Final Technical Report

PROJECT TITLE: Suppression Effectiveness of Aerosols

SERDP PROJECT IDENTIFIER: NGP 2b1

RESEARCH CATEGORY: 6.2 Applied Research

AGENCY: Navy

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THRUST AREA: 2B New and Improved Aerosol Suppressants

PROJECT DATES: April 1997 – May 2002

REPORT DATE: October 1, 2003

Sponsored by:
The Department of Defense
Strategic Environmental Research and Development Program

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I. EXECUTIVE SUMMARY

A. TASK OBJECTIVES

The objective of this project was to quantify flame suppression effects of various aerosols and relate these observations to properties of the aerosol. Both liquid drops as well as solid powders were investigated.

B. TECHNICAL PROBLEMS

Experiments in this project were carried out primarily in non-premixed counterflow flames. Gas-phase suppression agent behavior in counterflow flames is very similar, especially at low strain rates, to other non-premixed flames, specifically cup burner flames. The requirements for generating and working with aerosols typically demands air flow rates that puts the experimental conditions at a higher strain rate. Screens can be used in counterflow burners to make them more stable, especially at low strain rates. For best results when working with aerosols, burner tubes should be reasonably open (no or only very coarse screens). Screens are problematic especially for aerosols with larger drop size. In this project a compromise was made between achievable strain rate ranges and quality of aerosol seeding in the flow.

C. GENERAL METHODOLOGY

The project was carried out in the Combustion Dynamics Section of the Navy Technology Center for Safety and Survivability at the Naval Research Laboratory (NRL). Well-characterized aerosols were injected into premixed gas/air mixtures for studying the effect on burning velocity in premixed flames and into the air side of non-premixed counterflow diffusion flames to study the effects on extinction. Powder aerosols were generated by first sieving the powders into discrete size categories and then entraining them into the air stream. Liquid aerosols were generated using various drop generators depending on the drop size desired. Particle, drop, and gas stream velocities throughout the flow field were measured using laser Doppler velocimetry. Light scattering was used to determine particle delivery rates. Drop size and number density as a function of position in the flow field were determined with phase Doppler particle anemometry.

D. TECHNICAL RESULTS

- The theoretical achievable thermal effect for water, a physical agent, in reducing the burning velocity of premixed methane-air flames was demonstrated. Water drops ~ 0.3 μm diameter were found to be comparable on a mass basis to Halon 1301 in reducing the burning velocity.
- Water drops equal to and smaller than ~ 30 μm diameter were found to be more effective than Halon 1301 at extinguishing non-premixed counterflow propane or methane-air flames.
- Water extinction effectiveness was observed to correlate with the degree of drop evaporation.
- Suppression behavior of very small water drops is consistent with multi-phase modeling predictions in premixed flames.

- Suppression behavior of water drops ~ 14 – 52 μm diameter is consistent with modeling predictions based on a multi-phase Lagrangian-Eulerian treatment of the two phases in non-premixed opposed flow flames.
- Aerosols of alkali bicarbonate powders were determined to be very effective at extinguishing non-premixed counterflow flames. Comparison of the suppression effect for potassium and sodium compounds indicate that suppression correlates with the chemical participation of the alkali metal atom in the reduction of flame radicals.
- Powders of potassium bicarbonate were found to be more effective than sodium bicarbonate at extinguishing non-premixed counterflow flames.
- There is a monotonic increase in the flame extinction efficiency based on weight with decreasing particle size for all powder particle sizes studied.

E. IMPORTANT FINDINGS AND CONCLUSIONS

- Water is capable of achieving suppression effectiveness comparable to or greater than that of Halon 1301 in flame suppression if delivery issues inherent to the condensed phase fire suppressant can be successfully addressed.
- Water drops must evaporate in the flow field and the cooled gases conducted into the flame (without exchanging heat with the surroundings) in order to achieve suppression effectiveness comparable to Halon 1301.
- The amount of water required in flame velocity reduction studies is consistent with estimated theoretical maximum effectiveness for water based on an empirical model (developed previously by Sheinson at NRL) comparing water's properties with those of other gaseous agents.
- Powders of alkali compounds suppress flames through both a chemical and physical process. Very high levels of effectiveness are dominated by a chemical suppression mechanism. Powder particle size and residence time in the flame control the relative contribution of chemical to physical suppression processes.
- Residence time dominates the effectiveness of any aerosol in inhibiting or extinguishing a flame. In general, the residence time for aerosols in premixed flames is much shorter than for non-premixed flames. This translates to a general higher effectiveness of aerosols in non-premixed flames than in premixed flames for a given particle/drop size.
- For suppression evaluation of heterogeneous suppression, extinction concentration data in a characteristic particle/drop size that assures complete vaporization of the aerosol at a fixed strain rate (residence time correlates with strain rate) should give the maximum suppression effectiveness per mass of the added aerosol.
- For a given flow field and residence time, the transition diameter from very effective smaller particles/drops to larger less effective particles/drops will depend on the aerosol physical properties (boiling point, characteristic size, and density).

F. SIGNIFICANT HARDWARE DEVELOPMENTS

A powder delivery system capable of controlling the delivery of small amounts of small particle size powder samples was developed. The powder flow rate was maintained by the physical agitation of the powder reservoir by a rotating ridged shaft. The powder delivery rate could be varied by changing the frequency of rotation of the shaft.

G. IMPLICATIONS FOR FUTURE RESEARCH

Building on the information and understanding gained in this project to encompass a greater range of conditions and for more varied, realistic systems will require validated multi-phase aerosol/flame models. Further development is needed before these codes are generally available. For the understanding of more realistic platforms, it would be very worthwhile to study the behavior of aerosol suppression agents in cup burner flames. Cup burner flames (co-flow, non-premixed flames) have a more complex flowfield than the counterflow flame flowfield studied in this project. Because of this complexity, understanding the aerosol/flame interaction in cup burner flames without the aid of models is very challenging. Such models are not generally available. Characterization of the cup burner flowfield and development of suitable flame models should be pursued in order to make this experimental platform more tractable for key, informative research in this widely used flame configuration.

