

Title: Extinction of Cup-Burner Diffusion Flames by Catalytic and Inert Inhibitors

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EXTINCTION OF CUP-BURNER DIFFUSION FLAMES BY CATALYTIC AND INERT INHIBITORS

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SUMMARY

The first tests of super-effective flame inhibitors blended with CO₂ have been performed in methane-air co-flow diffusion flames. Although the organometallic agents used are typically one or two orders of magnitude more effective inhibitors than CF₃Br when evaluated in premixed and counterflow diffusion flames, they have been found to be surprisingly ineffective compared to CF₃Br in cup-burner flames. In order to understand the poor performance, the CO₂ volume fraction required for extinction was determined for a range of added catalytic inhibitor volume fraction. When added at low volume fraction, the agents TMT, Fe(CO)₅, and MMT, were effective at reducing the volume of CO₂ required for extinction, with a performance relative to CF₃Br of 2, 4, and 8, respectively. However, as the volume fraction of each metallic catalytic inhibitor was increased, the effectiveness diminished rapidly. The greatly reduced marginal effectiveness is believed to be caused by loss of active gas-phase species to condensed-phase particles. Laser scattering measurements in flames with Fe(CO)₅ / CO₂ blends detected particles both inside and outside (but not coincident with) the visible flame location. The peak scattering cross section for vertically polarized light was 220 times the value for room temperature air. For the metallic inhibitors, their effectiveness is believed to be reduced because of particle formation, followed by thermophoresis, which prevents the inhibiting species from reaching the relevant zone of the flame. The results indicate that the appropriate flame configuration for evaluating the effectiveness fire suppression agents must be carefully considered, since in some cases, different flame configurations can switch the relative performance of an agent by an order of magnitude.

1. INTRODUCTION

Finding replacements for the effective but ozone-destroying fire suppressant CF₃Br and related compounds is a continuing research challenge. Metal compounds have attracted attention because it has been found that some metals recombine radicals in the post-combustion region of premixed H₂/O₂ flames [Bulewicz and Padley, 1971] and that several metallic compounds are one to two orders of magnitude more effective than CF₃Br at reducing the burning velocity of premixed flames [Lask and Wagner, 1962; Bonne et al., 1962; Reinelt and Linteris, 1996; Linteris et al., 2000; Linteris et al., 2002]. If means could be found to incorporate such super-effective moieties in a practical fire suppressant (particularly for unoccupied spaces), very effective agents may be possible.

Premixed and counterflow diffusion flames have been used extensively for testing these agents since they provide easily measurable parameters which can be directly related to the effect of the agent on the overall reaction rate. For these super-effective agents, however, few detailed studies have been conducted in flames resembling fires. The present work remedies this deficiency by presenting results for addition of these highly effective agents to cup-burner flames. Not only do cup burners have flame structures that are a reasonable approximation to those in fires, but they are also widely used by the fire protection industry as a metric to assess fire suppressant performance[NFPA, 1999]. Hence, measurements of agent performance in cup burners have clear relevance to their eventual use. In the results described below, the catalytic agents are found to be surprisingly poor flame inhibitors in cup burners, relative to CF₃Br. Experimental results are presented which delineate the performance of these agents, and provide an initial explanation of their lack of effectiveness.

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2. BACKGROUND

The agents tetramethyltin ($\text{Sn}(\text{CH}_3)_4$, TMT), methylcyclopentadienylmanganese tricarbonyl ($\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, MMT), ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) and iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) have recently been studied in some detail [Rumminger et al., 1999; Linteris et al., 2000; Linteris et al., 2002]. Experiments and modeling of $\text{Fe}(\text{CO})_5$ have quantified its performance and explained its mechanism of inhibition for a variety of conditions [Rumminger et al., 1999; Rumminger and Linteris, 2000a; Rumminger and Linteris, 2000b]. For iron, the strong inhibition is believed to occur from a catalytic radical recombination cycle involving iron oxides and hydroxides: $\text{FeOH} + \text{H} \leftrightarrow \text{FeO} + \text{H}_2$; $\text{FeO} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2$; and $\text{Fe}(\text{OH})_2 + \text{H} \leftrightarrow \text{FeOH} + \text{H}_2\text{O}$, which yields the net reaction: $\text{H} + \text{H} \leftrightarrow \text{H}_2$. For manganese-containing inhibitors, the mechanism is believed to be similar (with Mn replacing Fe in the reaction sequence). At low volume fractions, $\text{Fe}(\text{CO})_5$ is about eighty times more effective than CF_3Br at reducing the burning velocity of premixed flames; however, at volume fractions above about $100 \mu\text{L/L}$ ¹, the marginal effectiveness of $\text{Fe}(\text{CO})_5$ is greatly reduced. This is believed to occur from condensation of the active iron-containing intermediates to particles [Rumminger and Linteris, 2000c]. In a similar fashion, MMT loses its effectiveness at about $300 \mu\text{L/L}$, and TMT, which is about three times as effective as CF_3Br in premixed flames, loses its marginal effectiveness at about $3000 \mu\text{L/L}$. Indeed, if added directly to a cup-burner flame alone, $\text{Fe}(\text{CO})_5$ is not expected to be a particularly effective suppressant because condensation of active iron-containing intermediates to particles limits their gas-phase volume fraction, restricting the potential of the gas-phase catalytic cycle. Any practical fire suppressant using these super-effective agents would require some method to overcome the loss of effectiveness.

