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Fire-suppression characteristics of CF₃H in a cup burner

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Abstract

A numerical investigation is performed to understand the inhibition characteristics of CF_3H in a periodically oscillating methane-air jet diffusion flame formed over a cup burner. A detailed chemical kinetic mechanism having 82 species and 1510 elementary-reaction steps is used. Calculations made without adding agent yielded an oscillating flame with a flicker frequency of 11 Hz, which compared well with that obtained in the experiment. The minimum concentration of agent required for extinguishing the cup-burner flame is determined by adding CF₃H to the air stream and by increasing its volume fraction gradually until the flame is completely extinguished. Addition of CF₃H at volume fractions up to 10.05% did not affect the cup-burner flame temperature significantly. Extinction of a cup-burner flame took place as the base of the flame became destabilized, and the unstable flame base moved downstream in search of a new stabilization location. The predicted minimum concentrations of CF3H for extinguishing the flame obtained by (1) replacing the air with CF_3H and (2) replacing the N₂ in the air with CF₃H are 10.1 and 19.2%, respectively. These concentrations compare favorably with the corresponding measured values of 11.7 and 20.3%, respectively. For validation, calculations are also made for the steady counterflow diffusion flames with different concentrations of CF_3H in the air stream and the predicted volume fractions of agent at extinction are in good agreement with the experimental values published in the literature. Examination of the reaction rates for the cup-burner flames indicates that the reactions with fluorinated species reduce the concentration of chain-carrying radicals in the flame. The effect is stronger at the flame base than further up in the trailing part of the flame, leading to destabilization at the flame base prior to extinction in the trailing region, and yielding the observed blowoff-type extinction.

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1. Introduction

Fire-extinguishing agents are known to function primarily via chemical or thermal mechanisms [1]. Trifluorobromomethane (CF₃Br, Halon 1301), which functions primarily through chemical mechanisms, is a widely used fire-suppression agent [2]. Numer-

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ous studies have been conducted with laboratory premixed and diffusion flames in attempts to understand the inhibitory mechanisms of trifluorobromomethane [3–5]. Since the production of Halon has been banned in industrialized nations due to its adverse effect on stratospheric ozone, more environmentally friendly replacements are being considered [6]. Understanding the inhibition mechanisms of these replacements as well as those of CF3Br is important for their efficient use and for developing alternative agents. Studies with CF3Br itself have provided insight into the inhibition contributions from the CF_3 [7], even though inhibition by CF3Br is dominated by the brominecontaining species. Similarly, even though the shortterm replacements for CF3Br are predominantly twoand three-carbon fluorinated agents [6], insight into their flame inhibition mechanisms can be obtained from the study of simpler agents such as CF₃H, which are more amenable to modeling [8,9]. For example, experimental studies on premixed CO and H₂ flames have identified the key decomposition steps of CF3H leading to CF_3 [10,11].

Because of their straightforward interpretation, the flame configurations used to study flame inhibition mechanisms have tended to be premixed flames [12–15] and counterflow diffusion systems [16–19]. Premixed flames have been selected mainly because the overall reaction rate, heat release, and heat and mass transport in these flames can be described with a single fundamental parameter-the laminar burning velocity—and because over certain regions, the flowfield can be considered one-dimensional (greatly simplifying data collection and numerical simulation). Similarly, counterflow diffusion flames can be considered one-dimensional along the centerline, and the extinction strain rate has been commonly used as the characteristic suppression parameter. In principle, such fundamental parameters can ultimately be used to relate the behavior of the agent in the laboratory flame to its behavior in suppressing a large-scale fire-although this scaling is difficult to achieve in practice. Under the influence of buoyancy forces, most common fires become dynamic in nature with large vortical structures entraining additional surrounding air, which could alter the effectiveness of the agent as determined using laboratory-scale steadystate flames. To gain a better understanding of agent behavior in common fires, it is advantageous to investigate fire-suppressant characteristics in a laboratoryscale nonpremixed flame that is dynamically similar to a common fire [20]. Nonpremixed co-flow diffusion flames formed on a vertically mounted cup burner [21] become unsteady with the development and convection of centimeter-size toroidal vortices along the flame surface. These cup-burner flames are widely used in the fire protection community as a metric for the performance of fire-suppression agents. Further, the concentration of agent in the air stream necessary for extinction of cup burner flames is believed to scale reasonably well to that required to suppress large-scale fires. The present work applies detailed numerical modeling to understand the action of a representative Halon replacement (CF₃H) in extinguishing cup-burner flames. In doing so, the present analysis obtains the benefits of comprehensive fluid dynamic and chemical kinetic descriptions of the flame structure (typical of models for premixed and counterflow diffusion flames) in understanding complex flame configurations that are more representative of fires.

Under normal operating conditions, a laminar coflow diffusion flame formed over a cup burner has a negligibly small fuel flow rate and a low-speed annular air flow and develops large-scale, low-frequency (typically 10-15 Hz) buoyancy-induced vortices on the air side, which are similar to the vortical structures seen in common fires. Numerical investigations using conserved-scalar, global-chemistry, and detailedchemistry models have been performed for jet flames that are similar to the flames formed over a cup burner. These studies have elucidated important aspects of combustion in jet flames, such as the effect of heatrelease rate [22], the role of buoyancy [23,24] the enhancement of soot formation [25], and the effects of Lewis number [26,27]. Such comprehensive computations have also been performed recently to predict the effects of various fire-suppressing agents [N2, CO2, He, Ar, and Fe(CO)5] on methane co-flow diffusion flames [28-32].

The present paper describes an experimental– numerical investigation performed to establish the extinction criterion for cup-burner flames using CF_3H as a fire-suppression agent. A two-dimensional numerical model with detailed kinetics that accurately simulates dynamic diffusion flames was employed. The numerical results are examined in detail to interpret the influence of CF_3H on the flame stabilization and extinction process.

