Numerical Simulations of Gas-Phase Interactions of Phosphorus-Containing Compounds with Cup-Burner Flames

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Abstract

Computation has been performed for a methane-air co-flow diffusion flame, in the cupburner configuration, with a phosphorus-containing compound (PCC), dimethyl methylphosphonate (DMMP) or phosphoric acid, added to the oxidizer stream. The timedependent axisymmetric numerical code, which includes a detailed kinetics model (77 species and 886 reactions), diffusive transport, and a gray-gas radiation model (for CH₄, CO, CO₂, H₂O, and soot), has revealed the interaction of the gas-phase mechanisms of PCCs with the flame structure. The PCCs behave similarly with regard to flame inhibition: both raise the maximum temperature in the trailing flame, lower radical concentrations, and lower the heat-release rate at the peak reactivity spot (i.e., reaction kernel) at the flame base where the flame is stabilized. The mechanism of lowered radical concentrations is primarily due to catalytic cycles involving phosphorus species in both regions of the flame. For DMMP, which contains three methyl groups, the flame exhibited higher temperature and combustion enhancement in the trailing flame, with unique two-zone flame structure.

Keywords

Fire retardant • Fire suppression • Dimethyl methylphosphonate • Phosphoric acid • Diffusion flame structure

1 Introduction

Phosphorus-containing compounds (PCCs) are known to be effective at reducing flammability of polymers, with some ambiguity as to whether their effectiveness is due to gas phase reactions involving phosphorus intermediates, or a condensed-phase action [1]. The use of PCCs as fire retardant (FR) additives to plastics has increased dramatically in recent years [2-6]. In this application, the relative importance of gas phase chemistry and solid-phase effects such as char promotion has been debated, with recent work suggesting comparable importance for the two mechanisms, depending on the specific PCC chemistry [3, 7-9].

Due to environmental and health concerns on the most common gas-phase active FR formulations, brominecontaining compounds, with antimony trioxide usually added as a synergist, PCCs are considered as the chemical systems of highest interest to polymer companies and fire retardant manufactures, and the subject of the most intense recent investigations [10, 11].

While FRs increase their ignition time and reduce their heat release rates when burning [4, 12-13], PCCs have also been evaluated as potential halon replacements for fire

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suppression using cup burner, streaming tests [14, 15], and opposed-jet diffusion flames [16]. Further understanding of how PCCs affect flames is important for their efficient use.

A gas-phase chemical kinetics model of phosphorus compounds has been developed [17-22] over the years. Our calculations demonstrate that decomposition of DMMP (or other PCCs) is a relatively fast complicated process in a flame reaction zone. Once it decomposed, its main products (PO₂, PO, HOPO and HOPO₂) participate in the cycling sequence of reactions leading to the inhibition influence on the reaction in a flame zone. Figure 1 shows the simplified picture of the main inter-conversions of phosphorus-containing species.



Fig. 1 The abbreviated inhibition reaction cycles of PCC agents.

The sensitivity and reaction pathway analysis show two main inhibition cycles involving reactions of PO₂, HOPO and HOPO₂ species (PO₂ \Leftrightarrow HOPO and PO₂ \Leftrightarrow HOPO₂):

(1)
$$\begin{array}{l} H + PO_2 + M \rightarrow HOPO + M \\ OH + HOPO \rightarrow H_2O + PO_2 \\ H + HOPO \rightarrow H_2 + PO_2 \\ O + HOPO \rightarrow OH + PO_2 \end{array}$$

(2)
$$OH + PO_2 + M \rightarrow HOPO_2 + M$$

 $H + HOPO_2 \rightarrow H_2O + PO_2$

Each step of these cycling sequences involves a scavenging of H, O, and OH radicals, decreasing the concentration of radical pool, and, correspondingly, decreasing the flame reaction rate.

