

# Extinguishment of Cup Burner Flames of Propane and the Aerosol Can Simulator Fuel by $\text{CF}_3\text{Br}$ and $\text{C}_2\text{HF}_5$

Fumiaki Takahashi<sup>1</sup>, Viswanath R. Katta<sup>2</sup>, Gregory T. Linteris<sup>3</sup>, *and* Oliver C. Meier<sup>4</sup>

<sup>1</sup> Case Western Reserve University, Cleveland, OH 44106, USA

<sup>2</sup> Innovative Scientific Solutions, Inc., Dayton, OH 45440, USA

<sup>3</sup> National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

<sup>4</sup> The Boeing Company, Seattle WA 98124, USA

Calculations have been performed for co-flow diffusion flames of propane and a propane-ethanol-water fuel mixture, prescribed for the Federal Aviation Administration (FAA) Aerosol Can Simulator, in the cup-burner configuration, with added  $\text{CF}_3\text{Br}$  and  $\text{C}_2\text{HF}_5$ . The time-dependent, two-dimensional numerical code, which includes a detailed kinetic model (177 species and 2986 reactions) and diffusive transport, has predicted the minimum extinguishing concentration of agent and revealed the unique two-zone flame structure causing combustion enhancement by  $\text{C}_2\text{HF}_5$  in zero gravity.

## 1. Introduction

Because of its destruction of stratospheric ozone, the use of the effective fire suppressant  $\text{CF}_3\text{Br}$  (Halon 1301) has been discontinued, except for certain critical applications such as the aircraft cargo-bay fire suppression. Recently, some halon replacement agents, including  $\text{C}_2\text{HF}_5$  (HFC-125), have been evaluated in a mandated Federal Aviation Administration (FAA) aerosol can test (ACT) [1], in which a simulated explosion of an aerosol can, caused by a fire, must be suppressed by the agent. Unlike  $\text{CF}_3\text{Br}$ , the other agents created a higher over-pressure in the test chamber (when added at less than the inerting concentration) and thus failed the test. Similar combustion enhancement by various fire-extinguishing agents has been described in other experiments for certain conditions.

Recent work [2, 3] employing thermodynamic equilibrium and perfectly stirred-reactor calculations (for premixed systems) indicated that higher overpressures in the FAA ACT might be due to higher heat release from reaction of the inhibitor itself. Nonetheless, the fire-extinguishing agents should still reduce the overall reaction rate and inhibit the reaction. For diffusion flames, however, the inhibition or combustion enhancement processes by halogenated agents are not yet fully understood. This paper extends previous work [4-10] on cup-burner flames to more realistic fuels and agents in zero-gravity to uncover essential physical and chemical processes.

## 2. Computational Method

A time-dependent, axisymmetric numerical code (UNICORN) [11, 12] solves the axial and radial ( $z$  and  $r$ ) full Navier-Stokes momentum equations, continuity equation, and enthalpy- and species-conservation equations on a staggered-grid system. A clustered mesh system is employed to trace the gradients in flow variables near the flame surface. The thermo-physical properties such as enthalpy, viscosity, thermal conductivity, and binary molecular diffusion of all of the species are calculated from the polynomial curve fits developed for the temperature range

300 - 5000 K. 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 was incorporated into the energy equation. Only radiation from  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  was considered in the present study.

The finite-difference forms of the momentum equations are obtained using an implicit QUICKEST scheme [11], 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) matrix-decomposition technique. The boundary conditions are treated in the same way as that reported in earlier papers [4-10].

A comprehensive reaction mechanism was assembled. The four-carbon hydrocarbon mechanism of Wang and co-workers [13, 14] (111 species and 1566 one-way reactions) was employed, and detailed reactions of ethanol (5 species and 72 reactions) by Dryer and co-workers [15-17] were added. For  $\text{CF}_3\text{Br}$  inhibition, the bromine parts of the mechanism of Babushok et al. [18, 19] (10 additional species and 148 reactions) were added. Finally, a subset (51 species and 1200 reactions) of NIST HFC starting mechanism [20-21] was used for HFCs. The final chemical kinetics model (177 species, 2986 reactions) is integrated into the UNICORN code. Validation of the code was performed. The predicted extinction strain rates for propane-air opposing-jet diffusion flames (no agent) were within 7.5% of the measured values by Zegers et al. [22]. The fuel is propane or the ACT fuel gas mixture (volume fractions:  $\text{C}_3\text{H}_8$ , 0.159;  $\text{C}_2\text{H}_5\text{OH}$ , 0.454; and  $\text{H}_2\text{O}$ , 0.387), and the agent is  $\text{CF}_3\text{Br}$  or  $\text{C}_2\text{HF}_5$  added to "air" (21 %  $\text{O}_2$  in  $\text{N}_2$ ).

