EXPERIMENTAL INVESTIGATION OF EXTINGUISHMENT OF LAMINAR DIFFUSION FLAMES BY THERMAL AGENTS

by

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INTRODUCTION

As part of the National effort to identify effective replacements for halon fire suppressants [1], NIST has been investigating whether highly effective thermal agents are feasible. Thermal agents are defined as those that obtain their effectiveness solely by heat extraction and dilution. Excluded from investigation are species that directly or indirectly disrupt the combustion chemistry such as halons, which derive much of their effectiveness by the release of bromine atoms that catalytically remove hydrogen atoms in the flame zone.

A NIST Internal Report is available describing the findings of the first year of this investigation [2]. A thorough search of NIST thermodynamic databases was performed to identify molecular species that might be particularly effective thermal agents. Detailed chemical kinetic modeling of laminar opposed jet diffusion flames was used to predict extinguishing concentrations and provide insights into extinguishment mechanisms. Methane flames burning in air diluted with the known thermal agents nitrogen (N_2), argon (Ar), helium (He), carbon dioxide (CO_2), and water (H_2O), as well as artificial surrogate agents, were considered. These findings were summarized during the 1999 HOTWC meeting [3]. The third part of the study was an analysis of the interaction of liquid droplets with surfaces in order to characterize the physical properties desirable for liquid agents.

The database search identified two chemicals that were predicted to be particularly effective at extracting heat from a flame zone. The first was methoxy-nonaflurobutane ($C_4F_9OCH_3$), also known as HFE7100, which was one of the highest rated thermal agents on both mass and molar bases. The boiling and freezing points are 334 and 138 K, respectively. Extinguishing molar concentrations in air for the gas were reported as 6.1% in a cup-burner test using heptane fuel* and in a "micro cup-burner" test burning butane [4]. No measurements of the effectiveness of this compound when released as a liquid were available.

The second compound identified was lactic acid ($CH_3C(OH)COOH$), which has an estimated boiling point of 455 K [2] and a melting point of 291 K. Clearly, this compound is not a potential candidate as a fire suppression agent due to its high boiling and melting points and caustic nature. However, based on its ability to extract heat, it is predicted to be nearly twice as effective on a mass basis as any of the other potential thermal agents considered, except water. Its ability to extract heat is predicted to be roughly 2/3 of that of water on a mass basis and 3.5 times greater on a molar basis. Since lactic acid is soluble in water, it is desirable to investigate the suppression characteristics of mixtures of these two polar liquids.

The detailed chemical kinetic modeling showed that the addition of N_2, CO_2, Ar, He, and H_2O to the oxidizer side of a methane flame lowered the calculated maximum flame temperature for given initial fuel and oxidizer flow velocities. Increasing flow velocities ultimately resulted in

*R.E. Tapscott, personal communication, February 1999: NMERI In-House Testing, June 2, 1997.

extinction of the flame. Both the flow velocities and maximum flame temperature at extinction decreased with increasing agent concentration. To relate the calculated flame results to the extinguishment of buoyancy dominated fires, it is necessary to identify representative conditions for extinction for such fires. Note that a nomenclature has been adopted in which "extinction" refers to the general process of a flame going out due to an increasing flow velocity variation across the flame, i.e., increasing strain rate; while "extinguishment" refers to extinction that takes place at flow conditions *characteristic* of those for a buoyancy-dominated flame.

Somewhat surprisingly, very few extinguishing concentrations have been reported for methane flames. A limiting oxygen index (LOI) of 0.139 (defined as the ratio of the mole fraction of oxygen in a N_2/air mixture below which a diffusion flame cannot be sustained) had been reported by Simmons and Wolfhard [5] for methane using a hemispherical burner located in a slow oxidizer counter flow. This value corresponds to an added N_2 mole fraction of 33.8%. Measurements by Ishizuka and Tsuji [6] in a similar burner yielded a value of 31.9%. These two values were averaged to obtain an estimate of 33% for the extinguishing concentration for use in the calculations [2, 3]. The model results indicated that extinction of the methane flame in a 33% N_2/air mixture occurred when the maximum flame temperature fell to 1550 K. Note that the extinction temperature for air was calculated to be 1785 K. By defining 1550 K to be the typical temperature for extinguishing methane flames, it was possible to calculate the extinguishing concentrations for the remaining thermal agents. Experimental data for methane fires were not available, but comparison of the calculated results with experimental cup-burner results burning heptane were in good agreement, indicating that the calculations were predicting the variation in extinguishing concentration for different thermal agents quite well.

One additional measurement of the LOI for methane had been identified in the literature. Puri and Seshadri [7] reported that a 28.6% N_2 mole fraction was sufficient to extinguish an opposed jet diffusion flame. At the time of our earlier work, we chose to discard this value because it was significantly lower than the values reported by Simmons and Wolfhard [5] and Ishizuka and Tsuji [6]. In a very recent study, researchers at NIST have made measurements in a similar low strain-rate flame and measured a value of 30.0% for the maximum N_2 mole fraction at extinguishment.* At the 1999 HOTWC meeting, Ural [8] reported a study of extinguishment of a methane flame in a cup burner apparatus. The extinguishing mole fraction of N_2 over a relatively wide range of fuel and oxidizer velocities was 27.1%. The range of values reported in the various investigations raises the question of what extinguishing concentration (or LOI) is appropriate for buoyancy-dominated methane diffusion flames.

