba.

As mentioned, dissimilar metals may behave very differently as regards soot suppression. This is strikingly evident in Fig. 12 below where Fe is seen to be unlike both Ba and K as a fuel additive. Here, as was the case for Ba, (D/D⁰) is nearly unity; but unlike Ba and K, Fe is seen to enhance soot concentration and volume fraction. The precision of the data at 13 mm in Fig. 12 is, for the present, relatively poor and, hence, inferences regarding soot suppression at 13 mm or lower are not possible. Data with consequences similar to those in Fig. 12 for Fe(NO₃)₃ have been obtained for FeSO₄, Mn(NO₃)₂ and for 1, 1'-ferrocene dicarboxylic acid in 14% NH₄OH (ferrocene = dicyclopentadienyl iron).

**Liquid Fuels**

Preliminary measurements have been carried out to determine the effectiveness of fuel additives as soot suppressants in liquid fueled flames. Primary emphasis has been given to ferrocene as an additive in both wick and counterflow diffusion flames.

For the wick flame, the sooting which occurred for a 5/1 iso-octane/toluene fuel mixture without additives present was compared with the case in which ferrocene was added to the fuel in varying, small concentration. For 0.25% ferrocene by weight, a heavy soot plume was suppressed as deter-
mined by visual observation. In order to make this test more quantitative, optical extinction measurements were made at different heights in the flame. The light extinction decreased in the presence of ferrocene, albeit differently for different points in the flame, thereby confirming and extending the visual observation of soot suppression. Attempts were made to evaluate other substances closely related to ferrocene, but these were either not successful or resulted in soot suppressions less pronounced than for ferrocene itself. For example, 1,1'-ferrocene dicarboxylic acid was insoluble in the above fuel mixture, and hydroxymethyl ferrocene, although soluble, was significantly less effective than ferrocene.

For the liquid counterflow diffusion flame, fuel penetrated to and evaporated from the outer surface of a porous cylindrical shell. There the fuel was ignited in the presence of flowing shroud air creating a reasonably well-defined diffusion flame. The flame was laminar at and near the forward stagnation zone of the fuel/air counterflow but became increasingly turbulent higher up in the flame. In order to evaluate ferrocene effectiveness in this case, optical extinction measurements were made in the laminar zone for the above fuel mixture and ferrocene concentration; the latter zone alone lends itself to optical probing. These measurements did not yield any demonstrable ferrocene effectiveness. In order to verify that ferrocene or its derivatives were indeed present in the flame, particulate samples were collected in the postflame zone and analyzed for Fe presence by SIMS (secondary ion mass spectrometry). In this way, Fe was detected leading to two presently indistinguishable conclusions. The first is that additive effectiveness, if present, occurs for long residence times in turbulent zones not readily amenable to optical extinction or scattering measurement. The second is that the relatively cool cylinder surface hinders efficient evaporation of ferrocene. The latter ambiguity has determined that in this program future emphasis in the liquid fuels area will be given to wick flames.

Summary/Achievements

For gaseous fuels, the accomplishments to the present are as follows:

1) Detailed particulate measurements have been made for Ba, Fe and K salts added to an ethylene/air diffusion flame. Soot size, concentration and volume fraction have been determined throughout the flame zone with and without the above additives present, and very significant soot suppression has been measured for Ba and K.

2) The metal atoms in the above salts have been correlated conclusively with additive effectiveness.

3) Spatial mapping of particulates has demonstrated that dissimilar metals behave differently as additives, particularly as regards their effect on particulate size and volume fraction. This leads strongly to the conclusion that different metals may suppress soot via unrelated mechanisms.
4) For a Ba seeded flame, the species Ba, BaO and BaOH have been identified as present from their optical emission spectra. Laser-induced fluorescence has been demonstrated for a molecule closely related to BaOH. Finally, a perturbative effect of Ba on OH emission has been observed.

For liquid fuels, the accomplishments to the present are as follows:

1) Pronounced soot reduction has been demonstrated in a wick flame with ferrocene added to the fuel. This was confirmed by observing the changes in soot loading induced by the additive both visually and by diminished laser optical extinction.

2) There is preliminary evidence that the exact chemical nature of the additive compound may be more critical than was the case for metal salts in gaseous fueled flames.

NEAR FUTURE WORK

In consideration of the technical objectives and current status outlined above, immediate attention will be given to the following areas. For gaseous fuels, the concentrations of additive derived species in the flame will be measured via laser-induced fluorescence. Further attention will be given to clarifying the role of OH in relation to Ba additive effectiveness. In addition, the importance of fuel type and flame temperature on additive effectiveness will be determined. In the liquid fuels area, spatial mapping of ferrocene effectiveness for the wick flame will be carried out, and Ce will be evaluated similarly in view of its recently demonstrated effectiveness in practical combustors (Ref. 10). Optical emission measurements will be made to identify both Fe and Ce additive derived species.