One approach for overcoming the loss of effectiveness is to combine catalytic agents with inert compounds. In this case, the overall reaction rate is lowered in part through radical recombination by the catalytic agent, and in part through the lower temperature caused by the added diluent. This approach has been discussed in work since the 1950's [Lippincott and Tobin, 1953; Rosser et al., 1959; Rosser et al., 1963; Lott et al., 1996; Noto et al., 1998; Rumminger and Linteris, 2000b] which suggested that combinations of thermally acting and catalytic agents might prove beneficial. These predictions have been confirmed in various studies with premixed and counterflow diffusion flames inhibited by $\text{Fe}(\text{CO})_5$ [Reinelt and Linteris, 1996], ferrocene [Linteris et al., 2000], CF_3Br [Saso et al., 1999], phosphorus compounds [Macdonald et al., 2001], and alkali metals [Williams and Fleming, 2001]. Tests and calculations show that addition of an inert compound lowers the temperature and in some cases, enhances the performance of the catalytic agent [Linteris et al., 2000]. The goal is to harness the very high efficiency of the metal species at low volume fraction while keeping its concentration below that which causes condensation. Nonetheless, it is generally not known *a priori* if the combination of an inert agent with the catalytic agents will be effective in a particular flame configuration. For example, the lower temperature (because of the inert additive) can cause higher radical superequilibrium [Rumminger et al., 1999], increasing the catalytic effect, but may also modify the flame structure, providing larger residence times for particle formation [Rumminger and Linteris, 2000c].

Based on these encouraging results, extinction experiments of ferrocene together with an inert compound generated by a solid propellant gas generator (SPGG) have recently been conducted in an enclosure containing a spray flame [Fallis et al., 2000]. Unfortunately, the combination did not have the intended high efficiency. Notwithstanding, few carefully controlled tests have been performed in cup-burner flames for agents more effective than CF_3Br . In order to gain insight into reasons for the lack of effectiveness of the ferrocene/SPGG combination in suppressing the spray flame and to provide data in a low-strain diffusion flame similar to a fire, we performed experiments with catalytic metal-based inhibitors and CO_2 added to the air stream in a cup burner.

The approach adopted for assessing the effectiveness of the catalytic agents in extinguishing cup-burner flames is to determine how the CO_2 volume fraction at extinction changes in the presence of the catalytic inhibitor. This approach is conceptually the same as the classic oxygen index test used for assessing material flammability [Fenimore and Jones, 1966]. In that test, the oxygen volume fraction in the air stream at extinction (i.e. the oxygen index) is determined for solid, liquid, or gaseous fuels with chemical additives in either the fuel or oxidizer. In the present tests, CO_2 (rather than N_2) is added as the diluent to facilitate comparisons with existing experimental data for other configurations. Although previous studies have been performed with heptane and

¹ Note that $\mu\text{L/L}$ is equivalent to ppm by volume.

methanol as the fuel [Linteris and Chelliah, 2001], the present experiments use methane. A gaseous fuel allows an approximately constant flame size and heat release rate, preserving many properties of the flow field (unlike a liquid pool fuel, for which fuel supply rate varies with inhibitor addition). These methane-air flames with CO₂ are also essentially non-sooting, which is desirable since the metal additives would change the production rates of soot (and thus the radiant heat transfer) which would complicate interpretation of the results. The iron, tin, and manganese compounds were selected because there exists recent experimental data on their performance in premixed methane-air flames for comparison.

Previous experiments have measured particle properties in premixed and counterflow diffusion flames seeded with Fe(CO)₅, and shown that particle formation is well correlated with the loss of effectiveness. In order to assess the role of particle formation in the effectiveness of Fe(CO)₅ in cup-burner flames, we also report the results of laser scattering measurements to characterize the formation of particles in the 2-D region above the fuel cup.

3. EXPERIMENT

The cup burner, described previously [Hirst and Booth, 1977; Linteris and Gmurczyk, 1995], consists of a cylindrical glass cup (28 mm diameter) positioned inside a glass chimney (53.3 cm tall, 9.5 cm diameter). To provide uniform flow, 6 mm glass beads fill the base of the chimney, and 3 mm glass beads (with two 15.8 mesh/cm screens on top) fill the fuel cup. Gas flows were measured by mass flow controllers (Sierra 860¹) which were calibrated so that their uncertainty is 2 % of indicated flow. To determine the extinction condition, the desired amount of catalytic agent was added to the co-flowing air (held constant at 41.6 L/min), and CO₂ was added to the flow (in increments of < 1 % near extinction) until lift-off was observed. The test was repeated at least three times.