This mechanism has been used [23-27] to model the inhibition of premixed and counterflow diffusion flames with reasonable results. Nonetheless, no researchers have modeled or extensively studied co-flow diffusion flames, for which poor performance has been observed [16]. The effectiveness of compounds in gaseous flame inhibition is quite complex, depending upon the additive type as well as flame properties. Different inhibitors can be more or less effective depending upon the flame type. Dimethyl methylphosphonate (DMMP, PO[CH₃][OCH₃]₂) is about 141 times as effective as CO_2 in a premixed flame [28], 30 times as effective in a counter-flow diffusion flame [16] but only 3 times as effective in a cup-burner flame [29]. For phosphorus, this large variation in effectiveness with flame type has not been explained. Since phosphorous is and will be used as a gas-phase active FR, it would be of great value to understand the conditions for which it is expected to work.

The effects of DMMP in methane-air co-flow diffusion flames, in the cup-burner configuration, have recently been investigated experimentally [30] at the National Institute of Standards and Technology (NIST). The inhibitor effectiveness was measured as the minimum extinguishing concentrations (MECs) of CO₂ (added to the oxidizer) as a function of the DMMP loading (added to the oxidizer or fuel stream), in a similar manner as reported [31] in the literature for n-heptane flames. The particle formation in the flame with added DMMP was studied using the laser scattering technique. In addition, premixed flame simulations were used to approximate the flame chemistry (in the flame stabilization region) at the measured extinguishing conditions [30].

By using comprehensive numerical simulations, the present authors [32, 33] have studied the flame structure and inhibition (or combustion enhancement) processes in the cup-burner flames and, more recently, extended the effort to DMMP [34]. As DMMP has a significant heating value (due to methyl groups attached to the phosphorus atom), phosphoric acid (PO[OH]₃) is also used in this report for a comparison (since it provide the chemical inhibition without the fuel effect). The effectiveness of the chemical additive affects the flame structure, which then changes the additive effectiveness, etc. The overall goal of the present work is to understand how the properties of flames interact with the gas-phase inhibition, in support of the experimental research at NIST. The knowledge of detailed flame structure (temperature, species concentration, flow field, etc.) that affects fire retardant effectiveness will help to understand the reasons for the variation of effectiveness for phosphorus with flame type, and to shed light on how fire retardants which act in the gas phase actually retard ignition or reduce heat release. Ultimately, this work aims to aid in the development and application of new compounds that are likely to be used in flame-retarded high-volume thermoplastics to replace the widely used brominated retardants (and their antimony synergist).

2 Computational Methods

time-dependent, axisymmetric А numerical code (UNICORN) [35, 36] is used for the simulation of diffusion flames stabilized on the cup burner. The code solves the axial and radial (z and r) full Navier-Stokes momentum equations, continuity equation, and enthalpy- and speciesconservation 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 K to 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 is incorporated into the energy equation. Radiation from CH₄, CO, CO₂, H₂O and soot is considered in the present study.

A comprehensive reaction mechanism (77 species and 886 elementary reactions) is assembled and integrated into the UNICORN code for the simulation of methane flames with DMMP added to either the fuel or air stream. A chemical-kinetics model is compiled from a detailed reaction mechanism of GRI-V3.0 [37] for methane-oxygen combustion and a phosphorus mechanism [38] (41 additional species and 448 reactions).

The finite-difference forms of the momentum equations are obtained using an implicit QUICKEST scheme [35], 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 the pressure Poisson equations simultaneously and using the LU (Lower and Upper diagonal) matrix-decomposition technique.

Unsteady axisymmetric calculations for the cup-burner flames are made on a physical domain of 200 mm by 47.5 mm using a 351×151 non-uniform grid system that yields 0.2 mm by 0.15 mm minimum grid spacing in the *z* and *r* directions, respectively, in the flame zone. The computational domain is bounded by the axis of symmetry and a chimney wall boundary in the radial direction and by the inflow and outflow boundaries in the axial direction. The outflow boundary in *z* direction is located sufficiently far from the burner exit (~14 fuel-cup radii) such 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. The cup burner outer diameter is 28 mm and the chimney inner diameter is 95 mm. The burner wall (1-mm long and 1-mm thick tube) temperature is set at 600 K, and the wall surface is under the no-slip velocity condition. The mean gas velocities and temperature are set at 1.24 cm/s and 15.5 cm/s, respectively, for the fuel (methane) and oxidizer streams and 374 K. The low fuel velocity represents low momentum conditions typical of condensed material fires. The air velocity is in the middle of the so-called "plateau region" [32], where the extinguishing agent concentration is independent of the oxidizer velocity.