In this work, measurements of extinguishment are reported for two diffusion flame burners available at NIST. Extinguishment by HFE7100 and water/lactic acid mixtures released as liquids are investigated in the Dispersed Liquid Agent Fire Suppression Screen (DLAFSS) using propane as fuel. This screen is based on an opposed flow porous burner, which is similar to that used in the earlier investigation of Ishizuka and Tsuji [6]. Extinguishment of methane and propane flames by known gaseous thermal agents was investigated using two burners—the DLAFSS and a laminar coflow burner, known as a Santoro burner, which has been used for a number of studies at NIST.

* A. Hamins, National Institute of Standards & Technology, personal communication, 2000.

EXPERIMENTAL

EXTINGUISHMENT BY AGENTS RELEASED AS LIQUIDS IN THE DLAFSS

Measurements of extinguishment effectiveness for the liquid agents were made in the DLAFSS. A detailed description of this device is available, and only a brief account is provided here [9]. The apparatus consists of a small vertical wind tunnel, a porous, 15.8 mm diameter cylindrical burner located at the test section, and a small nebulizer located in the settling chamber of the tunnel. The fuel is propane. Air is supplied to the tunnel via a frequency-controlled blower. The nebulizer is used to generate a small poly-dispersed spray of liquid droplets. The droplet Sauter mean diameters (measured using a phase Doppler interferometer) at the burner location without the flame, vary between 25 μm and 35 μm under the test conditions. The droplets were entrained by the air flow and were transported to the test section.

The experiments were conducted by increasing the air flow rate through the tunnel with a fixed liquid delivery rate to the nebulizer. The air velocity at which the flame at the forward stagnation region of the burner was blown-off was observed visually and recorded. These measurements were repeated for a number of liquid delivery rates. Since there are many liquid delivery rates that one can use in the screening procedure, a reference rate is needed to compare and interpret the fire suppression effectiveness of various liquid agents in a consistent way. The following protocol is used, which is based on the conditions commensurate with cup-burner results for N_2.

Hamins et al. [10] measured the N_2 mole fraction at extinction as 33% for a cup burner with propane fuel. This value is in excellent agreement with the later work of Ural [8]. An examination of the N_2 results for the DLAFSS indicates that a 33% N_2 mole fraction results in blow-off of the propane flame in the DLAFSS when the oxidizer velocity is ≈ 30 cm/s [9]. Similar reference blow-off velocities were obtained when the cup-burner results for other gases (Ar, He) were compared to the DLAFSS results [9]. For this relatively low reference velocity, there are apparatus limitations associated with the operation of the burner and the nebulizer [9]. Therefore, in order to determine extinguishment concentrations for the liquid agents, measured extinction conditions at higher velocities are extrapolated to the reference velocity of 30 cm/s.

HFE7100 was obtained from 3M Corporation* and has a molar purity of 99%. As mentioned above, it was not feasible to investigate pure lactic acid, but it was possible to make measurements in the DLAFSS for lactic acid/water mixtures. A lactic acid/water solution having a lactic acid mole fraction of 60.1% was obtained from Fischer Scientific. Three aliquots generated by dilution of the stock solution with water were tested. These had lactic acid mole fractions of 5.4, 13.7, and 22.4%. The undiluted stock solution was not tested because it was so viscous it stallled the current syringe pump used to deliver the liquid to the nebulizer.

EXTINGUISHMENT BY GASEOUS THERMAL AGENTS IN THE DLAFSS

The DLAFSS was also used to determine extinguishing concentrations for gaseous thermal agents (N_2 and CO_2) by operating the opposed flow flame at very low strain rates. The air and

* Certain commercial equipment, instruments, or material are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

thermal agents were mixed [9]. The agent concentration was increased by incrementing the agent flow rate while maintaining the air flow at the same level until extinguishment was observed. Unlike earlier work, the air volume flow rate was adjusted to the minimum value feasible with the apparatus, which corresponded to a flow velocity of 13 cm/s in the test section at the burner. Since flow volume calibrations were unreliable at these low flow rates, the concentration of added agent was determined by using a Servomex 570A meter to measure the O_2 concentration in the agent/air mixture and subsequently calculating the corresponding mole fraction of the agent. Extinguishment measurements were made using both propane and methane as fuels. Tests showed the results were independent of the fuel volume flow rates over a substantial range. Each measurement was made three times to assess the repeatability of the tests.

EXTINGUISHMENT BY THERMAL AGENTS IN A COFLOWING BURNER

An axisymmetric burner with a co-flow of oxidizer was employed to study the extinguishment of laminar hydrocarbon diffusion flames. The burner (Figure 1), is the so-called Santoro burner [11], which has been widely used for flame studies at NIST (e.g., [12]). The burner consists of a 1.27 cm outer diameter central fuel tube surrounded by a 10.2 cm diameter oxidizer co-flow, which passes through a ceramic honeycomb. The fuel tube inner diameter is 1.14 cm.