The organometallic inhibitors were added to the air stream using multi-stage saturators in controlled temperature baths. The Fe(CO)₅ and TMT used two-stage saturators of a design described previously [Rumminger and Linteris, 2000b], while the MMT used a three-stage saturator, with 50% larger stages, to insure saturation. A measured portion of the added CO₂ flowed as a carrier through each saturator. The volume fraction of the organometallic inhibitors in the air stream was calculated based on the measured air flow, measured carrier gas flow, and calculated vapor pressure of the agent at the bath temperature. The experimental vapor pressure data was obtained from refs. [Stull, 1947; Gilbert and Sulzmann, 1974; Patrick and Golden, 1984]. Since the vapor pressure of MMT is much lower than that of the other agents, the burner and lines were maintained at >(35.0 ± 0.5) °C before and during the tests to reduce the likelihood of MMT condensation. Tests to validate the assumption of agent saturation in the carrier gas have been described previously [Rumminger and Linteris, 2000b]. For bromine as the inhibitor, all flow tubes downstream of agent addition as well as the burner base were made of Teflon to avoid reaction. A computer-controlled syringe pump added the liquid Br₂ to a 2.1 m long tubing carrying the air and CO₂, and complete Br₂ evaporation was observed to occur within a tubing length of less than 1 m.

The fuel gas is methane (Matheson UHP, 99.9 %), and the air is house compressed air (filtered and dried) which is additionally cleaned by passing it through an 0.01 μm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. The chemicals used were Fe(CO)₅ (Aldrich), TMT (Alfa Aesar), MMT (Alfa Aesar), CH₃OH (Aldrich, 99.8 %), Br₂ (Aldrich, 99.5 %), CF₃Br (Great Lakes), N₂ (boil-off), and CO₂ (Airgas).

For the particle measurements, a 90° laser scattering system was used, as described in previous work [Rumminger and Linteris, 2000b; Rumminger and Linteris, 2002]. A 5W argon ion laser operating at 488 nm supplied the laser light to a single mode fiber which carried the beam to an optical table in a fume hood. To prevent laser light from scattering off of the cup-burner chimney walls, the round cup-burner chimney was cut off to a height 2 mm

¹ Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the procedure. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the intended use.

below the fuel cup rim and a second, square chimney with an additional co-flow of air enclosed the burner. A three-axis translator positioned the burner and chimney in the stationary optical path. The scattering measurements were made on horizontal paths across the flame at fixed heights above the fuel-cup rim. Tests with gases of known scattering cross section [Rudder and Bach, 1968] provided the calibration factors for the optical system.

An uncertainty analysis was performed, consisting of calculation of individual uncertainty components and root mean square summation of components. All uncertainties are reported as *expanded uncertainties*: $X \pm ku_c$, from a combined standard uncertainty (estimated standard deviation) u_c , and a coverage factor $k = 2$. Likewise, when reported, the relative uncertainty is ku_c/X . The expanded relative uncertainties for the experimentally determined quantities in this study are: CO₂ volume fraction, 4 %; inhibitor volume fraction for organometallics, CF₃Br, and Br₂: 5 %, 2.7 %, and 2.0 %, respectively.

4. RESULTS AND DISCUSSION

In the first tests, the amount of CO₂ required for extinction of the cup-burner flame was determined with Fe(CO)₅ added to either the air or methane stream. **Table 1** summarizes the results. The top line shows that for CO₂ alone, the volume fraction for extinction $X_{\text{CO}_2,\text{ext}}$ is (15.7 ± 0.6) . The next two lines show that addition of Fe(CO)₅ to the air stream at relatively high volume fractions (450 $\mu\text{L/L}$ or 924 $\mu\text{L/L}$) causes only a (9.6 ± 0.5) % or (13.5 ± 0.8) % reduction in $X_{\text{CO}_2,\text{ext}}$. If we add 1 % CH₄ to the air stream to change the flame location and hence the scalar dissipation rate, the reduction in $X_{\text{CO}_2,\text{ext}}$ with addition of 450 $\mu\text{L/L}$ of Fe(CO)₅ is slightly greater, but still only about (10.7 ± 0.6) %. Likewise, addition of Fe(CO)₅ to the fuel stream at either 450 $\mu\text{L/L}$ or 4500 $\mu\text{L/L}$ causes only a (1.3 ± 0.1) % or (2.6 ± 0.2) % reduction in the amount of CO₂ required for extinction. These results are completely unexpected since only 100 $\mu\text{L/L}$ of Fe(CO)₅ in a premixed flame halves the burning velocity [Linteris et al., 2000]. Hence, the higher volume fractions of Fe(CO)₅ added here would be expected to strongly influence $X_{\text{CO}_2,\text{ext}}$.

Table 1 : Extinction volume fraction of CO₂ $X_{\text{CO}_2,\text{ext}}$ in methane-air cup burner with and without various amounts of Fe(CO)₅ or CF₃Br added to the fuel or air stream (air flow =41.6 L/min).