2. Experiment

The cup burner used in the present investigations to evaluate effectiveness of various fire-suppression agents consists of a cylindrical glass cup (diameter 28 mm) positioned inside a glass chimney (53.3 cm in height, 9.5 cm in inner diameter) [33,34]. To provide uniform flow, the base of the chimney was filled with 6-mm glass beads, the fuel cup was filled with 3-mm glass beads, and the burner assembly was covered with two 15.8-mesh/cm screens. Gas flows were

measured using mass flow controllers (Sierra 860¹) that were calibrated so that their uncertainty would be 2% of the indicated flow. (All uncertainties are expressed as expanded uncertainties, with a coverage factor of 2.) The total flow rate of the outer co-flowing gas (air + agent) was held constant at a specified value. To determine the extinction condition, CF₃H was added to the airflow (in increments of <1% near extinguishment), while the corresponding flow rate of co-flow air was reduced until lift-off was observed. The nominal co-flow velocity with and without CF3H was 10.7 ± 0.21 cm/s, and the fuel jet velocity was 0.921 ± 0.018 cm/s. These velocities closely represent those of entraining air and evaporating fuel, respectively, of a liquid-fueled cup-burner flame. The test for each condition was repeated at least three times. The fuel gas used was methane (Matheson UHP, 99.9%); the agent was CF₃H (Dupont, Freon 23, 99%); and the air was house compressed air (filtered and dried), which was additionally cleaned by passing it through a 0.01-µm filter, a carbon filter, and a desiccant bed to remove small aerosols, organic vapors, and water vapor. Visual flame images were recorded on VHS videotape using a chargecoupled-device (CCD) camera (512×512 pixels) and subsequently analyzed with image-analysis software to determine the flame-base location.

3. Numerical model

A time-dependent, axisymmetric mathematical model known as UNICORN (unsteady ignition and combustion using reactions) [35] was used for the simulation of unsteady jet diffusion flames associated with the cup burner. This model solves axial- and radial-momentum equations, the continuity equation, and the enthalpy- and species-conservation equations on a staggered-grid system [35]. The body-force term due to the gravitational field is included in the axialmomentum equation to simulate vertically mounted flames in normal gravity. A clustered mesh system is employed to trace the gradients in flow variables near the flame surface. The methane cup-burner flames with added CF₃H are simulated using a detailed chemical kinetic mechanism having 82 species and 1510 elementary reaction steps, developed by the National Institute of Standards and Technology (NIST) [36] through addition of fluorine-species inhibition

¹ Certain commercial equipment, instruments, or materials are identified in this paper for adequately specifying 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.

Table 1

Lennard-Jones potential parameters for fluorine species used in transport property calculations

Species	ε/k	σ	Species	ε/k	σ
	(K)	(A)	•	(K)	(A)
F	330.0	2.750	CH ₃ CF ₂	323.4	4.798
HF	262.0	3.148	CH ₂ FCH ₂	312.2	4.583
CH ₃ F	262.0	4.123	CH ₂ FCHF	312.2	4.583
CH_2F_2	262.0	4.123	CH ₂ FCF ₂	323.4	4.798
CHF ₃	134.0	4.123	CHF ₂ CH ₂	323.4	4.798
CF ₄	262.0	4.662	CHF ₂ CHF	323.4	4.798
CH_2F	262.0	4.123	CHF ₂ CF ₂	323.4	4.850
CHF ₂	121.0	4.123	CF ₃ CH ₂	289.1	4.911
CF ₃	262.0	4.320	CF ₃ CHF	323.4	4.850
CHF	108.0	4.123	CF ₃ CF ₂	323.4	4.900
CF ₂	94.2	3.977	CH ₂ CHF	272.2	4.322
CF	350.5	3.635	CH_2CF_2	251.5	4.442
CF ₃ O	350.5	4.906	CHFCHF	251.5	4.442
CHFO	350.5	4.906	CHFCF ₂	251.5	4.442
CF ₂ O	860.0	4.906	CF_2CF_2	254.2	4.647
CFO	312.2	4.000	CH_2CF	272.2	4.322
CH ₃ CH ₂ F	323.4	4.583	CHFCH	272.2	4.322
CH ₃ CHF ₂	289.1	4.798	CHFCF	251.5	4.442
CH ₃ CF ₃	312.2	4.911	CF ₂ CH	251.5	4.442
CH ₂ FCH ₂ F	323.4	4.583	CF ₂ CF	251.5	4.442
CH ₂ FCHF ₂	323.4	4.798	C ₂ HF	225.0	4.250
CH ₂ FCF ₃	323.4	4.850	C_2F_2	240.0	4.400
CHF_2CHF_2	323.4	4.850	CHFCO	350.5	4.906
CHF ₂ CF ₃	231.8	4.900	CF ₂ CO	350.5	4.906
CF ₃ CF ₃	312.2	4.969	CFCO	350.5	4.906
CH ₃ CHF	330.0	4.583			

reactions to the GRI-V1.2 combustion mechanism [37] of the Gas Research Institute. The thermo-physical properties such as enthalpy, viscosity, thermal conductivity, and binary molecular diffusion are calculated for each species from the polynomial curve fits developed for the temperature range 300-5000 K. The enthalpy polynomials and transport data for the species included in the GRI-V1.2 mechanism are given in Ref. [37]. While the enthalpy polynomials for the fluorine species are given in Ref. [36], the transport data for these species are listed in Table 1. Mixture viscosity and thermal conductivity are then estimated using the Wilke and Kee expressions, respectively. Molecular diffusion is assumed to be of the binary-diffusion type, and the diffusion velocity of a species is calculated using Fick's law and the effective-diffusion coefficient of that species in the mixture. A simple radiation model based on the optically thin media assumption [38] was incorporated into the energy equation. Only radiation from CO₂, H₂O, CO, and CH₄ was considered in the present study.