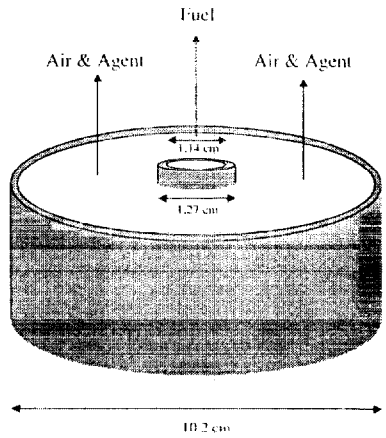


Figure 1. Schematic of the Santoro burner.

Previous experiments at NIST used air as the oxidizer. For the current experiments, oxidizer was supplied by a PC-based automated mixing system that controlled the volume flow rate and agent concentration for an agent/air mixture. The mixing system was based on the apparatus described by Pitts et al. [13], which utilized three mass flow controllers and an especially designed mixing chamber to generate prescribed mixtures. A fourth mass flow controller was added to meter the fuel, either propane or methane. New algorithms were written to control the mixing system for the various agents added to the air.

Each mass flow controller was calibrated using a Gilabrator-2 electronic soap-film flow meter. Most experiments were performed with average flow velocities, defined as the volume flow rates normalized by the nominal flow areas, for both the fuel and oxidizer matched at 7 cm/s. This is the base case employed in earlier studies as NIST. The sensitivity to velocity was investigated by varying the fuel and oxidizer flow rates. The control software provided the inputs required for the mass flow controllers to generate a given agent concentration while maintaining a constant flow velocity. During an experiment, the agent concentration was preset to an initial value, identified in a preliminary experiment as being near the extinguishing condition, and then increased in steps of 0.001 mole fraction at 40-s time intervals. While the agent mole fraction could be controlled with this precision, the uncertainty in concentration was estimated to be $\pm$ 0.004 (2σ). The effects of variations in the agent concentration on flame behavior were monitored visually.

RESULTS

EXTINGUISHING CONCENTRATIONS FOR HFE7100 AND LACTIC ACID/WATER MIXTURES

Figure 2 shows a plot of the measured velocity of the oxidizer at blow-off of the propane flame versus the liquid application rate in mL/min for liquid HFE7100. Extrapolation of the measured results to 30 cm/s yields a value of 17.6 mL/min. The measured distribution of the drops at the burner indicates that the agent concentration is roughly twice the value that would be obtained by assuming a uniform distribution across the cross sectional area of the test section [9]. This information allows the effective mole and mass fractions of HFE-7100 at the burner to be estimated as 3.8 and 25.6%, respectively, for the defined extinguishing condition. The estimated uncertainty for both values is ± 25%. Recall that the extinguishing mole fraction of gaseous HFE7100 in two independent cup burner tests was 6.1% [4].* When released as a liquid, HFE7100 is roughly two times more effective than when released as a gas.

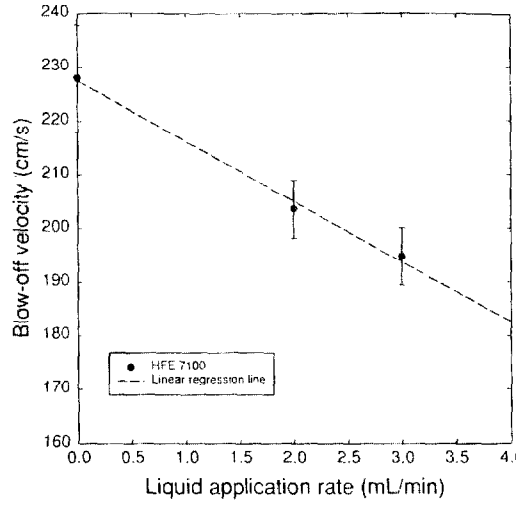


Figure 2. Fire suppression screening results for HFE7100.

Our earlier estimates of extinguishing capability, based entirely on a compound's theoretical ability to extract heat, indicated that liquid lactic acid could be roughly three times more effective than water on a molar basis and nearly 2/3 as effective on a mass basis. This is important, because water is predicted to be the most effective thermal agent, by a wide margin, in mass fraction terms.

Since a significant fraction of the predicted heat extraction for these compounds is due to the heat of vaporization, we estimated the heat of vaporization for lactic acid/water mixtures. These calculations involved construction of the equation of state for the liquid mixtures using the Peng-Robinson equation with an interaction parameter of 0.88 [14]. If one assumes that the entire sample is vaporized, then the integral heat of vaporization at constant pressure can be found using $\Delta H^{vap} = H_d - H_b$, where H_d is the enthalpy of the saturated vapor at the dew point and H_b is the enthalpy of the saturated liquid at the bubble point. Figure 3 shows the results of these calculations where the solid line is a fit to the calculated results.

It can be seen that the heat of vaporization increases substantially as the mole fraction of lactic acid is increased, reaching a maximum value at a water mole fraction of ~25%. Since the heat capacity of lactic acid should be much greater than that of water, the ability of the liquid mixtures to extract heat should increase substantially as the concentration of lactic acid increases.