II. ARTICLES PUBLISHED

Papers supported in whole or in part by this project

1. “Inhibition of Premixed Methane-Air Flames by Water Mist”, S.P. Fuss, E.F. Chen, W. Yang, R.J. Kee, B.A. Williams, and J.W. Fleming, *Proc. Combust. Inst.* **29**: 361-368 (2002).
2. “Water Mist Fire Suppression Research: Laboratory Studies”, J.W. Fleming, B.A. Williams, R.S. Sheinson, W. Yang, R.J. Kee, Proceedings of the Second National Research Institute for Fire Disaster Symposium: Technology Standards for Fire, 17 – 19 July, 2002, Tokyo, Japan, Paper 23, 2002.
3. “Suppression Effectiveness of Aerosols: The Effect of Size and Flame Type”, Fleming, J.W., Williams, B.A., and Sheinson, R.S., Paper 6-1, Proceedings of theHalon Options Technical Working Conference, Albuquerque, NM, 30 April – 2 May, 2002.
4. “Better Use of Water for Fire Suppression”, E.J.P. Zegers, P. Fuss, J.W. Fleming, B.A. Williams, A. Maranghides, and R.S. Sheinson, 2001 NRL Review, 102-104, 2001.
5. "Flame Suppression by Sprays of Aqueous Solutions Containing Phosphorus", T.M. Jayaweera, E.M. Fisher, and J.W. Fleming, Proceedings of the Second Joint Meeting of the U.S. Sections of the Combustion Institute, Oakland, CA, 25-28 March 2001.
6. “Dynamics and Suppression Effectiveness of Monodisperse Water Droplets in Non-Premixed Counterflow Flames”, E.J.P Zegers, B.A. Williams, R.S. Sheinson, and J.W. Fleming, *Proc. Combust. Inst.* **28**: 2931-2938 (2000).
7. "Reduction in Burning Velocity of Premixed Methane-Air Flames by Submicron Water Mist”, S.P. Fuss, D.J. Dye, B.A. Williams, and J.W. Fleming, 28th International Symposium on Combustion, Abstracts of Work-in-Progress Posters, Poster No. WIP 1-J13, p. 13, Edinburgh, Scotland, 31 Jul - 4 Aug 2000.
8. “Water Mist Suppression of Methane/Air and Propane/Air Counterflow Flames”, E.P. Zegers, B.A. Williams, R.S. Sheinson, and J.W. Fleming, Proceedings of the 2000 Halon Options Technical Working Conference, pp. 251-261, Albuquerque, NM, 2-4 May 2000.

9. “Inhibition of Premixed Methane-Air Flames by Submicron Water Mists”, S.P. Fuss, D.J. Dye, B.A. Williams, and J.W. Fleming, Proceedings of the 2000 Halon Options Technical Working Conference, pp. 242-250, Albuquerque, NM, 2-4 May 2000.
10. “Water Mist Suppression of Non-Premixed Counterflow Flames”, E. J.P Zegers, B.A. Williams, R.S. Sheinson, and J.W. Fleming, Proceedings of the Fall Technical Meeting of the Eastern States Section of the Combustion Institute: Chemical and Physical Processes of Combustion, pp. 109-112, Raleigh, NC, 11-13 Oct 1999.
11. “Inhibition of Premixed Methane-Air Flames by Water Mist”, S.P. Fuss, D.J. Dye, B.A. Williams, and J.W. Fleming, Proceedings of the Fall Technical Meeting of the Eastern States Section of the Combustion Institute: Chemical and Physical Processes of Combustion, pp. 105-108, Raleigh, NC, 11-13 Oct 1999.
12. “Flow Field Considerations for Counter Flow Burners”, M.P. Davis, J.W. Fleming, B.A. Williams, and H.D. Ladouceur, Proceedings of the Fall Technical Meeting of the Eastern States Section of the Combustion Institute: Chemical and Physical Processes of Combustion, pp. 200-203, Raleigh, NC, 11-13 Oct 1999.
13. “Suppression Mechanisms of Alkali Metal Compounds”, B.A. Williams and J.W. Fleming, Proceedings of the 1999 Halon Options Technical Working Conference, pp. 157-169, Albuquerque, NM, 27-29 Apr 1999.
14. “PDA Determined Sodium and Potassium Bicarbonate Particle Properties in Counterflow Diffusion Flames”, J.W. Fleming, M.D. Reed, E. J.P. Zegers, B.A. Williams, and R.S. Sheinson, 27th International Symposium on Combustion, Abstracts of Work-in-Progress Posters, W5E28, p. 495, Boulder, CO, 2-7 Aug 1998.
15. “Extinction Studies of Propane/Air Counterflow Diffusion Flames: The Effectiveness of Aerosols”, J. W. Fleming, M.D. Reed, E.J.P. Zegers, B.A. Williams, and R.S. Sheinson, Proceedings of the 1998 Halon Options Technical Working Conference, pp. 403-414, Albuquerque, NM, 12-14 May 1998.
16. “Fire Suppression by Bicarbonate Powders: The Influence of Particle Size”, J.W. Fleming, M.D. Reed, B.A. Williams, and R.S. Sheinson, Abstracts of the Third Annual SERDP Symposium, p. 16, Washington, DC, 3-5 Dec 1997.
17. “Laboratory Evaluation of Bicarbonate Powders as Fire Suppressants”, M.D. Reed, J.W. Fleming, B.A. Williams, and R.S. Sheinson, Proceedings of the International Conference of Ozone Protection Technologies, pp. 333-342, Baltimore, MD, 12-13 Nov 1997.
18. “Behavior of Bicarbonate Powders in Counterflow Diffusion Flames”, M.D. Reed, B.A. Williams, R.S. Sheinson, and J.W. Fleming, Proceedings of the Eastern States Section: The Combustion Institute, pp. 83-86, Hartford, CT, 27-29 Oct 1997.

III. DETAILED PROJECT DESCRIPTION

III A. Powder Aerosol Generation

Powder aerosols were created by first sieving prepared powder samples into separate discrete size bins (ROTAP Model RX-29, W.S. Tyler). Powders were delivered to the air stream though a tapered glass tube with a matching tapered brass rod to vary the opening size as shown in Figure 1. The powder tube reservoir was in contact with a variable frequency, rotating notched-shaft to control the powder delivery rate and maintain powder flow. Details of the powder delivery system can be found in [Reed, 1997]. This design was particularly effective for the control and delivery of small particle size samples. A modulated helium-neon laser beam with lock-in detection was used to monitor the powder flow delivered to the flame. The powder scattering signal intensity was calibrated to the powder mass flow for each air stream flow rate by determining the time-dependent weight of powder exiting the burner tube.