The finite-difference forms of the momentum equations are obtained using an implicit QUICKEST scheme [23], and those of the species and energy equations are obtained using a hybrid scheme of upwind and central differencing. At every time step, the pressure field is accurately calculated by solving all of the pressure Poisson equations simultaneously and utilizing the LU (lower and upper diagonal) matrixdecomposition technique.

Unsteady axisymmetric calculations for the cupburner flames are made on a physical domain of 200 and 47.5 mm in the axial (z) and radial (r) directions. A nonuniform grid system having a size of 421×201 is constructed in such a way that the grid spacing in the flame zone in both the z and the r directions is ~ 0.08 mm. The computational domain is confined by the axis of symmetry and wall in the radial direction and by the inflow and outflow boundaries in the axial direction. The outer boundary in the z direction is located sufficiently far from the burner exit (~15 fuelcup radii) so that propagation of boundary-induced disturbances into the region of interest is minimal. Flat velocity profiles are imposed at the fuel and air inflow boundaries, while an extrapolation procedure with weighted zero- and first-order terms is used to estimate the flow variables at the outflow boundary [39].

For accurate simulation of the flow structure at the base of the flame, which is very important in flameextinction studies, the fuel-cup rim was treated as a tube having a 1-mm-long, 1-mm-thick wall in the calculations. Note that even though this millimeter-size wall may not be sufficient for capturing the base structure of a well-anchored diffusion flame, it is sufficient for the flames that are near to extinction (lift-off), which are the main focus of the present study. For simulating the heat transfer between the burner rim and the flame, the temperature of the tubular rim was set at 600 K, which is close to that estimated from the experiments (500-600 K). Note that the temperature of the rim depends on the flame-base location; however, for the sake of simplicity and to be consistent with our previous investigations [28-32] we have used a 600-K rim temperature for all the flames simulated in this study.

The simulations presented here are performed on a 2-GHz Pentium IV-based personal computer with 1 GB of random access memory. Typical execution times using GRI-V1.2 and GRI + NIST mechanisms were \approx 52 and \approx 90 s/time-step, respectively. Stably oscillating flames are usually obtained in about 10,000 time steps (which corresponds to 300 ms real time).

4. Results and discussion

4.1. Uninhibited methane–air cup-burner flame structure

The nonpremixed flames established using the cup burner are laminar and nearly axisymmetric. Under



Fig. 1. Instantaneous flame simulated for cup burner with 10.7 cm/s annular airflow, 0.92 cm/s methane flow. Left image: temperature field; right image: oxygen volume fraction field and velocity vectors.

the influence of gravity, the low velocity of the coflowing air promotes buoyancy-induced instabilities outside the flame surface and causes the cup-burner flames to flicker at a low frequency. The fuel and air velocities of 0.921 and 10.7 cm/s, respectively, used in the present investigation represent a weakly strained flame that is stably attached to the burner lip. The computed instantaneous flowfield in the base region of the pure CH₄/air flame is shown in Fig. 1, in which temperature is plotted on the left half, and the velocity and O₂-concentration fields are plotted on the right half. Because of the very low fuel flow rate, the flame is squeezed inwardly by the buoyancyinduced flow and the velocity at the flame base is no longer parallel to the flame surface. As a result, the flame at the base is subjected to moderate strain that is induced by the entraining air. Except in the base region (0.1 < z < 4 mm), the peak temperature of the flame front is the same everywhere at 1880 K. The flame height at the instant shown in Fig. 1 is \sim 55 mm.

The computed flame is oscillating at a low frequency with large toroidal vortices forming naturally outside the flame surface. It is important to note that no artificial perturbation either in the calculations or in the experiment is required for the development



Fig. 2. Experimental (open symbols) and numerical (solid symbols) values of the volume fraction of CF_3H in the oxidizer stream required for extinguishing cup-burner flames as a function of co-flow oxidizer stream velocity. Data are shown for CF_3H replacing air (circles) or N_2 in the air (triangles).

of these outer vortices. The frequency corresponding to the passage of these vortices (also known as the flame-flickering frequency) is ~ 11 Hz, which compares well with the value of ~ 11 Hz measured in the experiments. However, a second frequency of 15 Hz was also observed in the photodiode signal. The bimodal flickering of the experimental flame is not yet understood and it could be specific to the setup used in the present study.

4.2. Cup-burner flame structure with added CF_3H

In the experiments, the extinction of the cupburner flame is achieved by adding CF₃H until the flame is destabilized and blows off (CF3H is added while simultaneously reducing the air flow to maintain the oxidizer stream velocity constant). Similarly, successive calculations are performed with increasing amounts of CF₃H in the air stream (again maintaining the co-flowing velocity constant) until a CF₃H volume fraction is reached that causes flame extinction. As an additional test of the capabilities of the numerical simulation, experiments and calculations were performed for particular cases in which the nitrogen (rather than the air) in the airflow was replaced by CF₃H. Compared to the traditional replacingair approach, for the given agent concentration, this replacing-N₂ method produces a flame with higher peak temperature, slightly higher reactant concentrations, and differing overall stoichiometry-which

should lead to a significantly different extinction criterion.