Figure 4 shows the test results for the various lactic acid/water mixtures. Each data point in Figure 4 is the average of at least 5 or more runs. The error bars represent one standard deviation. In each case, the blow-off velocities decrease with increasing liquid application rate. However,

*R.E. Tapscott, personal communication, February 1999: NMERI In-House Testing, June 2, 1997.

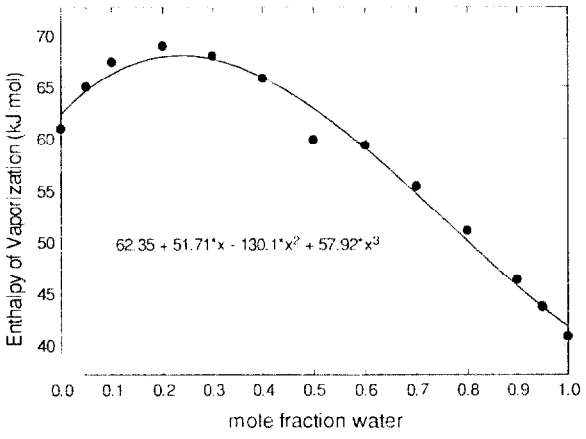


Figure 3. Heat of vaporization of lactic acid/water mixtures at p = 0.1013 MPa as a function of the mole fraction of water.

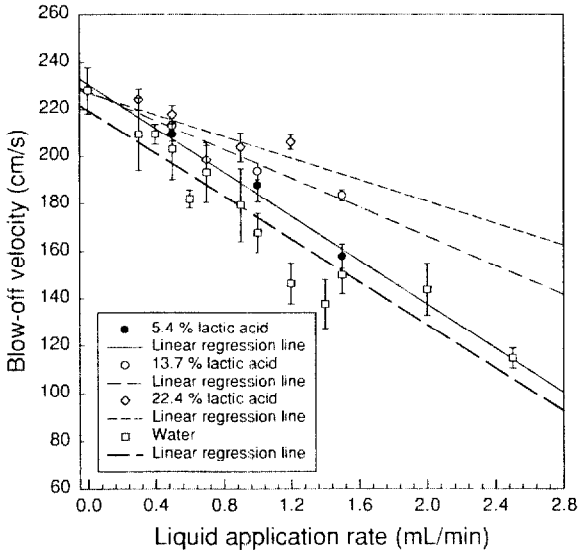


Figure 4. Fire suppression screening results for lactic acid/water mixtures.

higher flow velocities are required to blow off the flame mixtures having higher concentrations of lactic acid. This is an indication that the extinguishing ability of these mixtures is less than that of water alone or for the mixture with a 5.4% mole fraction of lactic acid. Extinguishing concentrations for the lactic acid/water mixtures have been estimated by extrapolating the results in Figure 4 to the reference velocity of 30 cm/s. These values are included in Table 1 along with corresponding values for water and HFE7100.

TABLE 1. CALCULATED EQUIVALENT MASS AND MOLE FRACTIONS AT THE REFERENCE BLOW-OFF VELOCITY.

Agent	Equivalent Mass Fraction (%)	Equivalent Mole Fraction (%)
Water	4.6	7.2
5.4% lactic acid (mole fraction)	5.0	6.5*
15.7% lactic acid (mole fraction)	7.6	7.9*
22.4% lactic acid (mole fraction)	10.2	8.8*
HFE 7100	25.6	3.8

* Mole fraction averaged molecular weight of lactic acid /water mixture is used in the calculation.

EXTINGUISHING CONCENTRATIONS FOR GASEOUS THERMAL AGENTS USING THE DLAFSS

The principal reason for making these measurements, as well as those discussed in the following section using a coflow burner, is to determine whether it is possible to identify a characteristic agent concentration for the extinguishment of a laminar diffusion flame. The existence of a characteristic value is implicit in the definition of the LOI [5] as well as in our earlier detailed chemical kinetic modeling investigation of extinguishment [2, 3], where a single extinguishment condition for N_2 was used to define conditions for extinguishment by other thermal agents. A similar assumption is made for the widely used cup-burner test.

The measurements were found to be highly reproducible. Uncertainties in the O_2 concentration at extinction are estimated as ±0.1% in mole fraction. This uncertainty is based on both the expected accuracy of the oxygen meter and the agreement of the meter reading when compared to known flow rates of the thermal agent and air at higher flow velocities where earlier calibrations are valid [9]. Table 2 lists the measured LOI and corresponding added N_2 extinguishing mole fraction for both methane and propane flames. The number of repeated measurements is denoted by "n"; the uncertainty limits represent one standard deviation. Nominal volume flow rates for the fuels are indicated. As noted above, the results were found to be independent of fuel velocity over a substantial range.

TABLE 2. SUPPRESSION RESULTS USING NITROGEN.

Fuel	Literature LOI [5]	LOI at blow-off (current measurements)	Mole fraction of added nitrogen
Methane (4 L/min)	0.139	0.140 ± 0.001 (n = 3)	33.3% ± 0.4 % (n = 3)
Propane (1.5 L/min)	0.127	0.128 ± 0.001 (n = 3)	39.0% ± 0.4% (n = 3)

The agreement between the current measurements and the earlier measurements of Simmons and Wolfhard is excellent [5]. This is true despite the fact that the burners had different configurations. Recall that the results reported by Ishizuka and Tsuji using a cylindrical porous burner were also in good agreement with those of Simmons and Wolfhard [6]. The close agreement suggests that the current results are typical of those to be expected for opposed flow flames stabilized on porous burners.