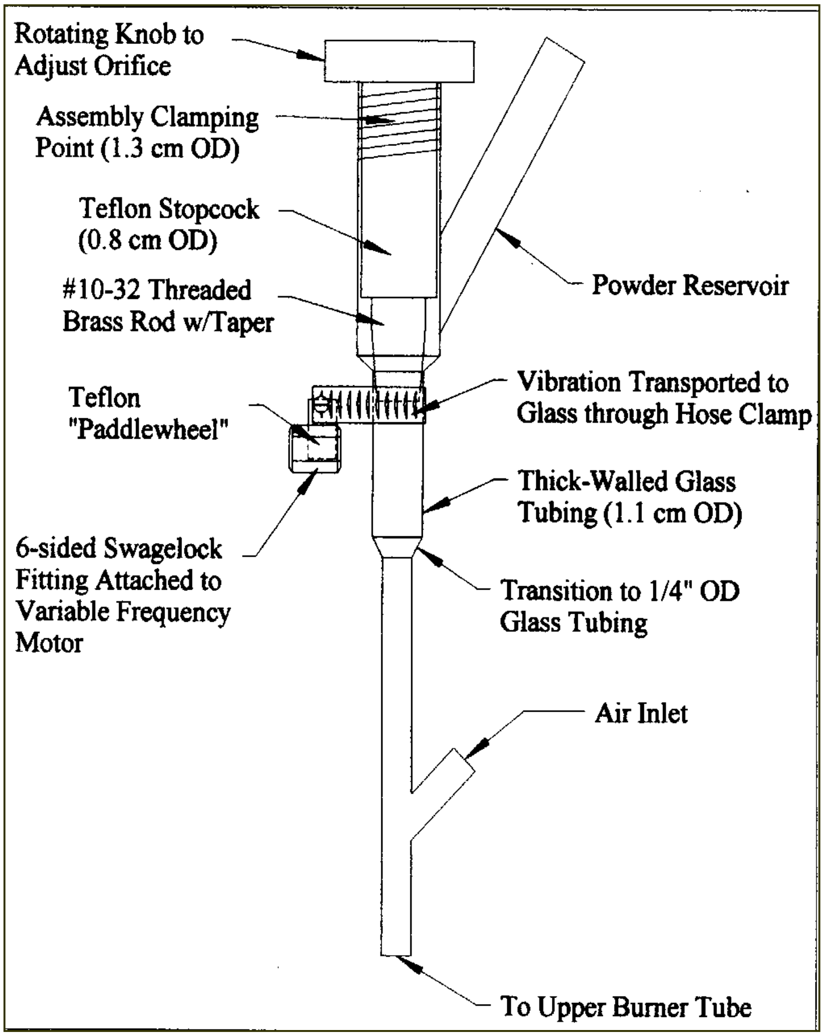
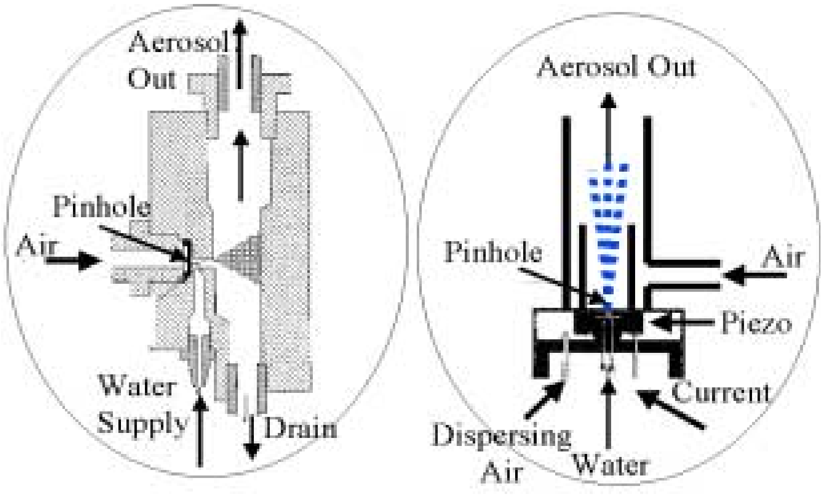


Figure 1. Powder delivery system [Reed, 1997].

III B. Liquid Aerosol Generation

To study the effect of drop size on suppression properties, mists were generated using various methods. Submicron size drops ($\leq$ 1 μm diameter) were generated using a venturi-based nebulizer (TSI Model 3076). A schematic of the nebulizer is shown in Figure 2a. Pressurized air, flowing through a small orifice, produces a high velocity air jet. The resulting pressure drop draws liquid from a reservoir through a small tube and entrains it in the air jet, breaking the liquid into drops. Larger drops impact the nebulizer wall and return to the reservoir. Drops small enough to remain entrained in the air flow are carried from the nebulizer. The amount of mist exiting the nebulizer was determined by measuring the change in mass of the liquid reservoir with time for a fixed air flow rate. Mists of polydisperse drops in the range of 1 to 20 μm were produced using a venturi-based nebulizer (Airlife Nebulizer with Air Entrainment and Heater Adapter), requiring a minimum air flow rate of ~ 2.9 SLPM to generate drops.

Monodisperse drops of larger size ($\geq$ ~15 μm diameter) were generated using a vibrating orifice aerosol generator (VOAG, TSI Inc. Model 3450). A schematic of the drop generator is shown in Figure 2b. To generate the mist, liquid is forced through a pinhole using either a syringe pump or a plastic bag under pressure inside a small chamber. A limited amount of control over the liquid flow could be accomplished using either method. The size of the pinhole ultimately determined how much liquid could be delivered to the burner. The pinhole is acoustically excited by a piezoelectric ceramic driven at specific frequencies to break up the liquid jet into a stream of extremely monodisperse drops. The drop size that could be produced depended on the pinhole diameter, the liquid flow rate, the forcing frequency, and the liquid properties. A dispersion cap was used to uniformly distribute the drop stream into a three-dimensional mist, although sacrificing some of the size monodispersity as shown in Figure 3. In the absence of the dispersion cap and dispersing air, all drops occupied a single PDPA size bin.



(a) (b)

Figure 2: Schematic of water aerosol generation methods. (a) venturi-based atomizer for generation of sub-micron diameter water drops (TSI Inc., Model 3076). (b) vibrating orifice aerosol generator (VOAG, TSI Inc., Model 3450) for generating mono-disperse water drops > ~ 15 μm diameter.

Drop size, velocity, and number density for drops > ~ 2 μm were measured using a phase Doppler particle anemometer (PDPA-Dantec Measurement Technology). For smaller drops (≤ ~1 μm diameter), water concentration in the reactant stream was monitored by 90^{o} scattering of a Helium-Neon laser at a wavelength of 0.6328 μm as shown in Figure 4. The scattered laser light was detected with a photomultiplier tube (PMT) using a narrow-line optical filter. The laser beam was modulated at 1 kHz by passing the beam through a rotating slotted wheel. The laser beam was positioned just above the burner exit. A reference beam was split off just before the burner and monitored by a photodiode. The scattered and reference signals were processed with a lock-in amplifier (EG&G Instruments, Model 7265 DSP) and integrated over a period of 0.5 s. The scattering intensity was calibrated to a mist delivery rate by correlating the scattering signal with the change in water mass of the reservoir.

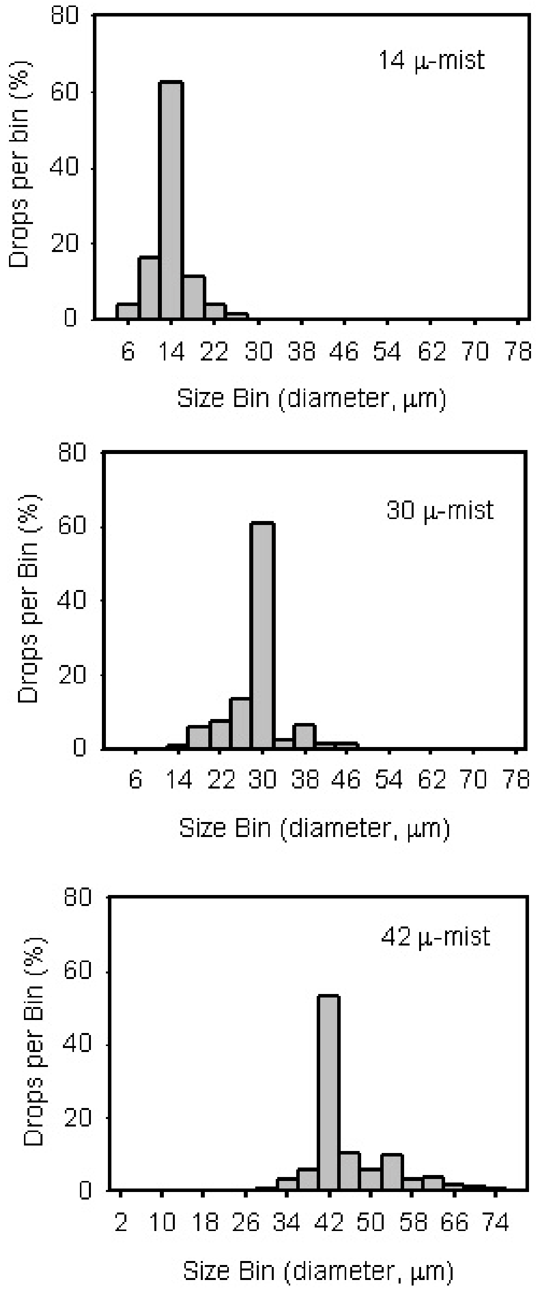


Figure 3. PDPA determined size histogram 2 mm above the air tube exit for the three water mists studied. In the absence of the dispersion cap and entrainment air stream, all drops exiting the VOAG occupied a single bin.