Catalytic Inhibitor	X_{inh} ($\mu\text{L/L}$)	Inhibitor Location	$X_{\text{CO}_2,\text{ext}}$ (%)	% Reduction from Pure CO ₂
None	-	-	15.7 ± 0.6	-
Fe(CO) ₅	450 $\mu\text{L/L}$	in Air	14.1 ± 0.6	9.6 ± 0.5
“	924 $\mu\text{L/L}$	“ “	13.5 ± 0.5	13.5 ± 0.8
“	450 $\mu\text{L/L}$	in Air w/ 1% CH ₄	14.0 ± 0.6	10.7 ± 0.6
“	450 $\mu\text{L/L}$	in Fuel	15.4 ± 0.6	1.3 ± 0.1
“	4500 $\mu\text{L/L}$	“ “	15.2 ± 0.6	2.6 ± 0.2
CF ₃ Br	1.3 %	in Air	4.4 ± 0.2	72.0 ± 4.1
“	11. %	in Fuel	8.7 ± 0.3	44.2 ± 2.5

CF₃Br is also believed to be a strong catalytic radical scavenging agent. As a test of the validity of the present approach, X_{CO₂,ext} was determined with CF₃Br added, to either the fuel or air stream, at a volume fraction which would halve the burning velocity of a premixed flame. These results are shown at the bottom of **Table 1**. In contrast to the results with Fe(CO)₅, addition of CF₃Br to either stream has a large effect on X_{CO₂,ext}, a reduction by factor of two to three. Clearly, CF₃Br and Fe(CO)₅ behave differently in the cup burner with respect to their ability to reduce the CO₂ requirement for extinction.

The results in Table 1 may lead one to conclude that although Fe(CO)₅ is highly effective in premixed flames, it has little effect in cup-burner flames. Conducting cup-burner extinction tests with added CO₂ for a *continuous* range of concentrations of Fe(CO)₅ in the air stream, however, shows that Fe(CO)₅ does, in fact, inhibit the flame. **Figure 1** shows the volume fraction of CO₂ required for extinction as function of the initial volume fraction of the catalytic inhibitor in the air stream (prior to CO₂ addition). Data are presented for Fe(CO)₅, as well as for the organometallic agents TMT and MMT. For comparison, tests were also performed for Br₂ and CF₃Br. For extinction of these methane-air flames, pure CO₂ is required in the air stream at volume fraction of (15.7 ± 0.6) %, whereas CF₃Br, a catalytic agent, is required at (2.4 ± 0.1) %. Moreover, as **Figure 1** shows, adding CF₃Br at volume fractions below the extinction value greatly reduces the amount of CO₂ required for extinction. For example, adding half of the extinction value of CF₃Br reduces the amount of CO₂ required by 70 %. The curvature in the line for CF₃Br in **Figure 1** indicates that, as described previously [Lott et al., 1996], the combination of CF₃Br and CO₂ is synergistic; that is, when combined, less of each is required for extinction than one would expect based on a linear interpolation of the individual results.

Figure 2 shows the data for the organometallic agents in more detail, and indicates that at low volume fraction, the organometallic agents are actually *more* effective than CF₃Br. For the sequence CF₃Br, TMT, Fe(CO)₅, and MMT, the relative magnitude of the slopes of the curves (at low volume fraction) are 1, 2, 4, and 8, so that Fe(CO)₅ is about four times as effective as CF₃Br. While this performance is noteworthy, it is far less than was observed in premixed flames or counterflow diffusion flames, for which the benefit was one to two orders of magnitude for Fe(CO)₅ as compared to CF₃Br. Also, the relative performance of Fe(CO)₅ and MMT is switched, with Fe(CO)₅ about twice as effective as MMT in premixed flames, while the opposite is true for the present cup-burner flames. Especially apparent in **Figure 2** is that the curve for each of the three agents, TMT, Fe(CO)₅, and MMT, all have a decreasing slope as their volume fraction increases. This behavior is similar to that in premixed and diffusion flames in which the loss of effectiveness was believed to be due to condensation of active species.

In previous work it has been argued that to obtain good performance by the super-effective agents, it might be possible to add small, non-condensing amounts of several catalytic agents together with an inert agent [Rumminger and Linteris, 2000b]. We tested this claim by adding a blend of the three catalytic metals MMT, Fe(CO)₅, and TMT to the air stream and then finding X_{CO₂,ext}. The bottom curve in **Figure 2** shows X_{CO₂,ext} for such a blend. MMT, Fe(CO)₅, and TMT are present in the molar ratio 1:2.1:15.5, and the curve is plotted as a function of the MMT volume fraction. Note that at the test point of the highest volume fraction, the three agents are added at 200 μL/L, 420 μL/L, and 3100 μL/L, respectively. (These values were selected since the individual curve for each agent is roughly linear up to these volume fractions; i.e. they have not yet lost their marginal effectiveness). As shown, the agents do work together to reduce the amount of CO₂ required for extinction, and, up to the maximum volume fractions added, the blend does not drastically lose its effectiveness. Amazingly, with addition of *three* catalytic inhibitors, *each* at a volume fraction which would easily reduce the overall reaction rate in a premixed flame by a factor of four, and each at a volume fraction at which the agent alone is not believed to lead to condensation, the combination still reduces the amount of CO₂ required for extinction by only 25 %.