The current result for the methane flame also agrees quite well with the extinguishing concentration assumed for N_2 in the earlier kinetic modeling study [2, 3]. To test the validity of these calculations, the CO_2 extinguishing mole fraction for the opposed flow methane flame was also measured, yielding 22.2 ± 0.3%. The value estimated based on the kinetic modeling was 22%. Obviously, the calculations predicted this experimental result very well.

EXTINGUISHING CONCENTRATIONS FOR GASEOUS THERMAL AGENTS USING A SANTORO BURNER

Even though the flame system and experimental measurements are quite simple, complex flame behaviors were observed for the flames on the Santoro burner. Consider first the methane flame burning in air diluted with N_2. With only air present, a blue flame was evident slightly below the exit and very close to the fuel tube. Further downstream the flame was yellow indicating the presence of soot. As the N_2 concentration in the oxidizer was increased, the base of the flame gradually moved downstream and away from the burner tube, but the flame was still attached. At the same time, the fraction of the flame that appeared yellow decreased. When the N_2 mole fraction reached 20.3%, an up and down oscillation of the flame base suddenly appeared as indicated in Figure 5. This flame was entirely blue. The oscillating flame only existed over a

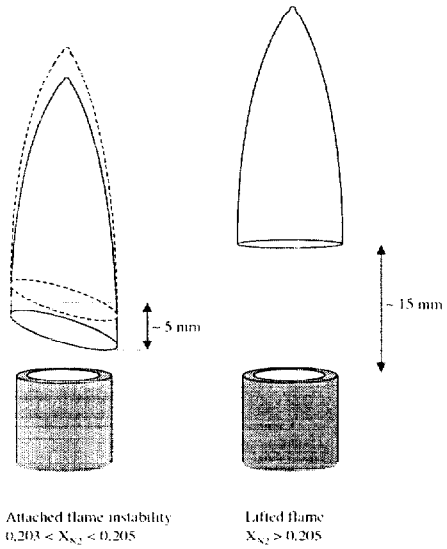


Figure 5. Sketch of a methane flame showing the attached flame oscillation and subsequent stabilized lifted flame that result from the addition of nitrogen to the air co-flow.

narrow range of N_2 mole fraction. Similar oscillations for flames near extinction have been reported previously in the literature [15, 16].

When the N_2 mole fraction was increased to 20.5%, the flame detached from the burner and moved downstream where it became stable and floated lazily up and down 15–20 mm above the burner. With further increases in N_2 concentration the flame moved further downstream, while becoming shorter and broader. These changes in appearance are shown in cartoon form in Figure 6. Similar lifted-flame structures have been observed in investigations with different fuels and burner configurations and are attributed to the presence of triple flames [17, 18, 19, 20]. When the N_2 mole fraction reached 21.9%, the lifted flame could no longer be stabilized and it simply floated away, i.e., it was blown off.

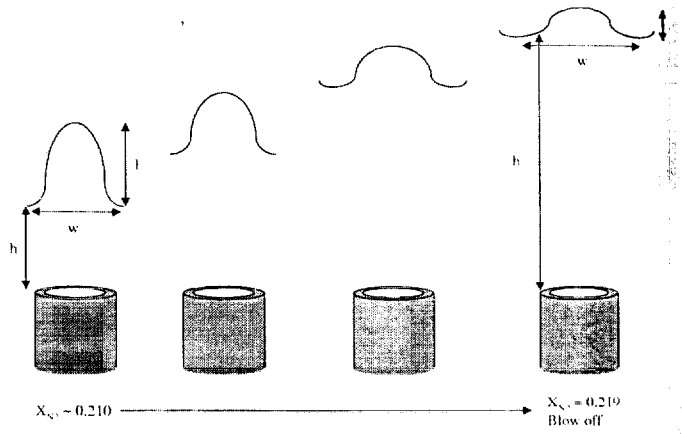


Figure 6. Evolution of the flame structure as additional N_2 is added to the co-flow air stream.

Increasing N_2 dilution of the air resulted in three distinct behaviors—attached flame instability, lift off, and blow off. The N_2 mole fraction range where these processes occur is narrow, ranging from 20.5–21.9%. It is difficult to define any of these processes as a true extinguishment, though blow off would seem to be the most appropriate. We chose to use the onset of attached flame instability as the basis for comparison of results for reasons that will be apparent shortly.

No matter how it is defined, it is clear that extinguishment of a methane flame by N_2 occurs at a much lower concentration on a Santoro burner than for the other diffusion flame types discussed in the Introduction. In particular, this is true for the cup-burner measurements of Ural [8], for which the extinguishing N_2 mole fraction was 27.1%. This difference is remarkable since both experiments involve coflowing diffusion flames with similar oxidizer flow velocities (Ural's

base case corresponded to an average velocity of 14 cm/s). Interestingly, Ural also reports flame lift off just prior to extinguishment.