III C. Flame Configurations

III C 1. Premixed Flames

The laminar burning velocity is a fundamental property of a flammable gas mixture and is frequently used as an indicator of the effectiveness of an inhibiting agent [Noto, 1996]. There are a variety of methods to measure laminar burning velocity [Andrews, 1972]. We employed the total area method to quantify the reduction in burning velocity as a function of added mist in premixed conical flames. A schematic of the arrangement is shown in Figure 4. The burner is a converging nozzle with an exit diameter of 1.0 cm. An entrainment device to straighten the flow and uniformly seed drops in the gas flow utilized a perforated disk. The sub-micron size mist drops were small enough to pass through the ~ 0.16 cm diameter perforation holes. Larger drops (≥ 5 micrometer diameter) were introduced through an opening in the middle of the perforated disk. The burner was enclosed inside a 13 cm diameter inner diameter acrylic tube that allowed optical access to the flame. The acrylic chamber was vented to an exhaust hood through a conical metal covering open at the top. A ~ 3 SLPM flow of nitrogen introduced through a sintered disk in the bottom of the chamber was used to purge the chamber of excess oxygen and product gases.

Video images of the flame were recorded to determine the burning surface area. Burning velocities for the inhibited flames are reported relative to the uninhibited burning velocity, thereby minimizing systematic errors in determining an absolute value for the burning velocity. Relative values derived from schlieren images for some of the flames are in good agreement with values derived from the visible flame surface. The presence of the aerosol reduces the flame burning velocity, which results in a taller flame with a larger flame surface area for a fixed fuel-air flow. To minimize any systematic effects due to varying flame height, fuel and air flows were adjusted to maintain a stoichiometric mixture and a flame height of 1.0 ± 0.15 cm. The measured burning velocities of nitrogen-inhibited flames were found to be insensitive to flame height over this range.

III C 2. Non-Premixed Flames

Water mist suppression effectiveness in non-premixed flames was quantified by determining the extinction strain rate in counterflow flames. Details of the experiments are reported in [Zegers, 2000]. A schematic of the experimental configuration is shown in Figure 5. The burner consisted of two 50-cm long stainless steel tubes (1 cm inner diameter), with outer concentric tubes for a co-flow. The upper tube has a jacket for cooling water. The two tubes were aligned vertically and colinearly with a separation of 1.00 ± 0.05 cm. The end of the each tube was plumbed through the center of stainless steel plates on the top and bottom of a 22 cm inner diameter, 19 cm long acrylic tube. The acrylic tube has flat windows for good optical access. These windows are critical to both the position of the laser beam overlap for the PDPA measurements and the detection angle of the scattered light. A ~ 4 SLPM purge flow of nitrogen was introduced into the bottom of the chamber. All gases exited through the top plate of the combustion chamber through a 5 cm diameter exhaust port.

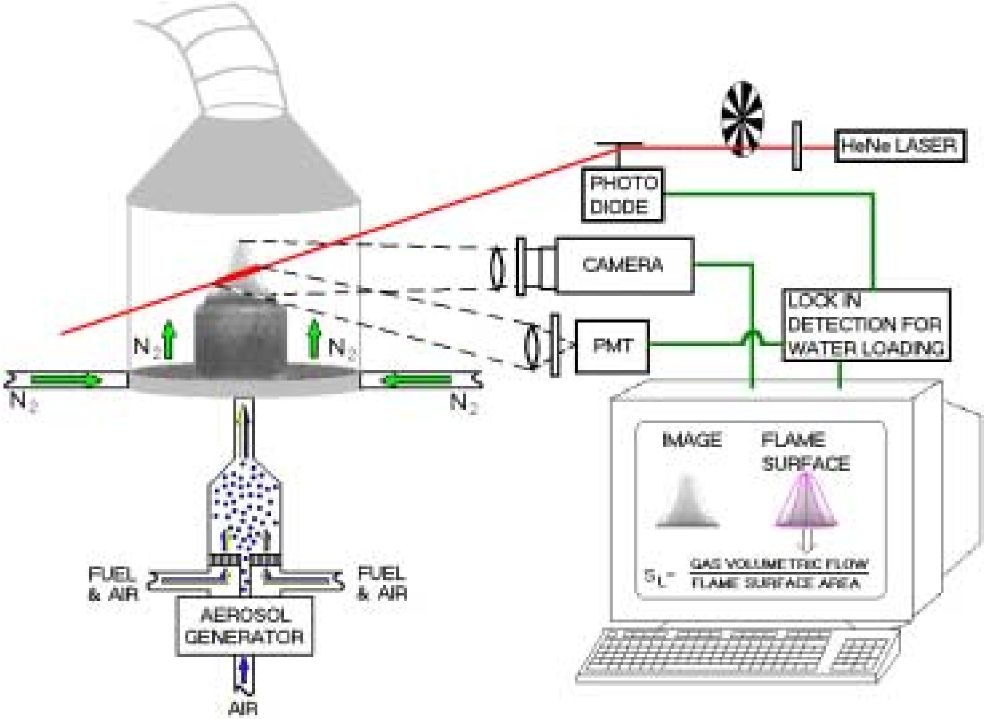


Figure 4: Schematic for the mist inhibited burning velocity determination in premixed flames. Water mist aerosols are seeded into the premixed gases. The flame is contained in an acrylic chamber, purged with a flow of nitrogen. Flame images are recorded using a CCD camera and a value for the total flame surface is determined. Burning velocities are determined by comparing the total flame surface to the volumetric flow of gases in the burner. Light from a modulated He-Ne laser, scattered from the aerosol in the premixed flow and detected with a lock-in detector, is used to determine the amount of water aerosol in the form of small drops introduced into the flame. PDPA is used to quantify the water concentration for mists of larger drops.

Flames were started using an arc igniter for a standard fuel and air flow configuration. For hydrocarbon fuels burning in air, stoichiometry dictates that the non-premixed flame reside on the air side of the stagnation plane. Mist was added with the air, typically supplied from the bottom tube. Air side introduction of the mist is relevant to real fire, total flooding fire suppression scenarios. Representative centerline temperature and axial velocity profiles are indicated in Figure 5, as is the strain rate, the maximum gradient in the axial velocity on the air side of the flame. Experimental strain rates were evaluated using Laser-Doppler Velocimetry (LDV) by seeding the flows with ~ 0.35 μm diameter alumina particles or sub-micron water drops. In this flow field, stable flames can be maintained if a sufficient amount of heat and flame radicals generated from the combustion process can be conducted to the unreacted fuel and air as they flow into the reaction zone. Extinction occurs when the flow rate is too fast to maintain the flame. Under these conditions the flame strain rate exceeds a critical value referred to as the *extinction strain rate*. Suppression agents lower the extinction strain rate and this reduction is used to measure suppression effectiveness.