The measured and calculated extinguishing conditions for the cup-burner flames with added CF₃H are shown in Fig. 2, for tests performed for a range of oxidizer co-flow velocities. The experimental results indicate mild variation of the extinguishing volume fraction of CF3H for oxidizer velocities in the range from 3 to 15 cm/s. The calculations made with CF₃H replacing the air indicated that a stable flame could be obtained for agent volume fractions in the oxidizer stream of 10.05%. Above that value, however, the flame extinguished. Similarly, for CF3H replacing the nitrogen in air, stable flames were obtained for CF₃H volume fractions up to 19.1%, but blew off for values of 19.2% or higher. As the figure shows, the predicted minimum volume fraction of CF₃H for extinction of the cup-burner flame (10.1%) is reasonably close, about 9% lower, compared to the experimental value (11.2 ± 0.8) %. For the case of CF₃H replacing the N₂ in the air, the predicted value of 19.2% is again about 9% lower than the measured value of (21.0 ± 1.5) %. Considering the fact that the actual velocity profiles in the experiment, especially near the burner rim, could deviate from the flat profiles used in the calculations, the 9% difference between the measured and computed extinction limits seems reasonable. Of course, the discrepancy could also be due to limitations in the chemical kinetics. The agreement between the predicted and measured limiting



Fig. 3. Simulated cup-burner flames with CF_3H replacing air in the oxidizer stream: (a) 5%, (b) 10.05%, and (c) 10.1%. Left side of each image shows the temperature field, while the right side shows the CF_3H volume fraction field.

volume fractions of CF_3H in the present study and that of CO_2 in the previous study [28,29] suggests that the present two-dimensional, detailed-chemistry model is reasonably accurate in simulating both the chemical kinetics of the methane flames with CF_3H and CO_2 and the extinguishment process associated with the buoyancy-dominated dynamic flames.

Instantaneous images of the flames obtained from the calculations performed for 5, 10.05, and 10.1% CF₃H in the air stream (replacing-air method) are shown in Figs. 3a, 3b, and 3c, respectively. Here, distributions of temperature and CF₃H concentration are plotted on the left and right halves. The dynamic nature of the cup-burner flame is evident in this figure. The peak temperature for the 10.05% CF₃H flame is about 50 K lower than that of the pure methane-air flame (1880 K). Fig. 3 implies that for agent (CF₃H) concentrations less than 10% (i.e., oxygen >18.9% and nitrogen >71.1%), the global structure of the flame is not changed much. That is, the formation of outer vortices and the oscillatory behavior of the flame are similar in all the flames with agent volume fraction less than 10%. Significant differences exist, however, at the flame base. As the agent volume fraction was increased, the base of the flame got detached from the burner and stabilized at a location slightly downstream of the burner edge; this distance, for example, was about 3 mm for 10.05% added CF₃H. (For convenience, location of the flame base is defined

as the bottom most location of the 1500-K contour line in the flame base region, a definition consistent with that used in previous studies [28].) As indicated in Fig. 3b, the 3-mm separation between the burner edge and the flame base allows air and CF_3H to enter the fuel stream and provides partially premixed conditions in the base region. The entrained CF_3H is transported with the fuel jet all the way up to the flame tip (see Fig. 3b).

When the volume fraction of CF₃H was increased to 10.1%, the flame separated from the burner tip and was completely blown out of the computational domain with time. The flame image shown in Fig. 3c was captured at an intermediate time during the blowout process. Calculations made with CO₂ as the fire-suppressing agent [28,29] also predicted such extinction behavior (i.e., through the blowout process); however, the transition from attached to blowout condition is more abrupt with CF₃H. The flame base was shifted by only 3 mm before the flame, whereas, it shifted nearly 6 mm in the case of CO₂-added flames [28,29].

The computed evolutions of temperature at 20 mm above the burner for the 0, 5, 10.05, and 10.1% CF_3H cases are shown in Figs. 4a–4d, respectively, while the corresponding evolutions at 40 mm above the burner are shown in Figs. 4e–4h, respectively. While the images in Figs. 1 and 3 represent many locations in



Fig. 4. Evolutions of temperature distribution at 20 mm above burner for (a) 0%, (b) 5%, (c) 10.05%, and (d) 10.1% CF_3H in airflow, and at 40 mm above the burner (e), (f), (g), and (h), respectively. Traces of flame surfaces are marked by the shaded region.

the flame at one particular time, those in Fig. 4 represent the temperature at a particular height (20 or 40 mm) over varying time (approximately one flicker cycle, i.e., \approx 100 ms). A trace of the flame surface at a given height is shown with a shaded region in which temperature is in the neighborhood of its peak value. Note that temperature at the flame surface varies with time (Figs. 4e–4h) during an interaction between the buoyancy-induced vortex and the flame surface due to preferential diffusion effects [40]. The global characteristics of these cup-burner flames, such as flame oscillation in radial direction and the puffing action of fuel jet (closed contours at the center), are evident in these evolution plots. The vortices formed outside the flame surface have grown significantly by the time they reached a height of 40 mm (Figs. 4e–4h). Appearance of lower temperature contours along the center (r = 0) in flames with higher agent concentration (Figs. 4c–4d and 4g–4h) indicates that more cold air and CF₃H are penetrating into the fuel jet as the separation between the burner lip and the flame base increased with the agent concentration. Note that the flame shown in Figs. 4d and 4h is eventually blown out of the computational domain.



Fig. 5. Experimentally measured flame area for cup-burner flame with added CF₃H or CO₂.