Validation of the UNICORN code has been performed for a variety of flame systems, fuels, and inhibitors with the kinetic model used. The predicted global strain rates at extinction of methane-air opposing-jet flames at the reactant temperature of 100 °C are 380 s⁻¹ without the inhibitor, which is close to the measured value (360 s⁻¹) [16], and those with DMMP added to the flames with different stretch rates are within a range of 10 % of the experiments.

3 Results and Discussion

The numerical simulations reported previously [39, 40] show that the flame-base region supports a trailing flame and controls the flame attachment, detachment, and oscillation processes. Near the extinguishment limit, small variations in the agent volume fraction in the oxidizing stream result in profound changes in the flame structure. The calculated inner structure of the flame base region provides detailed physical and chemical insights into the flame stabilizing mechanism and inhibition processes.

Figure 2 shows the calculated structure of near-limit flames in air with (a) DMMP at $X_{DMMP-O} = 0.012$ and CO_2 at $X_{\text{CO2}} = 0.032$ (Fig. 2a) and (b) PO(OH)₃ at $X_{\text{PO(OH)3-O}} =$ 0.011 (with no CO₂ added) (Fig. 2b). The variables include the velocity vectors (v), isotherms (T), and heat-release rate (\dot{q}) . Although unsteady code is used, the calculated flames are nearly steady state without flame flickering or base oscillations throughout the entire process because of the relatively high oxidizer flow velocity and temperature. The base of both flames is detached and lifted above the burner rim at the height from the burner rim, $z_k = 3.4$ mm (Fig. 2a) and 4.2 mm (Fig. 2b) in the nearly horizontal entrainment flow. The velocity vectors show longitudinal acceleration in the hot zone due to buoyancy. As a result of the continuity of the fluid, surrounding air is entrained into the lower part of the flame. The entrainment flow inclines inwardly as a result of the overall stream-tube (streamline spacing) shrinkage due to the significantly low velocity of the fuel compared to that of the oxidizer as well as the flow



Fig. 2 Calculated structure of methane cup-burner flames with agents added to the oxidizer: (a) DMMP at $X_{DMMP-O} = 0.012$, $X_{CO2} = 0.032$ and (b) PO(OH)₃ at $X_{PO(OH)3-O} = 0.011$.

acceleration downstream. The heat-release rate contours show a peak reactivity spot (i.e., the reaction kernel [39]) at the flame base, where the chain-carrier radicals (H, O, and OH), as well as heat, diffuse back against the oxygen-rich incoming buoyancy-induced flow, thus promoting chain-



Fig. 3 Calculated maximum temperature and reaction-kernel heat-release rate in methane cup-burner flames with DMMP or $PO(OH)_3$ added to the oxidizer.

branching (H + O₂ \rightarrow OH + O) and subsequent vigorous reactions to form the reaction kernel.

For DMMP (Fig. 2a), the heat-release rate contour shows a weak branch on the oxidizer side extending downstream from the reaction kernel. This feature was similar to the two-zone flame structure for halon replacement fireextinguishing agents with fuel components, as found previously [33]. The two-zone flame structure is formed due to burning of the fuel component of DMMP, while for $PO(OH)_3$, no outer branch is formed.

Figure 3 shows the maximum temperature in the trailing diffusion flame and the peak heat-release rate at the reaction kernel in the flame with pure DMMP or PO(OH)₃ in the oxidizer. As DMMP or PO(OH)₃ is added to the oxidizer, T_{max} increases, whereas the reaction kernel weakens (the heat-release rate decreases linearly). T_{max} in the trailing flame with DMMP added to the oxidizer is higher than that with PO(OH)₃ possibly due to combustion enhancement by additional heat release.