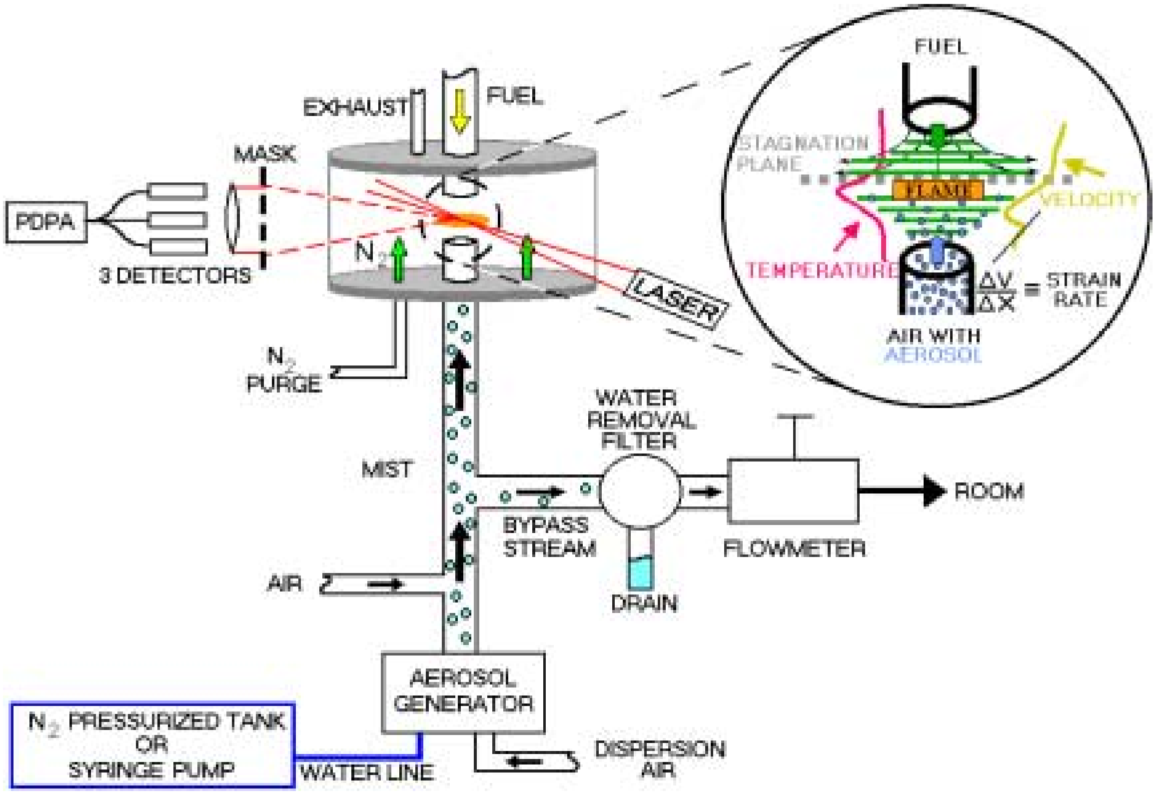


Figure 5: Schematic for studying aerosol inhibited non-premixed flames. Liquid mist aerosols are generated and seeded in the air flow in the lower tube. Fuel is introduced from the top, water-cooled tube. Powder studies were conducted with the air and powder introduced from the top tube and fuel introduced from the bottom tube. Flames are stabilized in a 1-cm gap between the two tubes. The burner is contained in an acrylic chamber, purged with a flow of nitrogen. The chamber has flat windows for optical access. Strain rates are determined from discrete velocity measurements using Laser Doppler Velocimetry. Phase Doppler Particle Anemometry is used to measure drop size, number density, and velocity through the flow field by vertically translating the burner assembly. The aerosol generator requires a ~1-1.5 SLPM flow of air for proper operation. In order to examine flames of lower strain rate, part of the air stream containing drops was diverted from the burner. Drops from the excess stream were removed by filtering and the resulting air flow measured to determine the amount of air sent to the burner.

III D. MODELING

Modeling of sub-micron mists in premixed flames was done in collaboration with Prof. Robert Kee at the Colorado School of Mines. The suppression effects of gas-phase agents were modeled using PREMIX [Kee, 1987] and OPPDIFF [Lutz, 1997]. The chemical reaction mechanism and the associated thermodynamic and transport properties were taken from GRI-Mech 3.0 [Smith, 2001] but with the nitrogen chemistry removed. The inhibition effects of water aerosols on premixed flames were calculated using a multiphase combustion model [Yang, 2002]. The multi-phase model solves conservation equations for mass, momentum, and energy for the water drops within a Lagrangian framework. One-dimensional conservation equations in an Eulerian framework are used to solve the physics of the gas-phase flame propagation. Coupling of the two phases is achieved through addition of drop-evaporation related source terms in the PREMIX software. Boundary conditions for the drop-evaporation dynamics are obtained from the PREMIX solution.

Modeling of micron size drops in counterflow flames was carried out in collaboration with Prof. Harsha Chelliah at the University of Virginia. The UVa multi-phase model is based on a hybrid Eulerian-Lagrangian formulation with a solution algorithm developed to predict the interaction between water mist and a laminar counterflow flame [Lentati, 1998]. Comparison of the modeling predictions with experimental results have provided valuable insights regarding the experimental observations reported here [Chelliah, 2003].