A comparison of temperature evolutions shown in Fig. 4 for different amounts of added CF₃H suggests that the amplitude of the flame oscillation, determined based on the maximum and minimum radial locations of the flame surface, is more in flames with higher CF₃H (7 mm for 0%, 11.4 mm for 5%, and 10 mm for 10.05% in Figs. 4e, 4f, and 4g, respectively). This increase in flame fluctuation correlates with the vortex growth noted in CF₃H-added flames. This phenomenon was also observed experimentally. Fig. 5 shows the experimentally measured flame area for methane-air cup-burner flames with added CF3H or CO₂ in the air stream up to their extinction value. The error bars represent the standard deviation of the variation in area for the approximately 30 images taken for each value of X_{CO_2} or X_{CF_3H} . Nearly all of that variation occurs from the natural fluctuation in the flame size as the flame flickers. Hence, the larger error bars denote more flame size fluctuation. As indicated, adding CF₃H increases both the flame size and the fluctuation in the flame size, whereas adding CO2 results in a smaller flame size increase and no increase in the flame size variation. These observations are consistent with CF3H's reaction in the flame. The increase in flame size is expected since CF₃H dilutes the oxidizer stream, and also acts as a fuel species, which increases the overall O₂ demand (both of which increase the flame height) [41,42]. The increase in flame fluctuation is due to the higher buoyancy force: with added CF₃H the total heat release is larger (about a factor of 2, as estimated from the larger flame size), and the density of the oxidizer stream is about 13% higher. This increased fluctuation may have bearing when comparing fire suppressant agents applied to flames in 1g vs reduced gravity environments. The density of the agent, its heat release, and the density of its decomposition products (if any) will all affect the buoyancy forces, and hence the flame flickering and agent entrainment in extinguishing the flame.

4.3. Comparison of flame suppression in cup and counterflow burners

Since counterflow diffusion flames are commonly used to assess the performance of fire-suppressant compounds [18,19,43-45], it is of value to compare the present measurements in the cup burner to those in the counterflow diffusion flames. Data exist in the literature concerning CF3H addition to methaneair counterflow diffusion flames, both in experiments [18,46] and numerical calculations [47]. Since experiments have shown [43] that the extinguishment concentrations for inhibitors added to cup-burner flames are closest to counterflow diffusion flames at low strain, it is most relevant to compare the present cupburner flames with counterflow diffusion flames at these low strain rates ($\sim 50 \text{ s}^{-1}$). Of the previous work, only the data of Papas et al. [18] go to strain rates near 50 s⁻¹, and we use those here.

The present 2-D time-dependent code with full chemistry was used to calculate the flame structure for two strain-rate conditions corresponding to those of Papas et al. A low global strain rate of 30 s⁻¹ was achieved by forcing a 0.2-m/s fuel jet toward a 0.2-m/s air jet with a separation distance of 13 mm. Similarly, a moderate global strain rate of 90 s⁻¹ was obtained from the use of 0.6-m/s velocity fuel and air jets. Complete axisymmetric simulations (not just along the stagnation line) were made using the CFD code employed for the simulation of cup-burner flames. The calculated peak temperature in the flame as a function of the inhibitor volume fraction is shown in Fig. 6 for the counterflow flames with added CF₃H



Fig. 6. Decrease in peak flame temperature up to extinction in counterflow diffusion flame with added CO_2 or CF_3H in the air stream, for flow conditions corresponding to global strain rates of 30 and 60 s⁻¹. Extinction conditions of cup-burner flames with added CO_2 or CF_3H shown by vertical bars.

or CO₂ and global strain rates of 30 or 90 s⁻¹. Also shown (vertical bars) are the extinction conditions of the cup-burner flames with added CF₃H (described above) and CO₂ (described previously [28,29]). As the figure shows, for the low- and moderately-strained counterflow flames, the minimum CF₃H volume fractions required to extinguish the flames were found to be 11.95 and 8.04%, which compare well with the experimental results [18] of 11.0 and 8.0%, respectively. These results provide additional support of capabilities of the present numerical code and kinetic mechanism to predict the extinction conditions of methane–air flames with added CF₃H.

As Fig. 6 shows, the flame temperature decreases with the addition of the inhibitor, and decreases more gradually with the addition of CF3H as compared to that of CO₂. The weakly strained (30 s⁻¹) flame extinguished when the temperature dropped to 1810 or 1570 K with the addition of CF₃H or CO₂, respectively, while the moderately strained (90 s⁻¹) flame extinguished when the temperature dropped to 1755 or 1585 K for the respective agent. Previous calculations [48] for a 23%-diluted methane/air counterflow diffusion flame suggest that flame extinction occurs when the global strain rate is increased to 120 s^{-1} , and at this strain rate the flame temperature would decrease to 1500 K. The extinction temperature of CO2-added flame is close to that of the pure methane flame indicating that addition of CO2 alters chemical

kinetics minimally. On the other hand, the higher temperature at extinction for counterflow diffusion flame with CF_3H suggests significant changes in chemical kinetics with the addition of CF_3H . Consequently, the chemical agent CF_3H is more effective in extinguishing cup-burner flame compared to the inert agent CO_2 .

Fig. 6 further suggests that the extinction conditions (agent concentrations) for the cup-burner flames with added CF3H or CO2 fall in between the conditions obtained with the counterflow diffusion flames with low (30 s^{-1}) and moderate (90 s^{-1}) strain rates. The flame extinction process itself is markedly different in the two flame types. In the cup-burner, the flame base first detaches from the burner rim, similar to lifting of jet diffusion flames [49], and then moves downstream until it blows out of the computational domain. This blowoff behavior is maintained even for cases with CF₃H volume fractions much greater than 10.1% (although with higher CF₃H volume fractions, the time required for complete blowoff decreases sharply). In contrast, the counterflow diffusion flames extinguish nearly instantaneously and uniformly over the flame surface when the extinction concentration is reached and hence, flame stability becomes irrelevant (unless the applied strain rate is varied using methods such as variable burner separation [33] or jets with varying velocity profiles [50]).



Fig. 7. Reaction-kernel structure of cup-burner flame with 5% CF_3H added to airflow. (a) Heat-release-rate (J/cm³/s) contours are superimposed on velocity field. Dotted lines represent locations of maxima in heat release rate at different heights. Isocontours of volume fraction (broken lines) and rate of production (solid lines) of (b) O_2 , (c) H, (d) OH, (e) CF_3H , and (f) CF_2O .