### 3. Results and Discussion

The flame-base region supports a trailing flame and controls the flame attachment and detachment processes [23]. Small variations in the agent mole fraction in the coflowing oxidizing stream ( $X_a$ ) result in profound changes near the extinguishment limit. Figure 1 shows the calculated structure of a zero-gravity ( $0g_n$ ) near-limit propane flame with agent ( $\text{C}_2\text{HF}_5$ ) added at  $X_a = 0.093$ . The variables include the velocity vectors ( $\mathbf{v}$ ), isotherms ( $T$ ), and heat-release rate ( $\dot{q}$ ). The flame base is already detached and lifted above the burner rim. The contours of the heat-release rate showed a peak reactivity spot (i.e., the *reaction kernel* [23]) at the height from the burner rim,  $z_k = 10.9$  mm. The chain radical species as well as heat diffused back against the incoming flow at the flame base (edge), thus promoting vigorous reactions to form the reaction kernel.

Figure 2 shows the radial and axial variations of the species mole fractions ( $X_i$ ), temperature, and

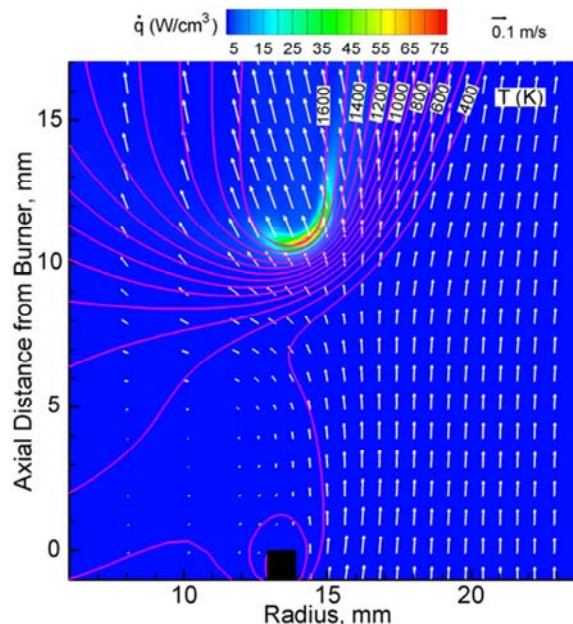


Fig. 1. Calculated structure of a  $0g_n$   $\text{C}_3\text{H}_8$  flame in air with added  $\text{C}_2\text{HF}_5$  at  $X_a=0.093$ .

heat-release rate (HRR) crossing the reaction kernel of the flame at  $X_a=0.093$ . The general trend in the radial plot at  $z = 10.9$  mm (Fig. 2a) is similar to that in the methane flame with added nitrogen [10], except that  $X_{CO}$  was much larger,  $X_{H_2O}$  was much smaller, and there are broad and large concentrations of HF,  $CF_2O$ , and minor fluorinated intermediates on both fuel and oxidizer sides. The heat-release rate peak was formed on the oxidizer side. The axial plot (Fig. 2b) revealed the premixed-like nature of the unique flame-base structure. At increasing axial distances along  $r = 14.4$  mm, the mole fractions of the reactants ( $C_3H_8$ ,  $O_2$ , and  $C_2HF_5$ ) decreased, intermediate species and chain radicals (H, O, and OH) peaked, the temperature increased, the heat-release rate peaked, and the final products ( $CO_2$ , HF, and  $CF_2O$ ) were formed. Surprisingly,  $H_2O$  and  $H_2$  formed by hydrocarbon- $O_2$  reaction were completely converted to HF and  $CF_2O$ . Notice that  $X_O$  was much higher than  $X_H$  and  $X_{OH}$ .