Similar experiments were conducted using CO_2, Ar, and He as diluents. The effects of these agents on the methane flame were somewhat different from those observed for N_2. For all three, the initial effect of increasing their concentration in air was the appearance of the attached flame instability. The required concentration varied with the agent. Similar to the results for N_2, additional small increases in the mole fractions of CO_2 and Ar resulted in detachment of the flame from the burner with stabilization further downstream. At first these flames moved further downstream with additional increases in diluent concentration, but eventually the flames reached lift-off heights where further concentration increases appeared to have little effect. The most likely reason for this is that the flames reached a downstream location where room air was able to diffuse through the oxidizer coflow and provide sufficient O_2 to sustain combustion. For these cases, it is impossible to define the concentration required for flame blow off.

The behavior of the methane flame burning in air diluted with He was quite different. After a few oscillations following the onset of the attached flame instability, the flame was extinguished without further increases in helium concentration. Apparently, the onset of the attached flame instability was sufficient to extinguish the methane burning in the He/air mixture.

To test the sensitivity of the observed behaviors to the oxidizer and fuel velocities, the measurements were repeated using different velocities for each. Table 3 lists agent mole fractions for which the attached flame instability developed for the four thermal agents and indicated flow velocities V_{fuel} and V_{ox}. Where observed, values are also included for the concentration required for flame blow off or blow out. While minor differences seem to be present, the dependence on velocity is much too small to explain the difference between the current results for N_2 and those reported by Ural [8].

TABLE 3. AGENT MOLE FRACTIONS RECORDED AT ONSET OF ATTACHED FLAME INSTABILITY (AFI) AND FLAME BLOW OFF OR BLOW OUT (BO) AS A FUNCTION OF FUEL (V_{FUEL}) AND OXIDIZER (V_{OX}) FLOW VELOCITIES.

V_{fuel}	V_{ox}	N_2		CO_2		AR		He	
(cm/s)	(cm/s)	AFI %	BO %	AFI %	BO %	AFI %	BO %	AFI %	BO %
7.0	7.0	20.2	21.9	12.0	-	29.0	-	19.9	19.9
3.5	7.0			12.1	12.8	29.1	-	19.8	19.8
1.8	7.0	20.4	23.3	12.3	13.1	29.6	30.9	19.9	19.9
7.0	3.5			12.4	-	29.4	-	20.5	20.6
7.0	1.8	20.6	-	12.7	-	30.1	-	23.2	-

Similar measurements of extinguishing concentration were made for propane flames. The results are not presented here in detail due to space limitations. Suffice it to say that a variety of flame behaviors were observed, including the attached flame instability. While higher concentrations of thermal agents were required to induce the instability than were observed for the methane flame, the required mole fractions were considerably less than observed in cup-burner experiments using propane fuel [8, 10].

DISCUSSION

FLAME EXTINGUISHMENT BY HFE7100 AND LACTIC ACID

The experimental measurements in the DLAFSS confirmed the prediction, based purely on its ability to extract heat, that liquid HFE7100 would be an effective thermal agent. On a molar basis, this compound is comparable to the efficiency of Halon 1301 and is better than liquid water. On a mass basis, the efficiency is somewhat lower than observed for both of these compounds, but is still quite good. The results indicate that there is a significant advantage to be gained by releasing HFE7100 as a liquid as opposed to a gas. In some ways this seems to be contrary to the overall purpose of identifying suitable replacements for the total-flooding firefighting agent Halon 1301. However, one the most often mentioned alternatives for Halon 1301 is water mist, so it is appropriate to compare liquid HFE7100 and water as firefighting agents. HFE7100 would seem to have several advantages. The ether has a lower boiling point so it is likely to be vaporized more quickly. One result of its lower boiling point is that, unlike water, the room temperature vapor pressure of the ether corresponds to a concentration that is higher than the extinguishing value, so it should be possible to inert an enclosure [2]. The freezing point of the ether is also much lower than H_2O, 138 K versus 273 K, and it is very likely that it will be useful in much lower temperature environments than H_2O. The ether is also much less conductive than H_2O and will therefore be more compatible with energized electronic equipment. The fluid properties of the ether will be much different than water. Testing would be required to determine whether or not these differences are an advantage or disadvantage with regard to piping and distributing the fluids within an enclosure. One area where H_2O is likely to have a decisive advantage is in the formation of byproducts. Similar to the halons or fluorinated halon replacements such as HFC-125 or HFC-227, combustion will certainly decompose the ether, and HF and other fluorinated compounds will be generated. Testing will be required to determine whether the amount of HF generated precludes the use of HFE7100 in particular applications.

The results for lactic acid demonstrate clearly that chemical effects can counteract the expected thermal effectiveness of a particular compound. Perhaps it is not too surprising that lactic acid, which only contains C, H, and O atoms, would generate excess heat when oxidized. Based on the current findings, the amount of heat generated is slightly greater than that absorbed by the vaporization and heating of this compound. Clearly, lactic acid should not be considered for firefighting applications.