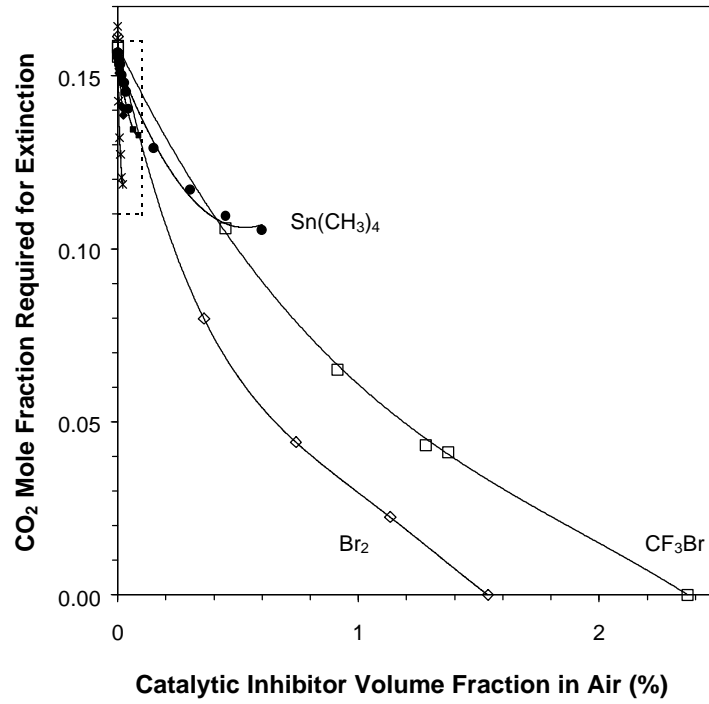


Figure 1 : Volume fraction of CO₂ required for methane-air cup-burner flame extinction as a function of catalytic inhibitor volume fraction, CF₃Br, Br₂, Fe(CO)₅, TMT, MMT, or a blend of the last three. The boxed region in the upper left is expanded in **Figure 2**.

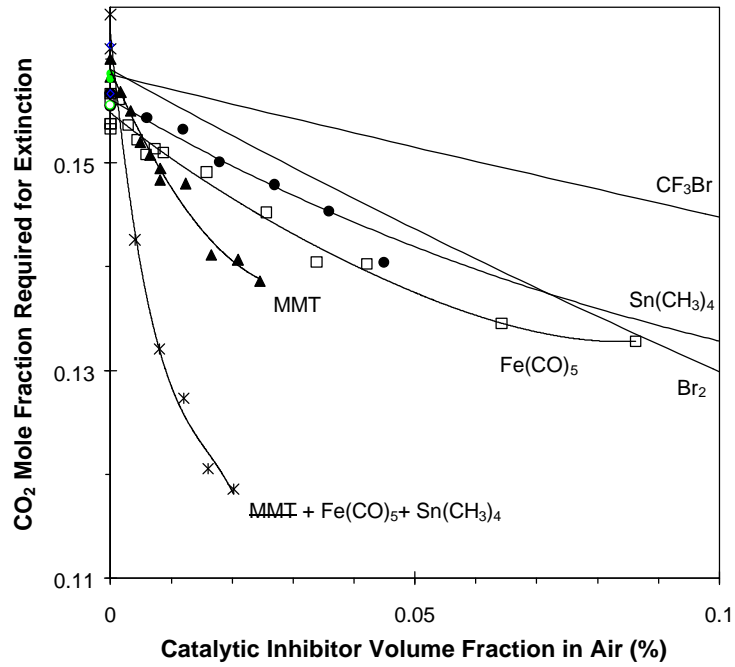


Figure 2 : Data of Fig. 1 with expanded x- and y-axis to show influence of metallic inhibitors in more detail.

Although the organometallic compounds *are* effective at reducing the amount of CO₂ required for cup burner extinction as compared to CF₃Br, their relative performance is drastically poorer than one would expect based on their behavior in premixed flames, and it is of interest to try to understand why. Two possible causes of the loss of effectiveness are the same as were discussed previously for premixed and counterflow diffusion flames, namely: 1.) saturation of the catalytic cycles and 2.) condensation of active gas-phase species. The saturation of the catalytic cycles is defined as a state in which the chain-carrying flame radicals have already been reduced to near equilibrium levels, so that additional catalytic inhibitor has no further benefit. This explanation of the lack of effectiveness is deemed to be unlikely, based on two results shown in **Figure 1** : those for Br₂, and those for the blend of MMT, Fe(CO)₅, and TMT. The experiments with Br₂ were designed to test the action of a catalytic agent without the confounding effects of condensation of inhibiting species. Further, it is an improvement over tests with CF₃Br for this purpose, since CF₃Br, because of its carbon content and use at relatively high volume fraction (>2 %), can have fuel-like behavior, moving the flame location, changing the scalar dissipation rate, and affecting the extinction condition. Bromine, added at half the volume fraction, and having no reducing species, does not have a fuel effect. As **Figure 1** shows, the curve for Br₂ is linearly decreasing in the region where the other curves are starting to flatten out—that is, it keeps working, implying radical depletion is not the cause of the loss of effectiveness of the metals (otherwise, Br₂ would stop working at about the same value of X_{CO₂,ext}). The data for the blend of metallic inhibitors shows a similar result. If each of the agents added alone was losing its effectiveness due to radical depletion, adding a second (or third) catalytic agent to the mix would not provide additional inhibition (since radicals are already reduced to their equilibrium levels). In the bottom curve of **Figure 2**, however, the blend of all three agents clearly shows additional inhibition over MMT alone, providing evidence against saturation of the radical scavenging by the metals.