Figure 3 shows the radial variations of calculated variables crossing the trailing flame at  $z = 15.9$  mm ( $z_k + 5$  mm). At this height, the flame structure is characterized by two zones (inner and outer) as is evident from two heat-release rate peaks. In the inner zone ( $11 < r < 15$  mm),  $T$ ,  $X_H$ ,  $X_O$ , and  $X_{OH}$  peaked, and hydrocarbon fuel fragments and, more importantly  $X_{H_2O}$  and  $X_{H_2}$  from the fuel side, diminished, unlike in a neat diffusion flame without a halogenated agent [10]. As the case at the reaction kernel,  $X_O$  peak was much larger than  $X_H$  and  $X_{OH}$  and penetrated into the outer zone. In the outer zone ( $15 < r < 18$  mm), the agent ( $C_2HF_5$ ) from the air side decomposed and diminished, the mole fractions of many fluorinated species ( $CF_2O$ ,  $CF_4$ ,  $CF_3-CF_3$ ,  $CHF_3$ , etc.) peaked.

Figure 4 shows the radial variations of the calculated production(+)/consumption (-) rates (Fig. 4a) and heat-release rates (Fig. 3b) of species  $i$  crossing the trailing flame at  $z = 15.9$  mm. In the inner zone,  $H_2$ ,  $H_2O$ , CO,  $O_2$ , F, and  $CF_2O$  were consumed, HF and  $CO_2$  were

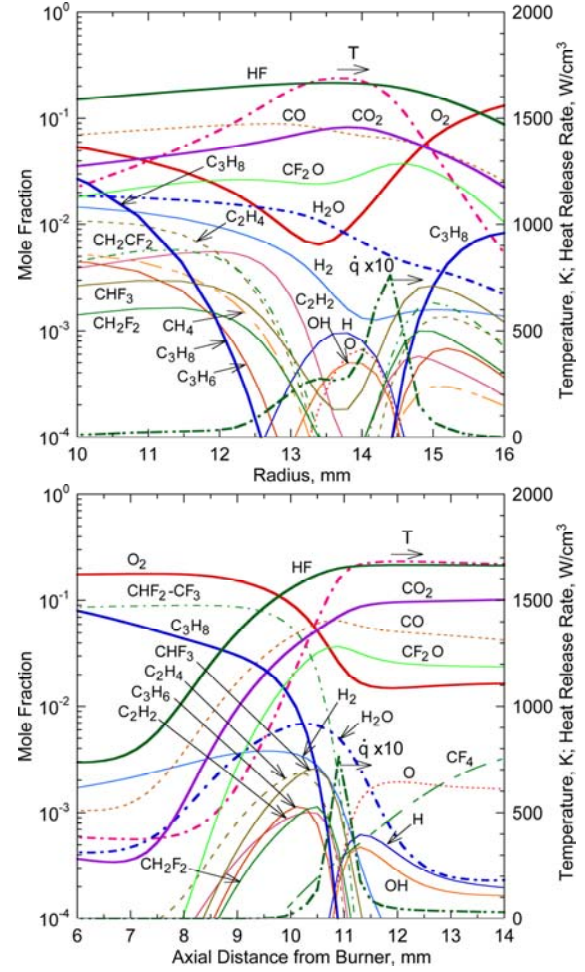


Fig. 2 Calculated structure through the reaction kernel for a  $0g_n$   $C_3H_8$  flame in air with  $C_2HF_5$  at  $X_a=0.093$ . (a) Radial ( $z=10.9$  mm) and (b) axial ( $r=14.4$  mm) variations.

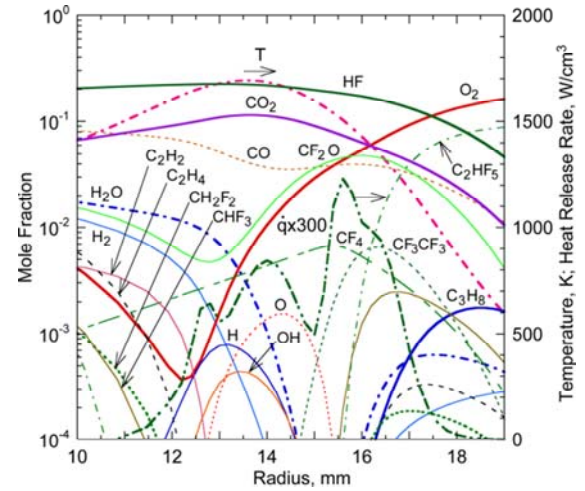


Fig. 3 Calculated structure across the trailing flame for a  $0g_n$   $C_3H_8$  flame in air with  $C_2HF_5$  at  $X_a=0.093$  ( $z_k=15.9$  mm).