It should be remembered that HFE7100 will also be oxidized in the combustion zone of hydrocarbon flames. Thermodynamics analysis indicates that there will be significant heat release associated with these reactions. The fact that the effectiveness of this compound is similar to that predicted by assuming only thermal processes are important indicates that the heat release effect is being counteracted in some way. The most likely explanation is that the fluorine atoms in the molecule that are released in the combustion zone have a moderating chemical effect on the flame. The same is true for other fluorinated agents.

EXTINGUISHMENT OF DIFFUSION FLAMES AND IMPLICATIONS FOR DETAILED CHEMICAL KINETIC MODELING

The current findings on the extinguishment of various types of diffusion flames by N_2, CO_2, Ar, and He certainly lead one to question the assumption that a unique condition, e.g., maximum flame temperature or local strain rate, characteristic of laminar diffusion flames can be defined.

Different types of flames and even similar types of flames extinguish at different concentrations of the thermal agents.

A likely explanation for the variations observed between the different coflowing diffusion flames is that a diffusion flame is not actually being extinguished in these experiments. In order for a diffusion flame to attach to a burner, it is necessary for some premixing of the fuel and oxidizer to occur. To stay attached, the flame must propagate against the flow within the boundary layer separating the fuel and air, which is due to the initial flow velocities of the gases, as well as flow induced by buoyancy. This type of flame is sometimes referred to as an "edge" flame. The edge flame acts as an ignition source for the more diffusion-like flame that burns downstream of the burner. Similar considerations apply to flames lifted off of the burner. Here an edge flame or more fully developed triple flame serves to anchor the flame at its base.

Both analytical models [21] and detailed chemistry and flow models [22] are being developed to better understand the behavior of edge and triple flames. These models are not yet well enough advanced to explain the observations reported in the current study. However, a simple argument can provide some insight. The actual velocities against which the edge or triple flame must propagate will depend on the burner configuration at the flame base. For instance, a larger burner thickness should generate a wider wake region with the result that an edge flame is more easily stabilized. The burner wall thickness for a cup burner (4.8 mm [8]) is much wider than that for the Santoro burner (0.7 mm) employed in the current investigation. This difference provides a plausible explanation for the observed differences between extinguishing concentrations measured by Ural [8] and those observed using the Santoro burner.

Apparent differences between measured extinguishing concentrations for different types of opposed flow burners are more difficult to understand. To first order, diffusion flames formed by two laminar jet flows and those formed by flowing fuel through porous bodies into an oxidizer flow have the same flame structure. However, there are secondary differences. For instance, flames typically burn closer to solid surfaces for porous burners placed in a flow than in opposed jets. Heat losses to the burner surface may therefore be higher than in the opposed jet type of burner. The porous burners also form flames that are somewhat curved as opposed to the flat flames typical of the opposed jet flames. These differences may be responsible for the different extinguishing concentrations observed for the different configurations, but additional analysis and/or modeling is necessary to understand the physical mechanisms fully.

The different extinguishing concentrations observed in the current experiments imply that it may be inappropriate to specify a single criterion for the extinguishment of buoyancy dominated laminar diffusion flames. This is particularly true for cases where edge or triple flames are present. The implications for our earlier detailed chemical kinetic investigation, where the maximum flame temperature at extinction was used as a criterion for the extinguishing concentration, are evident. On the other hand, as the successful prediction of the extinguishing concentration for CO_2 in the DLAFSS demonstrates, for a given flame system the approach works quite well. It seems likely that by choosing a slightly higher maximum flame temperature at extinguishment, it will be possible to predict extinguishing concentrations for thermal agents in the opposed jet flames as well.

One would not expect the modeling of opposed jet diffusion flames to quantitatively predict the effects of thermal agents on flames stabilized by edge or triple flames. However, as can be seen in Figure 7, where the measured mole fractions of thermal agents necessary to induce attached methane flame instabilities and flame blow off or blow out are compared with the predictions of the earlier detailed chemical kinetic modeling study, the model captures the qualitative dependence on thermal agent well. This suggests that the effects of thermal agents on the stability of edge or triple flames are quite similar to those responsible for the extinguishment of pure diffusion flames.

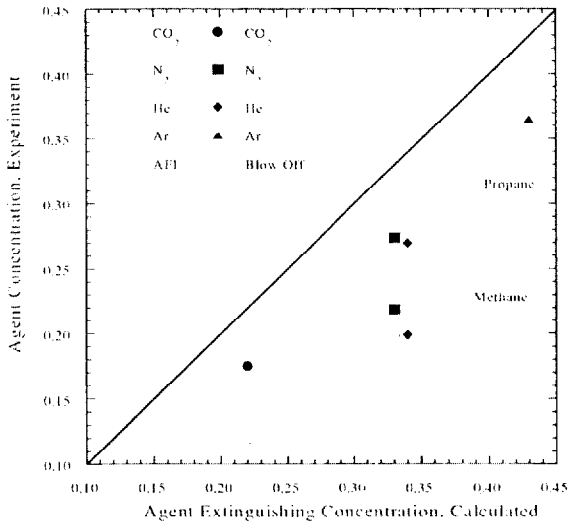


Figure 7. Thermal agent mole fractions measured at onset of attached flame instability (AFI) and blow off or out are compared with the results of the modeling study of opposed jet diffusion flames [2, 3].