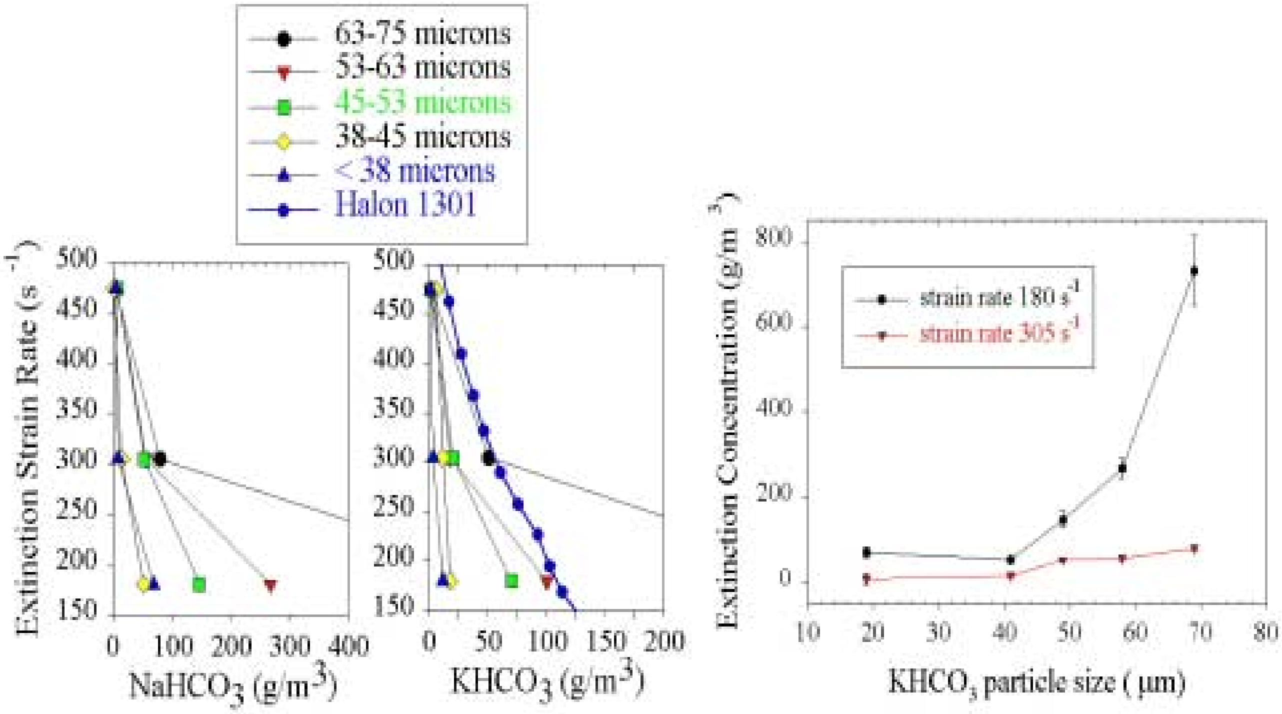
As part of this project, two other modeling approaches were explored. One publicly available code advertised as capable of modeling suppression of counterflow flames by aerosols is RUN-1DL (Rogg and Wang, U. Bochum). Available documentation on the treatment of drops was very sparse. The code as delivered only treats a single droplet stream and thus was not immediately capable of modeling our flame conditions involving an ensemble of water drops. Further development and code modification to model our experimental conditions were deemed too time consuming in light of the limited documentation.

We also investigated the use of PHOENICS to model the interaction of drops in the counterflow flame. PHOENICS is a finite volume code for calculating fluid flow. It had previously been used to model the flow field in this burner [Davis, 1999]. PHOENICS was configured to treat the full flame chemistry. Stable gas-phase flames could be modeled. The calculation was very sensitive to the inclusion of the aerosol/flame interaction due to the time and spatial scale dynamic ranges. Further development and code modification were not pursued as part of this project.

III E. RESULTS AND DISCUSSION

III E 1. Extinction Strain Rate Lowering by Powder Aerosols

The extinction strain rate for sodium bicarbonate ($NaHCO_3$) and potassium bicarbonate ($KHCO_3$) suppressed non-premixed counterflow flames were measured [Fleming, 1998]. Powders were mechanically sieved into size ranges of <38 μm, 38-45 μm, 45-53 μm, 53-63 μm, and 63-75 μm. Silica (2% by mass) was added to the powder samples to minimize clumping. Both powders flowed freely with almost no agglomeration noticed. Powder suppression efficiency was evaluated by adding powder to the air stream of non-premixed propane/air and methane/air counterflow flames. Extinction strain rate versus bicarbonate powder mass results are presented in Figure 6a for $NaHCO_3$ and Figure 6b for $KHCO_3$. Also plotted in Figure 6b are the results for CF_3Br. As can be seen in the figure, alkali metal bicarbonate powders are very effective at flame extinction, from 2 to 10 times more effective than CF_3Br. It will be noted from the mass scales in Figure 6 that K and Na exhibit similar behavior, and K is ~ twice as effective as Na. Their effectiveness is strongly dependent on size as seen in Figure 6c for K. A 50% decrease in $KHCO_3$ particle size increases the suppression effectiveness by a factor of 50. A similar dependence on particle size is also observed for $NaHCO_3$. The effectiveness approaches a limit at small particle size, below ~ 40 µm. Hamins measured extinction concentration values for three $NaHCO_3$ aerosols (all < 20 µm) inhibiting several different fuels in a modified cup burner [Hamins, 1998]. The cup burner extinction values agree with the low strain rate counterflow flame extinction values in the limiting particle size region. The effectiveness at small particle size can only be accounted for by a significant chemical contribution to the suppression mechanism [Hamins, 1998; Williams, 2002].



(a) (b) (c)

Figure 6. Extinction of propane-air non-premixed counterflow flames: extinction strain rate versus mass of powder sieved according to the indicated sizes for (a) $NaHCO_3$ and (b) $KHCO_3$. (c) Extinction mass concentration versus particle size for $KHCO_3$ inhibited flames.

III E 2. Burning Velocity Reduction of Premixed Flames by Water Mist

The inhibition effect of sub-micron diameter water drops (nominal 0.35 µm) on the normalized burning velocity of a methane-air flame is plotted in Figure 7. Details of the experiment and results are reported in [Fuss, 2002]. Also shown are the inhibition effect of N_2, CF_4, and CF_3Br. The CF_3Br data are modeling results considering full chemistry [Noto, 1996; Parks, 1979]. On a mass basis, the inhibition effectiveness of water mist is comparable to that of CF_3Br.

A summary of an evaluation of the thermodynamic properties of the agents investigated in Figure 7 is listed in Table 1. Column 2 lists the sensible enthalpy per unit mass (per mole listed in column 3) required to raise the temperature of each agent from 300K to 1600K [Chase, 1985]. On a mass basis N_2 and CF_4 should contribute similarly to the inhibition. The sensible enthalpy for water mist, including the heat of vaporization at 1 atm, is roughly twice that of water vapor and 3.5 times higher than for the same mass of N_2 or CF_4. These predictions are consistent with the experimental observations. The mass of inhibitor required to reduce the burning velocity by 20% is listed in Column 4 and the molar amount in Column 5. The mass of liquid water needed to reduce the burning velocity by 20% is one third of that required for N_2 or CF_4, which is in good agreement with the thermodynamic estimate. The value for water is comparable to published measurements for CF_3Br. Thus, small water drops acting thermally exhibit a comparable effectiveness on a mass basis in premixed flames as CF_3Br with its chemical effect.

Both theoretical [Mitani, 1981; Blouquin, 1998] and computational [Yang, 2002] models have been developed to predict premixed flame structure and extinction characteristics as a function of water-mist properties. Figure 8 illustrates the predicted dependence of the burning velocity on drop size and water loading [Yang, 2002]. For small drops, the burning velocity decreases monotonically as a function of water loading. Also, for sufficiently small drops, the burning velocity becomes independent of drop size but still depends on water loading. For stoichiometric, methane-air, premixed flames, this small-drop limit is achieved for a drop diameter of approximately ten micrometers [Yang, 2002].

Experimental validation of the small-drop limiting behavior is presented in Figure 9. The sub-micron mist inhibition results are in excellent agreement with modeling predictions of Yang and Kee, requiring no adjustable parameters [Fuss, 2002]. Water vapor is both observed and predicted to be less effective than water aerosols of drop sizes less than ~ 15 μm. There is an increase in effectiveness of liquid water as the drop size is reduced down to ~ 10 μm. Below this size limit, there is no increase in suppression effectiveness with decreasing drop size. This limiting drop size correlates with those drops that completely evaporate in this flow field.