formed, and the chain radicals (H O, and OH) were formed and consumed depending on the radial location. In the outer zone,  $C_2HF_5$ , and  $O_2$  were consumed, HF,  $CF_2O$ , and CO were formed, and F was formed on the fuel side and consumed on the air side. The major contributors to the overall heat-release rate (Fig. 4b) were the formation of  $CO_2$  and HF in the inner zone and  $CF_2O$  and HF in the outer zone.

Figure 5 shows the maximum heat-release rate of each elementary step crossing the reaction kernel and the trailing flame ( $z = 10.9$  mm and  $15.9$  mm, respectively). At the reaction kernel, many steps for  $CF_2O$  and HF (and  $CO_2$ ) formation contributed to overall HRR, while in the trailing flame, HF formation from  $H_2O$  and  $H_2$  in addition to the  $CO_2$  formation (inner zone) and the HF from  $C_2HF_5$  and the  $CF_2O$  from  $CF_3$  (outer zone) were the main contributors.

The structure of the ACT fuel flame (not shown) was very similar to that of the propane flame, except for generally larger  $X_{H_2O}$  and  $X_{C_2H_5OH}$ , and smaller  $X_{C_3H_8}$  because of the initial fuel composition.

Figure 6 shows the effects of the agent volume fraction in the coflowing oxidizer on the calculated axial ( $z_k$ ) and radial ( $r_k$ ) positions of the reaction kernel from the burner exit on the axis in both propane and ACT fuel flames with added  $CF_3Br$  or  $C_2HF_5$ . As  $X_a$  was increased, the axial standoff distance of the reaction kernel increased steeply as the calculated minimum extinguishing concentration (Table 1) approached, while the radial location remained nearly constant.

**Table 1 Minimum Extinguishing Concentrations**

Fuel	$C_3H_8$		ACT Fuel	
	$CF_3Br$	$C_2HF_5$	$CF_3Br$	$C_2HF_5$
Agent	$CF_3Br$	$C_2HF_5$	$CF_3Br$	$C_2HF_5$
MEC (%)	2.54	9.7	2.08	11.2

Figure 7 shows the temperature, heat-release rate, and a ratio of the heat-release rate and the total velocity at the reaction kernel. As  $X_a$  was

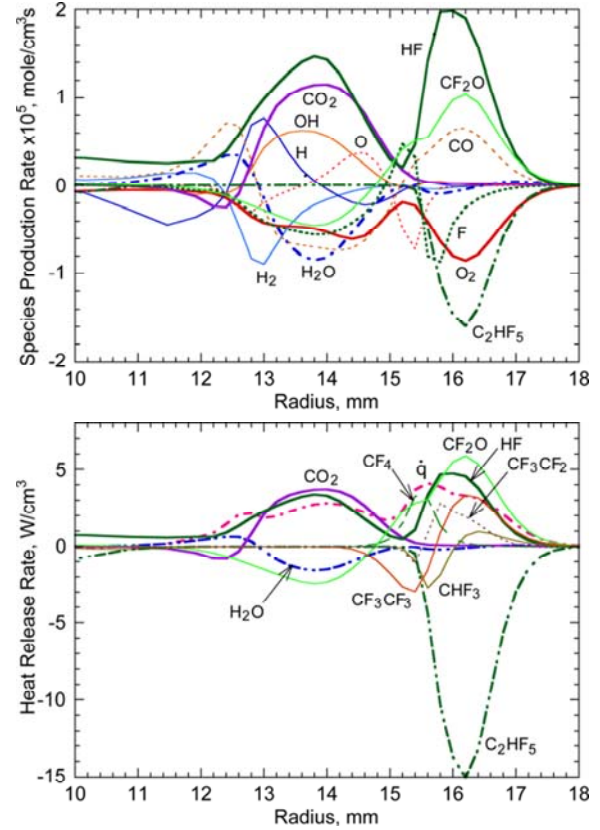


Fig. 4 (a) Species production rates, and (b) species and total heat-release rates crossing the trailing flame for a  $0g_n$   $C_3H_8$  flame in air with  $C_2HF_5$  at  $X_a=0.093$  ( $z=15.9$  mm).