Figure 4 shows the radial variations of calculated temperature and the heat-release rate crossing the reaction kernel at $z_k = 3.4$ mm and the trailing flame at z = 6.4 mm ($z_k + 3$ mm) in the near-limit flame with DMMP at $X_{DMMP-O} = 0.012$ and CO₂ at $X_{CO2} = 0.032$ (see Fig. 2a). At $z_k = 3.4$ mm, the heat-release rate peak resides slightly on the oxidizer side of the temperature peak, as the reaction kernel broadens as a result of fuel-air mixing in the region between the flame base and the burner rim. At z = 6.4 mm, the trailing diffusion flame is characterized by "two-zone" structure [33] (inner and outer) as evident from two heat-release rate peaks. The inner zone (10 mm < r < 11.4 mm) is formed by the hydrocarbon-O2 combustion with the



Fig. 4 Calculated radial variations of the temperature and heatrelease rate at z = 3.4 mm and 6.4 mm in a methane cup-burner flame with DMMP and CO2 added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$ and $X_{\text{CO2}} = 0.032$, respectively.

heat-release rate peak residing on the temperature peak. The outer zone (11.4 mm < r < 13 mm) is formed by exothermic reactions of the retardant itself.

Figure 5 shows the radial variations of the volume fractions (X_i) of phosphorus-containing species and the chaincarrier radicals (H, O, and OH) crossing the reaction kernel at $z_k = 3.4$ mm (Fig. 5a) and the trailing flame at $z_k =$ 6.4 mm (Fig. 5b) with DMMP added at $X_{\text{DMMP-O}} = 0.012$ and CO_2 at $X_{CO2} = 0.032$. In the region surrounding the reaction kernel (Fig. 5a), DMMP in the oxidizer stream reacts with O₂ and the radicals and is fragmented and diminished. As a result, the concentration peaks of species such as PO(OH)₃, CH₃PO₂, and P(OH)₃ are formed in this peripheral region. Relatively high concentrations (X_i in the order of 10^{-3}) of active phosphorus intermediates (HOPO₂, HOPO, and PO₂) present in the high-temperature central region, where the peaks of the chain-carrier radicals (H, O, and OH) are formed. Consequently, the afore-mentioned phosphorus inhibition reactions of radical recombination cycles are taking place vigorously at the reaction kernel. In the trailing flame (Fig. 5b), as a result of the two-zone flame structure and higher temperature, the DMMP fragments, active phosphorus intermediates, and radicals spread radially at higher concentrations.

Figure 6 shows the radial variations of calculated temperature and the heat-release rate crossing the reaction kernel at $z_k = 4.2$ mm and the trailing flame at z = 7.2 mm ($z_k + 3$ mm) in the near-limit flame with PO(OH)₃ at $X_{PO(OH)3-O} = 0.011$ (see Fig. 2b). As described above, no outer zone with a significant heat-release rate peak is formed in the trailing flame.



Fig. 5 Calculated radial variations of the volume fractions in a methane cup-burner flame with DMMP and CO2 added to the oxidizer at $X_{\text{DMMP-O}} = 0.012$ and $X_{\text{CO2}} = 0.032$, respectively, at (a) z = 3.4 mm and (b) z = 6.4 mm.

Figure 7 shows the radial variations of the volume fractions (X_i) of phosphorus-containing species and the chaincarrier radicals (H, O, and OH) crossing the reaction kernel at $z_k = 4.2$ mm (Fig. 7a) and the trailing flame at $z_k =$ 7.2 mm (Fig. 7b) with PO(OH)₃ added at $X_{PO(OH)3-O} =$ 0.011. At both $z_k = 4.2$ mm and 7.2 mm, the volume fractions of phosphorus intermediates on the air side of the



Fig. 6 Calculated radial variations of the temperature and heatrelease rate at z = 4.2 mm and 7.2 mm in a methane cup-burner flame with PO(OH)₃ added to the oxidizer at $X_{PO(OH)3-O} = 0.011$.

temperature peak are much smaller than the DMMP addition (Fig. 4).