REFERENCES


PUBLICATIONS


INTERACTIONS


2. P.A. Bonczyk was an invited participant in, "Oxidation Kinetics and Soot Formation," a research review held at NASA Lewis Research Center, Cleveland, Ohio, October 6, 1983.

3. P.A. Bonczyk gave the invited seminar, "In-Situ Laser Measurements of Additive Effects on Soot in Laboratory Diffusion Flames," to the Chemical Engineering Department, Yale Univ., November 17, 1983.

5. On April 5, 1984, P.A. Bonczyk made a presentation summarizing the status of research under the subject AFOSR contract to Mr. Anthony F. Klarman and associates at the Naval Air Propulsion Center, Trenton, N.J.


SOOT AND ADDITIVE MEASUREMENT SCHEMATIC

Figure 1

ETHYLENE/AIR DIFFUSION FLAME

Figure 2

SOOT SIZE DEPENDENCE ON ADDITIVE CONCENTRATION

Flame: Ethylene/air diffusion
Measurement height: 23 mm

Figure 3
SOOT VOLUME DEPENDENCE ON ADDITIVE CONCENTRATION

Flame: Ethylene/air diffusion
Measurement height: 23 mm

![Graph showing soot volume dependence on additive concentration.](image)

Figure 4

EFFECTIVENESS OF DISSIMILAR BARIUM ADDITIVE COMPOUNDS

Additive concentration: 0.1 Molar
Flame: Ethylene/air diffusion
Soot diameter without additive: 1664 Å

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<th>Additive compound</th>
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<td>Ba(CHO₂)₂, Barium Formate</td>
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Figure 5

BARIUM SEEDED ETHYLENE/AIR FLAME SPECTRA

![Graph showing barium seeded ethylene/air flame spectra.](image)

Figure 6
0-0 A-X OH EMISSION

![Graph showing intensity vs wavelength for O-O A-X OH emission.](image)

Figure 7

SPATIAL DEPENDENCE OF ADDITIVE EFFECTIVENESS

Flame: Ethylene/air diffusion
Measurement direction: Ascending flame edge
Additive: 0.2 M BaCl₂ · 2H₂O

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Figure 8

SPATIAL DEPENDENCE OF ADDITIVE EFFECTIVENESS

Flame: Ethylene/air diffusion
Measurement direction: Ascending flame center
Additive: 0.2 M BaCl₂ · 2H₂O

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Figure 9
SOOT SIZE DEPENDENCE ON ADDITIVE CONCENTRATION

Figure 10

SOOT VOLUME DEPENDENCE ON ADDITIVE CONCENTRATION

Figure 11

SPATIAL DEPENDENCE OF ADDITIVE EFFECTIVENESS

Figure 12
Experiments in progress are described which have as their objective the clarification of the mechanisms responsible for soot suppression in flames by fuel additives. Measurements have been carried out in small well-defined diffusion flames for both gaseous and liquid fuels. Data have been obtained for selected organic and inorganic compounds of Ba, Fe, K and Mn as additives. The experimental techniques either employed or projected for use in the near term are in-situ by virtue of their reliance on nonperturbing laser-optical diagnostics. These techniques are Mie scattering, laser-induced fluorescence and coherent anti-Stokes Raman scattering to measure soot size and concentration, additive and other species concentrations and flame temperature, respectively. For gaseous fuels, inorganic salts of the above metals have been evaluated as additives in an ethylene/air flame. Additive suppression of soot was demonstrated, and particulate size, concentration...
and volume fraction were measured throughout the flame. Significantly, additive effectiveness varied with measurement position, and dissimilar metals behaved differently with respect to their alteration of soot parameters. In addition to particulate measurements, Ba additive chemical states in the flame have been identified from their optical emission spectra, and laser-induced fluorescence measurement has been demonstrated for a molecule closely identified with one of the latter states. For liquid fuels, ferrocene (dicyclopentadienyl iron) has been evaluated as an additive in wick and cylindrical counterflow diffusion flames. Results for the counterflow flames were inconclusive, but for the wick very significant soot reduction was observed both visually and via optical extinction. For both gaseous and liquid fuels, future work will stress spatial mapping of soot and additive derived species concentrations as well as an assessment of the importance of fuel type and flame temperature on additive effectiveness.