4.4. Chemical description of cup-burner flame extinguishment

The structure of the peak reactivity spot (i.e., reaction kernel) formed in the flame base (edge) was found to be useful for understanding the stability of a *jet* diffusion flame [49,51] and is an important region in the present cup-burner flames also. Detailed base structures of the cup-burner flames with 5 and 10.05% CF₃H added to the air stream are shown in Figs. 7 and 8, respectively. Figs. 7a and 8a show the contours of heat release rate superimposed on velocity fields, with the locations of maximum heat release rate in radial scans connected using dotted lines. A comparison of these figures indicates that as the volume fraction of CF₃H increased from 5 to 10.05%, (1) the flame base has broadened, (2) the peak heat release rate at the reaction kernel decreased from 114 to 95 J/cm³/s, and (3) the shape of the hook-like flame-base structure transformed from air hook to fuel hook (compare 50-J/cm³/s contours). As pointed by Takahashi and Katta [51], the methane flames do not form tripleflame structures in the base regions. The shift in the hook-like flame structure results from the increase in



Fig. 8. Reaction-kernel structure of cup-burner flame with 10.05% (limiting value) CF_3H added to airflow. (a) Heat-release-rate $(J/cm^3/s)$ contours are superimposed on velocity field. Dotted lines represent locations of maxima in heat release rate at different heights. Isocontours of volume fraction (broken lines) and rate of production (solid lines) of (b) O₂, (c) H, (d) OH, (e) CF_3H , and (f) CF_2O .

air and fuel leakage through the increased separation between the flame base and burner lip (from 2.2 to 6.0 mm, based on the reaction kernel location), and the increased fuel load (resulting from the inhibitor) on the air side of the flame.

The production/destruction rates of O_2 , H, OH, CF_3H , and CF_2O are superimposed (solid lines) on their respective species concentration contours (dashed lines) in Figs. 7b, 7c, 7d, 7e, and 7f, respectively for the flames with 5% CF_3H , and in Figs. 8b, 8c, 8d, 8e, and 8f, respectively for those with 10.05%

 CF_3H . The contour showing the radial location of the maxima in heat release rate at each height is plotted in all these figures with dotted lines. From Figs. 7b and 8b, it is observed that the oxygen consumption rate is decreased with increased CF_3H , and the peak heat release rate in the reaction kernel is occurring at a lower oxygen concentration. While the former observation directly implies weakening of the flame base, the latter also suggests weakening of the local flame as a weaker flame consumes less oxygen and hence, moves toward a location where the concentration.



Fig. 9. Flame structures in (a) trailing flame and (b) reaction kernel of a cup-burner flame with 0, 5, and 10.05% CF_3H added to the airflow.

tration of oxygen is lower. The production and destruction rates of H and OH radicals are significantly decreased with increased CF₃H (compare Figs. 7c and 7d with Figs. 8c and 8d, respectively); however, while the concentration of the OH near the reaction kernel location has decreased from 1.0 down to 0.75, the concentration of H at this location has not changed much. Finally, while all the CF₃H diffusing into the flame is consumed, a significant amount of CF₂O is produced in the flame zone.

While the global features shown in Figs. 7 and 8 indicate a weakening of the flame base with addition of CF_3H , the mechanism of this weakening is not apparent from these figures. For understanding the chemical influence of the inhibitor on the stabilization region, the species volume fractions and reaction fluxes are examined in detail near the reaction kernel. The volume fractions of the chain-carrying radicals H, O, and OH, along with the temperature profile, are shown in Fig. 9 for radial line passing through the (a) trailing diffusion flame part and (b) reaction kernel of a cup-burner flame with CF_3H added to the air stream at 0, 5, and 10.05%. While the radial line for the base-region flame is obtained at locations where peak temperature just reached a value of

1600 K (2.0, 2.2, and 5.9 mm above the burner lip for CF₃H added at 0, 5, and 10.05%, respectively), the radial line for the trailing flames are obtained 10 mm above the burner lip. As mentioned earlier, the flame with 10.05% CF₃H represents the one very close to blow off condition.

Examination of Fig. 9a indicates that in the trailing-flame region, compared to the neat case (0% CF₃H), addition of 10.05% CF₃H decreases the peak temperature by only 49 K, while decreasing the volume fraction of OH by about 40%, and having little (about 10%) effect on H and O volume fractions. In contrast, in the reaction kernel (Fig. 9b), all three radicals are present (for the uninhibited flames) at about half the concentration as in the trailing flame, and more importantly, addition of 10.05% CF₃H reduces the concentrations of all radicals in the reaction kernel by about a factor of 4. Addition of CF3H above 10.05% causes further reduction in the concentrations of H, O, and OH radicals, which, in turn, initiates the flame-quenching process in the base region. It is known [49,52] that stability of the flame base (reaction kernel) depends not only on the chemical reactivity but also on the local velocity. The reduced concentrations of radicals in the base region for CF3H concentrations greater than 10.05% cannot sustain a flame in the prevailing velocity field, and the flame base moves downstream in search of another stabilization location. If the flame base finds a stabilization location before its global reaction rate falls below the absolute quenching limit, defined as the minimum reaction rate required for a flame to sustain itself in a zero-strain-rate flowfield, the flame reestablishes itself with a different standoff distance; otherwise, the flame extinguishes and the process is called blowoff.

Addition of CF_3H to a cup-burner flame is unlikely to lead to extinction everywhere simultaneously. As indicated in Fig. 9, the radical volume fractions are initially lower in the reaction kernel, and addition of CF_3H also has a larger effect there. The trailing part of the flame, with its higher temperature, lower strain and higher radical volume fractions, would require higher volume fractions of CF_3H than the base region to be extinguished first. Hence, the cup-burner flame will always be extinguished through a blowoff process starting at the flame base.