The effectiveness of phosphorus compounds in inhibition is quite complex, depending on the additive type and the flame structure, which depends on the region in the flame. As shown in Fig. 3, the PCC addition to the oxidizer results in higher T_{max} , which would increase the radical concentrations. On the other hand, the two-zone flame structure with DMMP generates more active phosphorus intermediates on the oxidizer side of the trailing flame, thus promoting the radical recombination cycles. In the reaction kernel, there is good upstream mixing of fuel and oxidizer because the base is lifted. Thus, the inhibition characteristics in the reaction kernel must be closer to those in premixed flames, where the species for the catalytic cycles are more readily available.

4 Conclusions

The effects of the PCCs (DMMP and PO[OH]₃) acting in the gas phase on the structure and inhibition of methane-air co-flow cup-burner flames have been studied computationally. The two-zone flame structure has been calculated with the DMMP addition to the oxidizer due to the reactions of the retardant itself, whereas PO[OH]₃ lacks it. The effectiveness of PCCs added to the oxidizer is outstanding. Although the PCCs in the oxidizer increased the maximum flame temperature, particularly for DMMP, in the trailing diffusion flame, it weakened the flame attachment point (reaction kernel) at the flame base, thereby inducing the detachment, lifting, and blowout extinguishment.



Fig. 7 Calculated radial variations of the volume fractions in a methane cup-burner flame with PO(OH)₃ added to the oxidizer at $X_{PO(OH)3-O} = 0.011$, at (a) z = 4.2 mm and (b) z = 7.2 mm.

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References

Linteris, G.T., 2007, Flame Suppression Chemistry, In: Advanced Technology for Fire Suppression in Aircraft, The Final Report of the Next Generation Fire Suppression Technology Program (R.G. Gann, Ed.), NIST Special Publication 1069,

National Institute of Standards and Technology, Gaithersburg, MD, pp. 119-338.