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REFERENCES

1. Next Generation Fire Suppression Technology Program, http://www.dtic.mil/ngp/

2. Pitts, W.M., Yang, J.C., Huber, M.L., and Blevins, L.G., *Characteristics and Identification of Super-Effective Thermal Fire-Extinguishing Agents—First Annual Report*, NISTIR 6414, Gaithersburg, MD, October, 1999.

3. Pitts, W.M., and Blevins, L.G., "An Investigation of Extinguishment by Thermal Agents Using Detailed Chemical Modeling of Opposed Flow Diffusion Flames," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 145-156, 1999.

4. Flynn, R.M., and Thomas, S.D., Fire Extinguishing Process and Composition, *US Patent 5,718,293*, February 17, 1998.

5. Simmons, R.F., and Wolfhard, H.G., "Some Limiting Oxygen Concentrations for Diffusion Flames in Air Diluted with Nitrogen," *Combustion and Flame* 1, pp. 155-161, 1957.

6. Ishizuka, S., and Tsuji, H., "An Experimental Study of Effect of Inert Gases on Extinction of Laminar Diffusion Flames," Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 695-703, 1981.

7. Puri, I.K., and Seshadri, K., "Extinction of Diffusion Flames Burning Diluted Methane and Diluted Propane in Diluted Air," *Combustion and Flame* 65, pp. 137-150, 1986.

8. Ural, E.A., "Measurements of the Extinguishing Concentrations of Gaseous Fuels Using the Cup Burner Apparatus," *Proceedings*, Halon Options Technical Working Conference, Albuquerque, NM, pp. 275-283, 1999.

9. Yang, J.C., Donnelly, M..K., Prive, N.C., and Grosshandler, W.L., *Dispersed Liquid Agent Fire Suppression Screen Apparatus*, NISTIR 6319, Gaithersburg, MD, July 1999.

10. Hamins, A., Gmurczyk, G., Grosshandler, W., Rehwoldt, R.G., Vazquez, I., Cleary, T., and Presser, C., "4. Flame Suppression Effectiveness," pp. 345-465 in Grosshandler, W. L., Gann, R. G., and Pitts, W.M. (eds.), *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*, NIST SP-861, Gaithersburg, MD, April, 1994.

11. Santoro, R.J., Semerjian, H.G., and Dobbins, R.A., "Soot Particle Measurements in Diffusion Flames," *Combustion and Flame* 51, pp. 203-218, 1983.

12. Smyth, K.C., Harrington, J.E., Johnsson, E.L., and Pitts, W.M., "Greatly Enhanced Soot Scattering in Flickering CH4/Air Diffusion Flames," *Combustion and Flame* 95, pp. 229-239, 1993.

13. Pitts, W.M., Mulholland, G.W., Breul, B.D., Johnsson, E.L., Chung, S., Harris, R., and Hess, D.E., "Real-Time Suppressant Concentration Measurement," pp. 319-585 in Gann, R.G. (ed.), *Fire Suppression System Performance of Alternative Agents in Aircraft Engine and Dry Bay Laboratory Simulations*, Vol. II, NIST SP-890, Gaithersburg, MD, November, 1995.

14. Abderafi, S., and Bounahmidi, T., "Measurement and Estimation of Vapor-Liquid Equilibrium for Industrial Sugar Juice Using the Peng-Robinson Equation of State," *Fluid Phase Equilibria* 162, pp. 225-240, 1999.

15. Chan, W.Y., and T'ien, J. S., "An Experiment on Spontaneous Flame Oscillation Prior to Extinction," *Combust. Sci. Tech.* 18, pp. 139-143, 1978.

16. Dietrich, D.L., Ross, H.D., and T'ien, J.S., "Candle Flames in Microgravity," *Proceedings*, Third International Microgravity Workshop, NASA Conference Publication 10174, Cleveland, OH, pp. 31-36, 1995.

17. Chung, S.H., and Lee, B.J., "On the Characteristics of Laminar Lifted Flames in a Non-premixed Jet," *Combustion and Flame* 86, pp. 62-72, 1991.

18. Lee, B.J., and Chung, S.H., "Stabilization of Lifted Tribrachial Flames in a Laminar Non-premixed Jet," *Combustion and Flame* 109, pp. 163-172, 1997.

19. Lee, B.J., Kim, J.S., and Chung, S.H., "Effect of Dilution on the Liftoff of Non-Premixed Jet Flames," Twenty-Fifth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 1175-1181, 1994.

20. Brooker J.E., Jia, K., Stocker, D.P., and Chen, L.-D., "Influence of Buoyant Convection on the Stability of Enclosed Laminar Flames," *Proceedings*, Fifth International Microgravity Combustion Workshop, NASA Conference Publication 208917, Cleveland, OH, pp. 97-100, 1999.

21. Wichman, I.S., Pavlova, Z., Ramadan, B., and Qin, G., "Heat Flux from a Diffusion Flame Leading Edge to an Adjacent Surface," *Combustion and Flame* 118, pp. 651-668, 1999.

22. Takahashi, F., Schmoll, W.J., and Katta, V.R., "Attachment Mechanisms of Diffusion Flames," Twenty-Seventh Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 675-684, 1998.