Particle formation is more likely the cause of the degraded performance of the metal agents. Evidence to support this is that the approximate agent volume fraction for the loss of effectiveness is an order of magnitude higher for TMT (4000 μL/L) than for the iron or manganese (400 μL/L) (as occurs in premixed flames) [Linteris et al., 2002], which is consistent with the higher vapor pressure for the tin compounds. Also, the manner in which Fe-, Sn- and Mn-containing compounds lose their effectiveness in premixed flames [Linteris et al., 2002] is comparable to that indicated in **Figure 2**. Finally a visible outer annulus, apparently particles, was observed in all flames with added metals, and the blackbody radiation from that region increased with higher agent volume fraction.

To more accurately detect the particles, we conducted laser-scattering experiments in the cup-burner flames with and without added Fe(CO)₅. The flames had CO₂ volume fraction of 8 % in the oxidizer stream, and Fe(CO)₅ added to the air stream at 0 or 200 μL/L. **Figure 3** presents radial profiles of the scattering cross section (arbitrary units) at heights above the burner rim of (3, 6, 10, 15, and 20) mm. Also shown in the figure is the location of the peak visible emission, obtained from a digitized video image of the flame with 0 μL/L of Fe(CO)₅. Since the oxygen demand of the Fe(CO)₅ in the oxidizer stream at 200 μL/L is less than 2% of that of the methane, the flame location should not be significantly modified by presence of this fuel-like agent in the co-flow [Roper, 1977]. The peak scattering cross section in the figure corresponds to 4.74×10^{-6} 1/(cm-sr), which is 220 times higher than the value for air at laboratory conditions, clearly indicating particle formation. The particles are present both inside and outside, but not coincident with, the visible flame location. Flames without Fe(CO)₅ (not shown) had scattering cross sections attributable to only the hot and cold product and reactant gases.

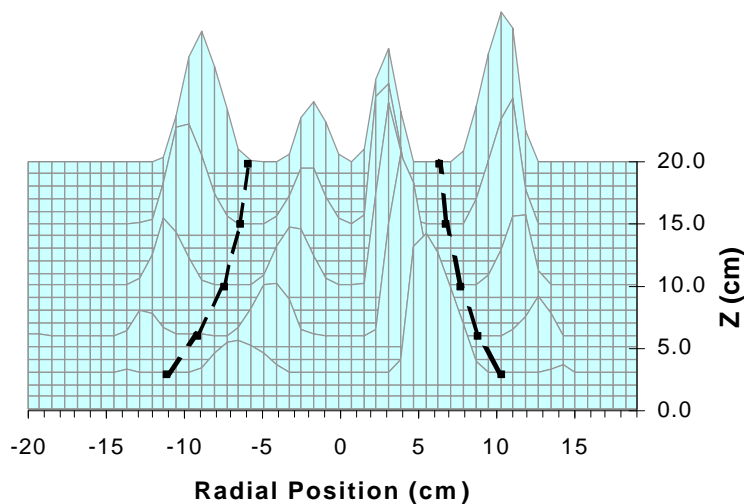


Figure 3 : Scattering cross section as a function of radial position in flame and height above cup-burner rim, with 200 $\mu\text{L/L}$ of $\text{Fe}(\text{CO})_5$ added to the air stream, and a CO_2 volume fraction of 8 %. Dotted lines show flame location from a digitized video image of the uninhibited flame.

In order to interpret the scattering results shown in **Figure 3**, it is useful to discuss previous results of particle measurements in both Bunsen-type premixed [Rumminger and Linteris, 2000b] and counterflow diffusion flames [Rumminger and Linteris, 2002] seeded with $\text{Fe}(\text{CO})_5$. A major finding of those studies was that the formation of particles leads to a loss of iron from active gas-phase inhibiting species to the condensed phase particles, which are much weaker flame inhibitors. If the characteristics of the flow field (including thermophoresis) allowed the particles to remove iron from the system, the active iron-containing inhibiting species could not reach the regions of high radical volume fraction, and $\text{Fe}(\text{CO})_5$ proved to be a poor inhibitor. The main factors found to affect the particle formation were the $\text{Fe}(\text{CO})_5$ loading and the residence time for condensation. At low enough volume fraction, the iron compounds were below their dew point at flame temperatures, so they remained effective in the gas phase. At higher volume fractions, particles were formed. Longer residence times were associated with larger particles and greater loss of effectiveness. The premixed flames had the shortest particle-formation residence times (on the order of 5 ms), and the peak scattering cross section for all of the flames tested with 200 $\mu\text{L/L}$ of added $\text{Fe}(\text{CO})_5$ was $1.6 \times 10^{-7} \text{ 1}/(\text{cm}\cdot\text{sr})$. Some of the counterflow diffusion flame configurations had much larger residence times (on the order of 50 ms), and also had much larger scattering cross sections, up to $4.7 \times 10^{-6} \text{ 1}/(\text{cm}\cdot\text{sr})$, which is about the same as the peak value in the present work. For those counterflow diffusion flames, virtually no flame inhibition was observed.