In order to determine the mechanism of CF_3H in reducing radical concentrations in the flame base, the chemical reactions involving H, O, and OH are examined in detail in the base region. The inhibition of premixed and counterflow diffusion flames by CF_3H has been shown to be due to reduction in the chaincarrying radical concentrations by radical trapping reactions to form HF [7,10,13,45,53,54]. It is of interest to determine whether radical trapping via HF formation is the inhibition mechanism through which CF_3H



Fig. 10. Sum of rates of reaction producing or consuming H atoms at a height that goes through the flame base, for CF_3H added at 5% (left) or 10.05% (right) to the air stream, as a function of radial position. (Key: F+/-, reactions which contain a fluorine-containing species; HC+/-, those that do not.)

works in the cup burner, and how the role of those reactions varies in the base and trailing region of the flame.

As in Fig. 9, the flame structure is examined via a radial slice at two heights: one in the trailing part of the flame, and one passing through the reaction kernel. For each radial profile, the reaction rates of all the reactions that are producing (or consuming) H, O, and OH are summed. For example, in Fig. 10, the net rates due to all reactions that produce (or consume) H atoms are shown for a radial slice that goes through the flame base. Data are shown for 5% (left) or 10.05% (right) CF₃H added to the air stream. The sum of all reactions of H with a fluorine-containing species (production F+, consumption F-, and the net Fnet of H atom) are shown, along with the sum for all other reactions (i.e., the hydrocarbon part of the mechanism) HC+, HC-, and HCnet and the sum of all reactions H_{net} (= F_{net} + HC_{net}). Note the three times larger scale for the 5% CF₃H case. As Fig. 10 shows, the production and consumption of H atom (as well as the net) by the hydrocarbon reactions is about three times lower in the flames with 10.05% CF₃H. Nonetheless, in both the 5 and 10.05% CF₃H cases, the net effect of the hydrocarbon reactions is to produce H atoms; in contrast, the net effect of the reactions containing F species is to consume H atoms. With the higher CF₃H loading, the consumption of the H atoms by the fluorine reactions is larger (relative

to the radical production by the hydrocarbon reactions); in fact, for the higher loading, there is a net loss of H atoms by all reactions, whereas in the 5% CF_3H case, this region of the flame is a net source of H atoms.

Because of the fast radical shuffle reactions in hydrocarbon systems, it is important to examine the reaction rate of other radicals as well. Fig. 11 shows the sum of the rate of all radical reactions involving H, O, and OH (Netnet) in the reaction kernel (lower figures) and trailing flame (upper figures) of the flame, with CF₃H added to the air stream at 5 (left figures) and 10.05% (right images). As in previous figures, curves are shown for the hydrocarbon (HC) and fluorine (F) reactions, the production (+) and consumption (-)reactions, and the net. Also shown are the heat release Q and temperature T. Note that in these figures solid and dashed lines show the results for 5 or 10.05% CF₃H, while in the left two figures (for 5% CF₃H) the solid lines with open circles show the result for 0% CF₃H.

Examining the lower images in Fig. 11 (for the reaction kernel) we see that in both 5 and 10.05% cases, the peak temperature is around 1600 K, and the heat release is monotonic, peaking near the radius of peak temperature. The hydrocarbon reactions produce chain-carrying radicals, while the net effect of the fluorine reactions is to consume them. With 5% CF_3H , there is a net production of radicals, whereas



Fig. 11. Sum of reaction rates of all reactions involving H, O, or OH, for addition of 5% CF₃H (left) or 10.05% CF₃H (right) to cup-burner flames. The upper figures are for the trailing part of the flame, and the lower figures, the reaction kernel. As in Fig. 9, curves are shown for production (+), consumption (–) and the net effect on radical reaction rates, for the fluorine (F) and hydrocarbon (HC) reactions. Also shown are the temperature and heat-release rate.

with 10.05% CF_3H , there is a net consumption of radicals in this reaction kernel.

For the trailing part of the flame (upper frames in Fig. 11), the behavior is different. Although the peak temperature is higher (near 1800 K), the sum of the rates of reactions involving radicals is significantly lower (note scale changes). As illustrated by both the reaction-rate and the heat-release curves, the flame in this region has a two-zone structure: the leftmost reaction zone (near r = 9 mm) is due to consumption of the methane and its fragments, while that near r = 10 mm is due to consumption of the CF₃H and its fragments (which approach from the air side). In fact, for the case of 10.05% CF₃H, there is some heat release and reaction rate near r = 7.5 mm which is due to reaction of the CF₃H that enters the fuel stream near the lifted flame base as described above. In the trailing region of the flame for both CF₃H loadings (upper frames, left and right images), the radicals are produced near the central range of radius (9 < r < 10 cm), but consumed outside this region.

Generally speaking, in the reaction kernel of the flame, the fluorine-containing reactions have the largest effect on H atoms (consuming them), a smaller effect on OH atoms (mildly consuming), and a small effect to increase O atoms. The effect in all cases increases with higher CF₃H loading. The net effect is that, in the base region, the fluorine-containing reactions account for about 7 or 10% of the total radical consumption for the two cases of 5 or 10.05% CF₃H addition, respectively. In the trailing part of the flame, it is more complicated because of the multizone structure; however, the fluorine reactions always have the Table 2

Fraction of total fluorine reaction radical consumption by specific reactions, for O, H, and OH, in the reaction kernel (RK) and trailing flame (TF) of cup-burner flames, with CF₃H added to the air stream at 5 or 10.05%