Complete evaporation of the sub-micron mist drops by the time they enter the luminous flame zone was confirmed by monitoring light scattered from the drops in the flame using laser sheet illumination. Drop size measurements using PDPA for larger drops as a function of position in the flame are shown in Figure 10: size versus position in Figure 10a and number density versus position in the flame in Figure 10b. Drops $\geq$ 27 μm diameter were reasonably monodisperse (generated using the VOAG) and survive travel through this flame (peak temperature ~2100K, determined using a radiation-corrected, coated Pt/Pt-Rh thermocouple). The smaller drops generated with a nebulizer (average diameter 6 μm and $D_{v=0.9} < 10$ μm) completely evaporate at the flame front. Thus, the experimental drop size for onset of complete evaporation in this flame is between 6 and 27 μm. These measurements are consistent with the predicted ~ 10 μm limiting drop size of the multi-phase model.

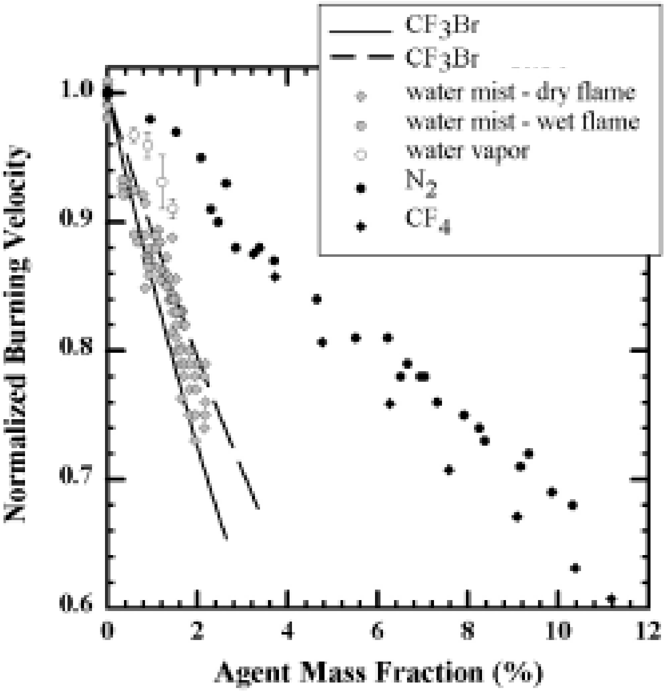


Figure 7: Normalized burning velocity reduction versus mass of added inhibitor: water in the form of sub-micron water drops in humidified flames (gray diamonds) and in un-humidified “dry” flames (gray circles), water vapor (open circles), N_2 (black circles), and CF_4 (black diamonds) [Fuss et al., 2002]. Results for CF_3Br are indicated by a dashed line [Parks et al., 1979] and a solid line [Noto et al., 1996].

Table 1: Relevant thermodynamic quantities and experimental suppression efficiencies for the thermal agents studied compared to CF_3Br. Columns 2 and 3 list the sensible enthalpy of each agent for a temperature range of 300K to 1600K. The value for water mist includes the heat of vaporization at one atmosphere. Columns 4 and 5 list the experimental mass and mole fractions of the total flow, respectively, from Figure 7 required to reduce the uninhibited burning velocity by 20%. Uncertainties are derived from the standard deviations in the fits to the burning velocity reduction versus mass.

Agent	$(H_f^{1600K} - H_f^{300K})$ [a]		Mass Fraction	Mole Fraction
	kJ/g	kJ/mol		
N_2	1.5	42	6.3 ± 0.4	6.2 ± 0.4
CF_4	1.4	122	5.5 ± 0.4	1.9 ± 0.2
H_2O (vapor)	2.9	53	3.3 ± 0.2	5.0 ± 0.3
H_2O (mist)	5.2	93	1.7 ± 0.1	2.6 ± 0.2
CF_3Br	0.85	126	1.9 [b]	0.4 [b]

[a] Calculated from data in [Chase, 1985]

[b] Data from [Noto, 1998]

Modeling predictions for the experimental conditions presented in Figure 10 are shown in Figure 11. Drop size versus position is shown in Figure 11a and relative drop number density versus position is shown in Figure 11b. Drop size behavior is in reasonable agreement in the post flame region. However, the experimental drop number density decay rates are much slower than the model predicts (note that the distance plotted in Figure 10b is four times that of Figure 11b.) The source of the difference can be attributed to the residence time of the drops in the flame. In the experiment, drops are traveling at the same speed as the gas phase, ~ 140 cm/s for these flames. In the one-dimensional freely propagating flame model, drops also travel at the same speed as the gas phase, but this is ~ 30 cm/s. Thus, the prediction of a higher evaporation rate (shorter evaporation time) for the longer residence time in the model is consistent. Experiments to quantify the effect of larger drops on the burning velocity are needed.

The model predicts a turning-point behavior for the effect of moderate and larger sized drops (above 25 μm for stoichiometric, premixed, methane flames) on burning velocity as seen in Figure 8. At the turning point the derivative of burning velocity with respect to the water mass loading is infinite. Turning points are caused by the drop dynamics within the flame. Specifically, longer drop residence time in a suppressed flame causes further increase of efficiency in flame suppression. Mathematically, at a turning point, an infinitesimally small increase of water mass loading causes the burning velocity to fall to the lower branch of the suppression curve. Such very-low-burning-velocity branches are experimentally not achievable due to the various heat-loss mechanisms that would prevent these flames from stabilizing. Therefore, it may be safe to interpret such turning points as flame extinction points.

The theoretical and computational analyses predict that the burning-velocity curves join together in the lower-burning-velocity region. This behavior can be attributed to a greater drop residence time in the slow-burning flames. If the burning velocity is sufficiently low, any drop can totally evaporate within the flame, leading to equivalent efficiency for flame suppression.

The turning points predicted for larger drops seen in Figure 8 can be important in fire suppression. Unfortunately, no direct observation or measurement of such behavior for inhibited premixed flames has been reported. The challenges to realizing such experiments include the generation of the mono-dispersed mists, the high water-mass loading required at turning points, and controlling the non-ideal conditions such as buoyancy and heat loss to the environment. Experiments that focus on the inhibition effects of larger drops are needed.

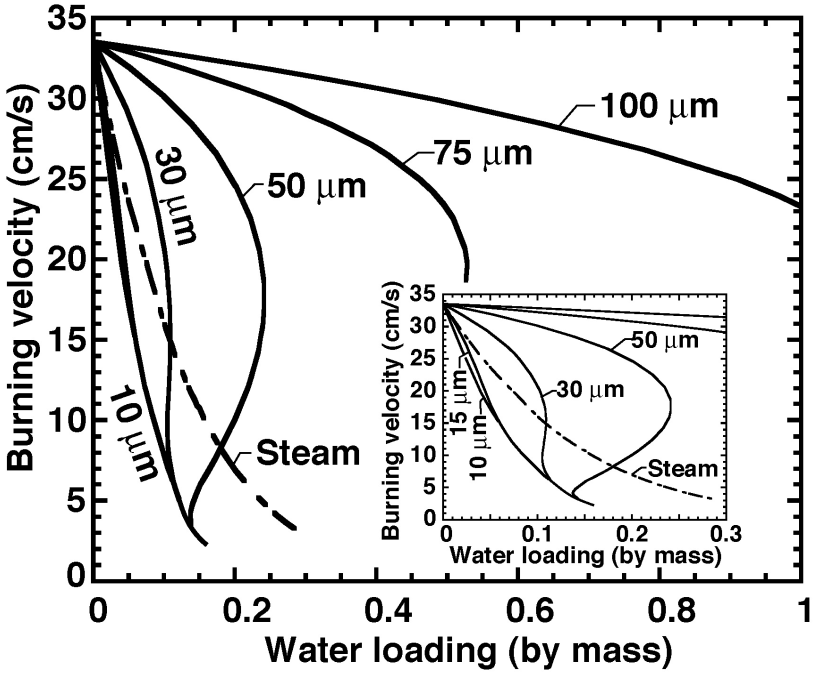


Figure 8: Predicted burning velocity for a stoichiometric, premixed, methane-air flame as a function of initial drop diameter and water mass loading [Yang and Kee, 2002].