Since the present cup-burner flames have quite different flow fields than either premixed or counterflow diffusion flames, it is likely that the condensation behavior in them is different. From **Figure 3**, it seems likely that metal compounds added to the air stream are sequestered as particles which are then moved away from the relevant radical recombination zones of the flame before they can affect the flame chemistry. Thermophoretic forces can have a strong influence on particle trajectories in flames [Gomez and Rosner, 1993]. Recent attempts to seed co-flow diffusion flames with TiCl_4 to provide very small TiO_2 for laser imaging of the velocity field proved ineffective due to strong thermophoresis of the particles [Wanigarathne, 2001]. In the present flames, the flow streamlines tend to be nearly parallel to the flame boundary [Urban et al., 1998], whereas the thermophoretic forces will be tangential, and may force the particles away from the flame boundary, preventing the iron-containing inhibiting species from reaching the flame. Given the data in **Figure 3**, it seems reasonable to deduce that particle formation followed by thermophoresis act to keep the inhibiting iron-containing species away from the regions of the flame where radical scavenging is the strongest, causing the loss of effectiveness shown in **Figure 2**. Nonetheless, the location of the stabilization region of the cup burner flame most sensitive to chemical inhibition is not known. Detailed numerical modeling would be helpful for delineating the actual causes of flame extinction in the cup burner caused by radical scavenging agents.

5. CONCLUSIONS

The first data on the extinction characteristics of highly effective catalytic agents added with CO_2 to a cup burner flame of methane and air have been measured. Although such catalytic agents have previously been found to be very effective in premixed and counterflow diffusion flames, they are surprisingly ineffective in cup-burner flames. The experiments have shown that for reducing the amount of CO_2 required for extinction, the order of increasing performance is: CF_3Br , TMT, $\text{Fe}(\text{CO})_5$, and MMT. Hence, the relative performance of $\text{Fe}(\text{CO})_5$ and MMT are switched relative to premixed flames. Further, a combination of three organometallic catalytic agents, each at a volume fraction which should reduce the overall reaction rate by a factor of four, reduced the amount of CO_2 required for extinction by only 25 %, a result which was strikingly unexpected. At higher volume fractions, each of the metal-based agents experienced a loss of effectiveness which is reminiscent of their behavior in premixed flames. In contrast, the agent Br_2 was effective alone or in combination with CO_2 , with a performance improvement over CF_3Br of about a factor of two.

The loss of effectiveness of the organometallic agents is believed to be caused by particle formation. Laser light scattering measurements with 200 $\mu\text{L/L}$ of $\text{Fe}(\text{CO})_5$ in the air stream and CO_2 added at a volume fraction of 8 % indicate particles with a peak scattering cross section 220 times higher than from air. The particles occur inside and outside of (but not coincident with) the visible flame location. The reason for the lower effectiveness in these diffusion flames as compared to either premixed or counterflow diffusion flames is believed to be particle formation and thermophoresis, which cause a sequestering of the active gas-phase inhibiting compounds away from the stabilization region of the flame.

The relative performance of these very powerful flame inhibitors has been found to be highly dependent upon the type of flame configurations used for the tests. Further research is recommended to understand the regions of cup burner flames most affected by radical scavenging agents and their influence on flame detachment.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