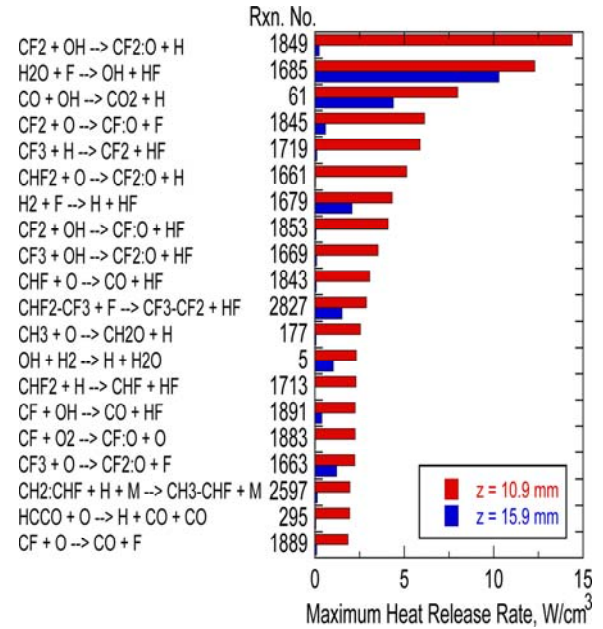


Fig. 5 Maximum heat flux of each step across the reaction kernel and trailing flame for a  $0g_n$   $C_3H_8$  flame in air with  $C_2HF_5$  at  $X_a=0.093$ .

increased for both fuels and both agents, the reaction kernel weakened (lower  $\dot{q}_k$ ), but the flame stabilized at higher  $T_k$ . The quantity  $\dot{q}_k/|v_k|$  (which relates to a ratio of the residence time and the reaction time, i.e., local Damkhöler number, at the reaction kernel [23]) decreased mildly, stayed nearly constant over a wide range, and decreased rapidly (just before lifted off) to a minimum level (3-4), which was comparable to the chemically passive agents [9, 10]. The reaction kernel lifted gradually downstream to seek a balance until blew out eventually.

Figure 8 shows the maximum temperature ( $T_{\max}$ ) in the trailing diffusion flame, the total heat-release rate ( $\dot{q}_{\text{total}}$ ) integrated over the entire flame, and the flame base region ( $\dot{q}_{<z_k+3 \text{ mm}}$ ) only. Unlike chemically passive agents [9, 10], which work thermally to reduce the flame temperature by dilution, the maximum flame temperature remained constant (or increased slightly) over an entire range of  $X_a$  varied until lifting. There was a striking difference between  $\text{CF}_3\text{Br}$  and  $\text{C}_2\text{HF}_5$  in  $\dot{q}_{\text{total}}$  over the entire flame.  $\dot{q}_{\text{total}}$  decreased (i.e., inhibition) with added  $\text{CF}_3\text{Br}$ , whereas it increased (i.e., combustion enhancement) with added  $\text{C}_2\text{HF}_5$ . On the other hand, for both fuels and both agents,  $\dot{q}_{<z_k+3 \text{ mm}}$  was nearly constant. Thus, the combustion enhancement occurred only in the trailing flame. In fact,  $(\dot{q}_{\text{total}} - \dot{q}_{<z_k+3 \text{ mm}})$  doubled with added  $\text{C}_2\text{HF}_5$  (at  $X_a \approx 0.1$ ). Although the volumetric heat-release rate in the trailing flame was an order-of-magnitude smaller than the peak  $\dot{q}_k$ , integration over the entire trailing flame zone made the total value much larger. This result suggests the significant implication that even if the reaction kernel, with premixed-like flame structure, is weakened by halogenated agent addition toward the flame stability limit, the trailing flame can burn more reactants (including the agent itself) because of the additional heat release to form HF and  $\text{CF}_2\text{O}$  in the aforementioned two-zone flame structure.