Reaction i	ω_i/ω_{all} fluorine reactions				
	5RK	5TF	10RK	10TF	
	O-atom	1			
$CF_2 + O = CFO + F$	0.24	0.27	0.27	0.34	
$CF_3 + O = CF_2O + F$	0.26	0.43	0.12	0.33	
$CF_3H + O = CF_3 + OH$	0.26	0.25	0.27	0.22	
$C_2HF + O = CFCO + H$			0.02	0.03	
$CH_3CH_2F + O = CH_2FCH_2 + OH$	0.08		0.19		
$O + H_2O_2 = OH + HO_2$			0.03		
$O + CH_2OH = OH + CH_2O$			0.02		
	H-atom	1			
$CF_2 + H = CF + HF$	0.40	0.23	0.52	0.44	
$CF_3 + H = CF_2 + HF$	0.35	0.37	0.22	0.26	
CF + H = C + HF		0.12		0.06	
$CF_3 + H_2 = CF_3H + H$	0.11	0.05	0.14	0.06	
$CH_2CHF + F = CH_2CF_2 + H$	0.02	0.03	0.04	0.03	
$CF_2O + H = CFO + HF$		0.10		0.03	
$CF_3CF_3 + H = CF_3CF_2 + HF$		0.04		0.02	
	OH-ator	n			
$CF_3H + OH = CF_3 + H_2O$	0.66	0.55	0.74	0.55	
$CF_3 + OH = CF_2O + HF$	0.22	0.36	0.12	0.33	
$CF_2 + OH = CF_2O + H$		0.03	0.03	0.04	
CF + OH = CO + HF	0.03	0.02		0.02	
$CH_2CF_2 + OH = CF_2CH + H_2O$	0.02		0.06		
$CH_2F + OH = CH_2O + HF$			0.01		

net effect of consuming radicals (for O, H, and OH), and form a larger fraction of the radical consuming reactions. Nonetheless, the flame in the trailing part is still robust since, even for the case of 10.05% CF₃H, there is a region (near r = 9 mm) at which the radical production can proceed in the absence of fluorine or fuel species.

The specific fluorine reactions responsible for the radical consumption are shown in Table 2. For O atoms, its consumption occurs mainly through reaction with CF2, CF3, and CF3H (in approximately equal proportions); in the base region, reaction with CH₃CH₂F is also quite large. For H atom, reaction with CF₂, and CF₃ are even more important, while reaction with CF₃H itself is important but less so than for O atom. In the trailing flame region, consumption of H by reaction with CF, CF₂O, and CF₃CF₃ are also noteworthy. For OH consumption, reaction with CF₃H itself is the largest sink of the radical, followed again by CF₃, CF₂, and CF. It is interesting to observe that for each CF₃H loading (5 or 10.05%), the reactions in the trailing region of the flame favor the CF₃H consumption intermediates which are further away from the parent molecule, as compared to in the base region. For example, for OH, the smaller fragments (CF₃, CF₂, etc.) are favored over CF₃H further up in the flame because they are more abundant there.

It is also noteworthy that in this system, like others with fluorinated species [7,10,13], there is no catalytic cycle (as there is with Br). That is, due to the stability of the HF molecule (which is the fate of fluorine atoms in the system), the radical trapping species are not reformed in significant quantities, so there is radical trapping, but not a catalytic cycle. It would be of interest to examine cup-burner flames with an agent which does have a catalytic cycle (such as CF_3Br).

5. Conclusions

A periodically oscillating methane–air diffusion flame formed over a cup burner was used to explore the inhibition characteristics of CF₃H. This laminar flame, established with a negligibly small fuel flow rate and a low-speed annular-air flow, generated large-scale, low-frequency (\sim 11 Hz), highly organized, buoyancy-induced vortices on the air side. A detailed chemical kinetic mechanism having 82 species and 1510 elementary reactions was incorporated into an axisymmetric CFD model for the investigation of cup-burner-flame extinction by CF₃H. The numerical model was used to predict the extinguishment condition for both the cup-burner flames and counterflow diffusion flames with CF₃H added to the air stream. For agent displacing air in the cup burner, the calculated extinguishment volume fraction of CF₃H was 10.1% compared to an experimental value of (11.7 ± 0.8) %; for agent displacing the nitrogen in air, these values were 19.2 and (20.3 ± 1.5) %, respectively. These results represent the first time that the extinguishment conditions of a cup-burner flame have been predicted for an agent which decomposes in the flame.

For comparison, the present 2-D, time-dependent code was used to predict the extinction conditions of counterflow diffusion flames at global strain rates of 30 and 90 s⁻¹ in which CF₃H was added to the air stream. The predicted extinction volume fraction was 11.95 and 8.04% for these two strains, respectively, compared to the documented values of 11.0 and 8.0%. Unlike the cup-burner flames for which the calculations showed blowoff-type extinguishment, the predicted extinction of the counterflow diffusion flames was uniform and abrupt, as in the experiments.

Addition of CF_3H had little effect on the calculated peak temperature of the cup burner flame, but with 10.05% CF_3H (the near-limiting value), the magnitude (but not frequency) of flame oscillation was larger, and the flame base was lifted about 4 mm higher than without CF_3H . Extinction of a cup-burner flame takes place as the base of the flame becomes destabilized and moves downstream in search of a new stabilization location, eventually being blown out of the computational domain (a process similar to that observed in the experiment).

The flame destabilization was shown to be due to lower chain-carrying radical production rates (and volume fractions) in the flames inhibited by CF₃H. Examination of the elementary reaction rates revealed that in both the base and trailing regions of the cup-burner flame, the reactions involving fluorinated species effectively trap radicals through reactions primarily with CF₃H, CF₃, CF₂, CF, and CF₂O, ultimately forming the relatively nonreactive species HF. Notwithstanding, the radical production and consumption in the base region are affected more strongly by addition of CF₃H, and the radical production rates are more effectively quenched there than higher up in the flame, leading to destabilization in the base region first.

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