- Bonne, U., Jost, W., and Wagner, H. G. (1962), "Iron Pentacarbonyl in Methane-Oxygen (or Air) Flames," *Fire Research Abstracts and Reviews*, 4, pp6-18.
- Bulewicz, E. M. and Padley, P. J. (1971), "Catalytic Effect of Metal Additives on Free Radical Recombination Rates in $H_2+O_2+N_2$ Flames," *Proceedings of the Combustion Institute*, 13, pp73-80.
- Fallis, S., Reed, R., Lu, Y.-C., Wierenga, P. H., and Holland, G. F. (2000), "Advanced Propellant/Additive Development for Fire Suppressing Gas Generators," *Halon Options Technical Working Conference*, pp361-370.
- Fenimore, C. P. and Jones, G. W. (1966), "Modes of Inhibiting Polymer Flammability," *Combustion and Flame*, 10, 3, pp295-301.
- Gilbert, A. G. and Sulzmann, K. G. P. (1974), "The Vapor Pressure of Iron Pentacarbonyl," *Journal of the Electrochemical Society*, 121, 6, 832.
- Gomez, A. and Rosner, D. E. (1993), "Thermophoretic Effects on Particles in Counterflow Laminar Diffusion Flames," *Combustion Science and Technology*, 89, pp335-362.
- Hirst, B. and Booth, K. (1977), "Measurement of Flame Extinguishing Concentrations," *Fire Technology*, 13, 4, 296.
- Lask, G. and Wagner, H. G. (1962), "Influence of Additives on the Velocity of Laminar Flames," *Proceedings of the Combustion Institute*, 8, pp432-438.
- Linteris, G. T. and Chelliah, H. K. (2001), "Powder-Matrix Systems for Safer Handling and Storage of Suppression Agents", National Institute of Standards and Technology, NISTIR 6766.
- Linteris, G. T. and Gmurczyk, G. W. (1995), in *Fire Suppression System Performance of Alternative Agents in Aircraft Engine and Dry Bay Laboratory Simulations* (R.G. Gann, Ed.), National Institute of Standards and Technology, Gaithersburg, MD, pp201-318.
- Linteris, G. T., Knyazev, K., and Babushok, V. (2002), "Inhibition of Premixed Methane Flames by Manganese and Tin Compounds," *Combustion and Flame*, 129, pp221-238.
- Linteris, G. T., Rumminger, M. D., Babushok, V., and Tsang, W. (2000), "Flame Inhibition by Ferrocene and Blends of Inert and Catalytic Agents," *Proceedings of the Combustion Institute*, 28, pp2965-2972.
- Lippincott, E. S. and Tobin, M. C. J. (1953), *Journal of the American Chemical Society*, 75, pp4141-4147.
- Lott, J. L., Christian, S. D., Sliepcevich, C. M., and Tucker, E. E. (1996), "Synergism Between Chemical and Physical Fire-Suppressant Agents," *Fire Technology*, 32, 3, pp260-271.
- Macdonald, M. A., Gouldin, F. C., and Fisher, E. M. (2001), "Temperature Dependence of Phosphorus-Based Flame Inhibition," *Combustion and Flame*, 124, 4, pp668-683.
- NFPA (1999), "Clean Agents Fire Extinguishing Systems", NFPA, 2001.
- Noto, T., Babushok, V., Hamins, A., and Tsang, W. (1998), "Inhibition effectiveness of halogenated compounds," *Combustion and Flame*, 112, 1-2, pp147-160.
- Patrick, R. and Golden, D. M. (1984), "Termolecular Reactions of Alkali-Metal Atoms With O_2 and OH ," *International Journal of Chemical Kinetics*, 16, 12, pp1567-1574.
- Reinelt, D. and Linteris, G. T. (1996), "Experimental Study of the Inhibition of Premixed and Diffusion Flames by Iron Pentacarbonyl," *Proceedings of the Combustion Institute*, 26, pp1421-1428.
- Roper, F. G. (1977), "The Prediction of Laminar Jet Diffusion Flame Sizes: Part I. Theoretical Model," *Combustion and Flame*, 29, pp219-226.
- Rosser, W. A., Inami, S. H., and Wise, H. (1959), "Study of the Mechanisms of Fire Extinguishment of Liquid Rocket Propellants", ASTIA Document No. AD 216355, WADC Technical Report 59-206.
- Rosser, W. A., Inami, S. H., and Wise, H. (1963), "The Effect of Metal Salts on Premixed Hydrocarbon-Air Flames," *Combustion and Flame*, 7, pp107-119.
- Rudder, R. R. and Bach, D. R. (1968), "Rayleigh Scattering of Ruby-Laser Light by Neutral Gases," *Journal of the Optical Society of America*, 58, 9, pp1260-1266.
- Rumminger, M. D. and Linteris, G. T. (2000a), "Numerical Modeling of Counterflow Diffusion Flames Inhibited by Iron Pentacarbonyl," *Fire Safety Science: Proc. of the Sixth Int. Symp.*, Int. Assoc. for Fire Safety Science, pp289-300.
- Rumminger, M. D. and Linteris, G. T. (2000b), "Inhibition of Premixed Carbon Monoxide-Hydrogen-Oxygen-Nitrogen Flames by Iron Pentacarbonyl," *Combustion and Flame*, 120, 4, pp451-464.
- Rumminger, M. D. and Linteris, G. T. (2000c), "The Role of Particles in the Inhibition of Premixed Flames by Iron Pentacarbonyl," *Combustion and Flame*, 123, 1-2, pp82-94.
- Rumminger, M. D. and Linteris, G. T. (2002), "The Role of Particles in the Inhibition of Counterflow Diffusion Flames by Iron Pentacarbonyl," *Combustion and Flame*, 128, 1/2, pp145-164.

- Rumminger, M. D., Reinelt, D., Babushok, V., and Linteris, G. T. (1999), "Numerical Study of the Inhibition of Premixed and Diffusion Flames by Iron Pentacarbonyl," *Combustion and Flame*, 116, 1-2, pp207-219.
- Saso, Y., Ogawa, Y., Saito, N., and Wang, H. (1999), "Binary CF_3Br - and CHF_3 -Inert Flame Suppressants: Effect of Temperature on the Flame Inhibition Effectiveness of CF_3Br and CHF_3 ," *Combustion and Flame*, 118, 3, pp489-499.
- Stull, D. R. (1947), "Vapor Pressure of Pure Substances Organic Compounds," *Ind. Eng. Chem.*, 39, pp517-540.
- Urban, D. L., Yuan, Z. G., Sunderland, P. B., Linteris, G. T., Voss, J. E., Lin, K. C., Dai, Z., Sun, K., and Faeth, G. M. (1998), "Structure and Soot Properties of Nonbuoyant Ethylene/Airlaminar Jet Diffusion Flames," *Aiaa Journal*, 36, 8, pp1346-1360.
- Wanigarathne, P. C. (2001), "Flame Suppression Studies with Particulates Containing Metallic Compounds", University of Virginia, MS Thesis.
- Williams, B. A. and Fleming, J. W. (2001), "On the suitability of CF_3Br as a benchmark for replacement fire suppressants.," *Halon Options Technical Working Conference*, pp144-154.