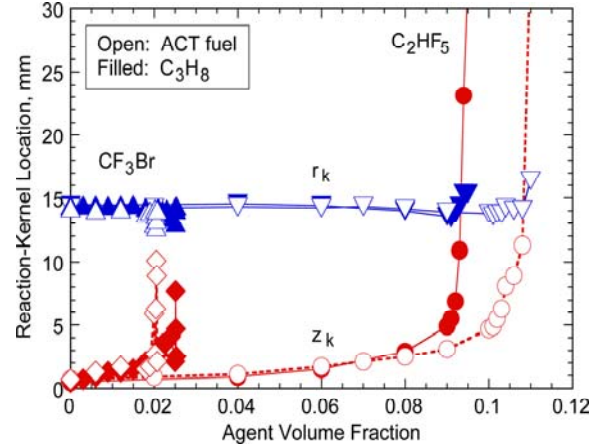


Fig. 6 Calculated reaction kernel coordinates of  $0g_n$   $\text{C}_3\text{H}_8$  and ACT fuel flames in air with added agent.

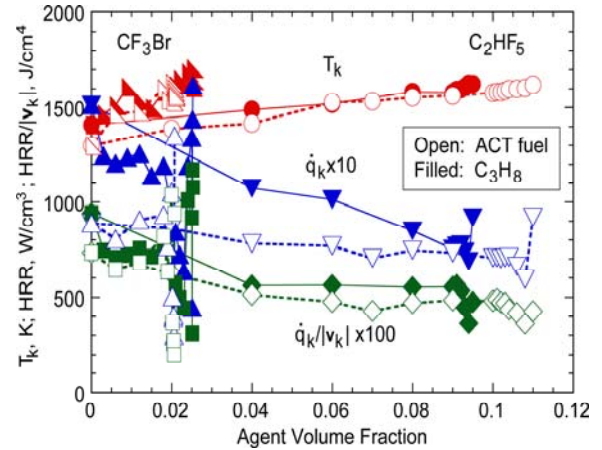


Fig. 7 Calculated heat-release rate, and its ratio to total velocity at the reaction kernel of  $0g_n$   $\text{C}_3\text{H}_8$  and ACT fuel flames in air with added agent.

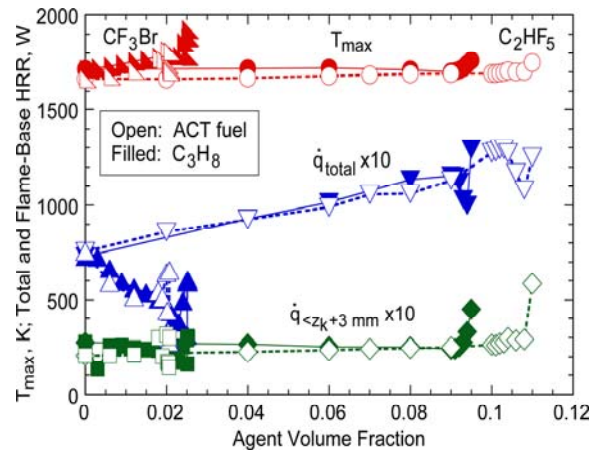


Fig. 8 Calculated maximum temperature, total heat release rate integrated over an entire flame, and the base region of  $0g_n$   $\text{C}_3\text{H}_8$  and ACT fuel flames in air with added agent.

#### 4. Conclusions

Addition of  $\text{CF}_3\text{Br}$  or  $\text{C}_2\text{HF}_5$  to the oxidizer weakened the flame attachment point (reaction kernel) at the flame base, thereby inducing the detachment, lifting, and blowout extinguishment eventually. Unlike chemically passive agents studied previously, the calculated maximum flame temperature in the trailing diffusion flame remained constant (or increased slightly) and the reaction kernel temperature increased, as a result of additional heat release from the inhibitor itself. Nevertheless,  $\text{CF}_3\text{Br}$  successfully inhibited the reaction and reduced the overall total heat release. By contrast, the  $\text{C}_2\text{HF}_5$  addition resulted in the combustion enhancement (increased total heat release) in the unique two-zone structure of the trailing flame: inner zone where  $\text{CO}_2$  was formed from  $\text{CO}$ , and  $\text{HF}$  from  $\text{H}_2\text{O}$  and  $\text{H}_2$ ; and outer zone where  $\text{CF}_2\text{O}$  and  $\text{HF}$  were formed from  $\text{C}_2\text{HF}_5$  and its fluorinated fragments.

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