- [2] Staendeke, H. and Scharf, D.J., 1989, Halogen-Free Flame-Retardant Based on Phosphorus-Compounds, Kunststoffe-German Plastics 79, 1200-1204.
- [3] Avondo, G., Vovelle, C., and Delbourgo, R., 1978, Role of Phospohorus and Bromine in Flame Retardancy, Combustion and flame 31, pp. 7-16.
- [4] Levchik, S.V., 2007, Introduction to Flame Retardancy and Polymer Flammability, In: Flame Retardant Polymer Nanocomposites (A.B. Morgan and C.A. Wilkie, eds.), John Wiley & Sons, Inc., pp.1-29.
- [5] Sherman, L.M., 1992, Flame Retardants Update: Phosphorus Expands Its Niche, Plastics Technology 38, pp. 102-105.
- [6] Shelly, S., 1993, Keeping Fire at Bay, Chemical Engineering 100, pp. 71-73.
- Brauman, S.K., 1977, Phosphorus Fire Retardance in Polymers.
 I. General Mode of Action, Journal of Fire Retardant Chemistry 4, pp. 18-37.
- [8] Green, J., 1996, Mechanisms for Flame Retardancy and Smoke Suppression: A Review, Journal of Fire Sciences 14, pp. 426-442.
- [9] Peters, E.N., 1979, Flame-Retardant Thermoplastics. 1. Polyethylene-Red Phosphorus, Journal of Applied Polymer Science 24, pp. 1457-1464.
- [10] Schartel, B., 2010, Phosphorus-based Flame Retardancy Mechanisms-Old Hat or a Starting Point for Future Development?, Materials 3, pp. 4710-4745.
- [11] Levchik, S.V. and Weil, E.D., 2006, A Review of Recent Progress in Phosphorus-Based Flame Retardants, Journal of Fire Science 24, pp. 345-364. General Mode of Action, Journal of Fire Retardnt Chemistry 4, pp. 18-37.
- [12] Fenimore, C.P, and Jones, G.W., 1966, Modes of Inhibiting Polymer Flammability, Combustion and Flame 10 pp. 295-301.
- [13] Linteris, G.T., 2002, Gas-phase Mechanisms of Fire Retardants, NIST IR 6889, National Institute of Standards and Technology, Gaithersburg, MD.
- [14] Kaizerman, J.A., and Tapscott, R.E., 1996, Advanced Streaming Agent Development, Volume II: Phosphorus Compounds, NMERI 96/5/32540, New Mexico Engineering Research Institute, Albuquerque, NM.
- [15] Lifke, J.L., Moore, T.A., and Tapscott, R.E., 1996, Advanced Streaming Agent Development, Volume V: Laboratory-Scale Streaming Tests, NMERI 96/2/32540, New Mexico Engineering Research Institute, Albuquerque, NM.
- [16] McDonald, M.A., Jayaweera, T.M., Fisher, E.M., and Gouldin, F.C., 1999, Inhibition of Nonpremixed flames by Phophorus-Containing Compounds, Combustion and Flame 116, 166-176.
- [17] Hastie J.W., and Bonnell D.W., 1980, Molecular Chemistry of Inhibited combustion Systems, NBSIR 80-2169, National Bureau of Standards, Gaithersburg, MD.
- [18] Twarowski, A., 1993, The Influence of Phosphorus Oxides and Acids on the Rate of H+OH Recombination, Combustion and Flame 94, pp. 91-107.
- [19] Werner, J.H., and Cool, T.A., 1999, Kinetic Model for the Decomposition of DMMP in a hydrogen/Oxygen Flame, Combustion and Flame 117, pp. 78-98.
- [20] Babushok, V.I., and Tsang, W, 1999, Influence of Phosphorus-Containing Fire Suppressants on Flame Propagation, In: Society of Fire Protection Engineers, Boston, MA.
- [21] Wainner, R.T., McNesby, K.L., Daniel, R.G., Miziolek, A.W., and Babushok, V.I., 2000, Experimental and Mechanistic Investigation of Opposed-Flow Propane/Air Flames by Phosphorus-Containing Compounds, Proceedings of the Halon Options

Technical Working Conference (HOTWC), Albuquerque, NM, May 2-4, pp 141-153.

- [22] Glaude, P.A., Curran, H.J., Pitz, W.J. Westbrook, C.K., 2000, Kinetic Study of the Combustion of Orgnophophorus Compounds, Proceedings of the Combustion Institute 28, pp. 1749-1756.
- [23] McDonald, M.A., Gouldin, F.C., and Fisher, E.M., 2001, Temperature Dependence of Phosphorus-Based Flame Inhibition, Combustion and Flame 124, pp. 668-683.
- [24] Korobeinichev, O.P., Bolshova, T.A., Shvartsberg, V.M., and Chernov, A.A., 2001, Inhibition and Promotion of Combustion by Organophosphorus Compounds Added to Flames of CH4 or H2 in O2 and Ar, Combustion and Flame 125, pp. 744-751.
- [25] Korobeinichev, O.P., Rybitskaya, I.V., Shmakov, A.G., Chernov, A.A., Bolshova, T.A., and Shvartsberg, V.M., 2009, Inhibition of Atmospheric-Pressure H₂/O₂/N₂ Flames by Trimethyl-Phosphate Over Range of Equivalence Ratio, Proceedings of the Combustion Institute 32, pp. 2591-2597.
- [26] Korobeinichev, O.P., Rybitskaya, I.V., Shmakov, A.G., Chernov, A.A., Bolshova, T.A., and Shvartsberg, V.M., 2010, Mechanism of Inhibition of Hydrogen/Oxygen Flames of Various Compositions by Trimethyl Phosphate, Kinetics and Catalysis 51, pp.154-161.
- [27] Bolshova, T.A., and Korobeinichev, O.P., 2006, Promotion and Inhibition of a Hydrogen-Oxygen Flame by the Addition of Trimethyl Phosphate, Combustion Explosion and Shock Waves 42, pp. 493-502.
- [28] Korobeinichev, O., Mamaev, A., Sokolov, V., Bolshova, T., Shvartsberg, V., Zakharov, L., and Kudravtsev, I., 2000, Inhibition of Methane Atmospheric Flames by Organophosphorus Compounds, Halon Options Technical Working Conference, Albuquerque, NM, May 2-4, pp. 164-172.
- [29] Tapscott, R.E., Mather, J.D., Heinonen, E.W., Lifke, J.L., and Moore, T.A., 1998, Identification and Proof Testing of New Total Flooding Agents: Combustion Suppression Chemistry and Cup-Burner Testing, NMERI 97/6/33010, Albuquerque, NM: New Mexico Engineering Research Institute.
- [30] Bouvet, N., Linteris, G.T., Babushok, V.I., Takahashi, F., Katta, V.R., and Krämer, R.H., 2015, Experimental and Numerical Simulations of the Gas-Phase Effectiveness of Phosphorus Compounds, Fire and Materials 2015, Interscience Communications Ltd, London, UK.
- [31] Shmakov, A.G., Korobeinichev, O.P., Shvartsberg, V.M., Knyazkov, D.A., Bolshova, T.A., and Rybitskaya, I.V., 2005, Inhibition of Premixed and Nonpremixed Flames with Phosphorus-Containing Compounds, Proceedings of the Combustion Institute 30, pp. 2345-2352.
- [32] Takahashi, F., Linteris, G., and Katta, V.R., 2007, Extinguishment Mechanisms of Coflow Diffusion Flames in A Cup-Burner Apparatus, Proceedings of the Combustion Institute 31, pp. 2721-2729.
- [33] Takahashi, F., Katta, V.R., Linteris, G.T., and V.I. Babushok, V.I., 2014, Combustion Inhibition and Enhancement of Cup-Burner Flames by CF₃Br, C₂HF₅, C₂HF₃Cl₂, and C₃H₂F₃Br, Proceedings of the Combustion Institute 35.
- [34] Takahashi, F., Katta, V.R., Linteris, G.T., and Babushok, V.I., 2015, Simulations of Gas-Phase Interactions of Phosphorus Flame Retardants with Diffusion Flame Structure, Fire and Materials 2015, Interscience Communications Ltd, London, UK.
- [35] Katta, V.R., Goss, L.P., and Roquemore, W.M., 1994, Numerical investigations of transitional H2/N2 jet diffusion flames, AIAA Journal 32, p. 84.
- [36] Roquemore, W.M., and Katta, V.R., 2000, Role of Flow Visualization in the Development of UNICORN. Journal of Visualization 2, 3/4, pp. 257-272.

- [37] Frenklach, M., Wang, H., Goldenberg, M., Smith, G.P., Golden, D.M., Bowman, C.T., Hanson, R.K., Gardiner, W.C., Lissianski, V., 1995, GRI-Mech—An Optimized Detailed Chemical Reaction Mechanism for Methane Combustion, Report No. GRI-95/0058, Gas Research Institute, Chicago, IL.
- [38] Korobeinichev, O.P., Shvartsberg, V.M., Shmakov, A.G., Bolshova, T.A., Jayaweera, T.M., Melius, C.F., Pitz, W.J. and Westbrook, C.K., 2004, Flame Inhibition by Phosphorus-Containing Compounds in Lean and Rich Propane Flames, Pro

ceedings of the Combustion Institute 30, pp. 2350-2357.

- [39] Takahashi, F., and Katta, V.R., 2000, A Reaction Kernel Hypothesis for the Stability Limit of Methane Jet Diffusion Flames, Proceedings of the Combustion Institute 28, 2071-2078.
- [40] Takahashi, F., Linteris, G.T., and Katta, V.R., 2007, Vortex-Coupled Oscillations of Edge Diffusion Flames in Coflowing Air with Dilution, Proceedings of the Combustion Institute 31, pp. 1575-1582.