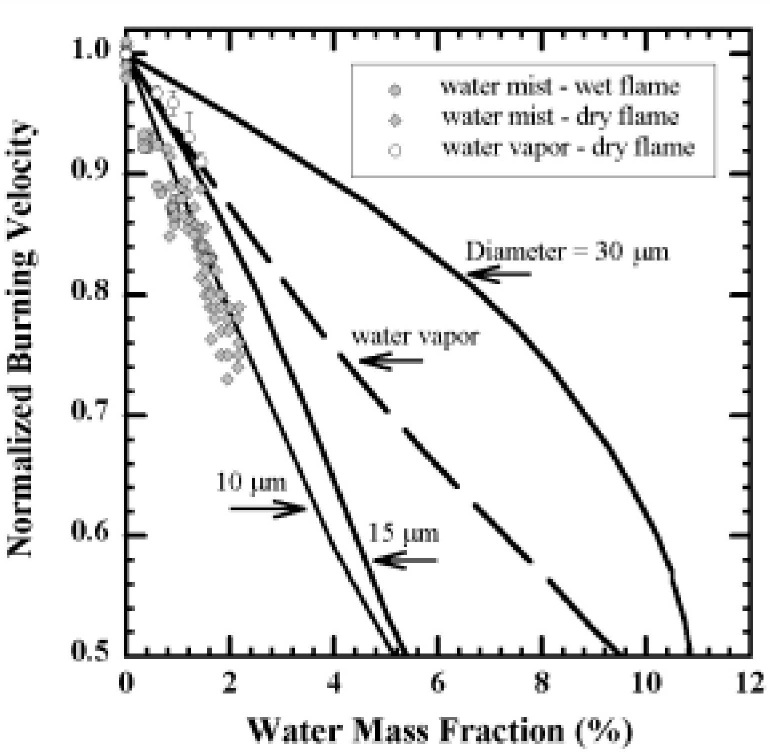
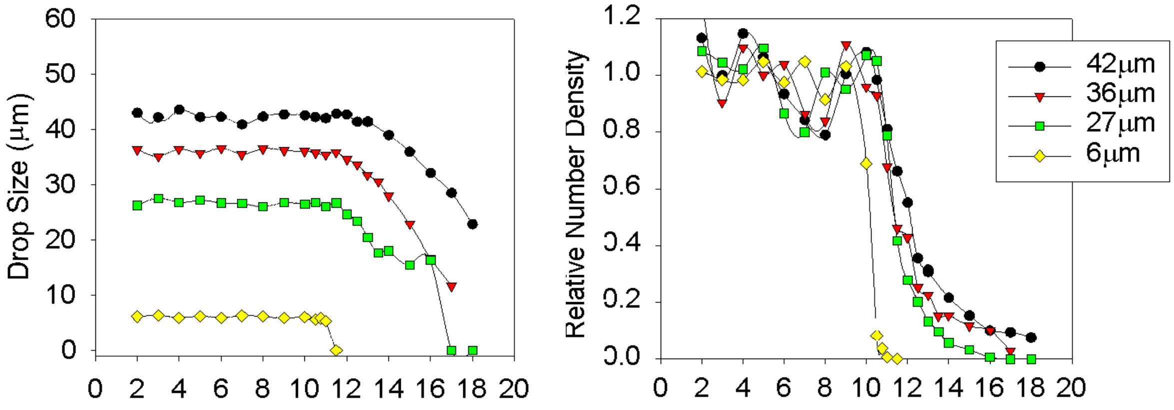
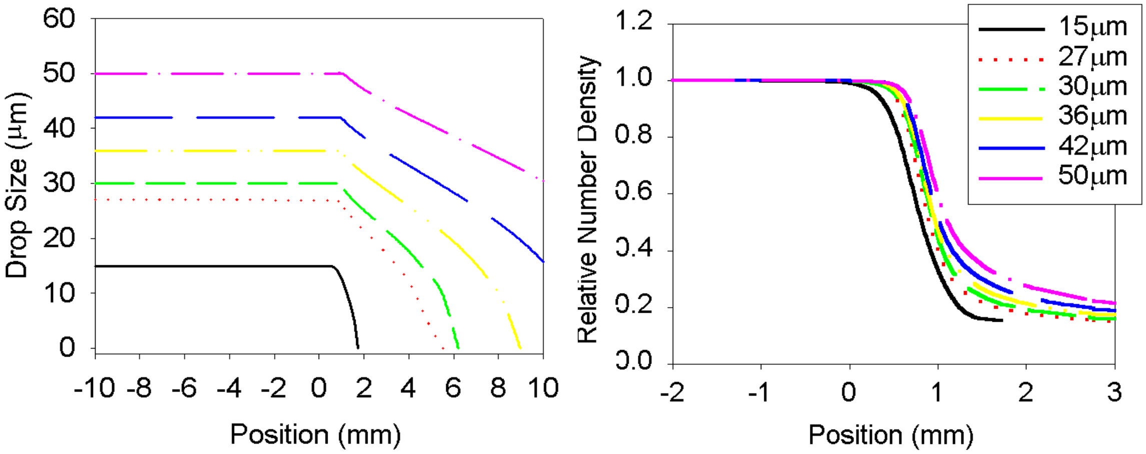


Figure 9: Normalized burning velocity for a water inhibited methane-air premixed flame showing the experimental results from Figure 7, and multi-phase flame modeling results for the indicated water drop sizes (solid lines) and PREMIX results for water vapor inhibited flame (dashed line) [Fuss et al., 2002].



(a) (b)

Figure 10: Experimental measurements of water drop behavior in a stoichiometric premixed methane-air flame as a function of height above the burner exit; (a) average drop size and (b) relative drop number density versus position for water aerosols of the indicated drop size. The relative burning velocity for the aerosol laden flames was ~ 90% that of the uninhibited flame.



(a) (b)

Figure 11: Multi-phase flame modeling predictions of water mist behavior in a stoichiometric premixed methane-air flame: (a) average drop size versus position in the flame and (b) relative number density versus position in the flame. The water mass fraction is 5%. The 0 mm position is the 300 K left boundary for the freely propagating flame solution. Figures 10a and 11a are plotted over the same distance of 20 mm. The distance plotted in Figure 10b is four times that of Figure 11b.

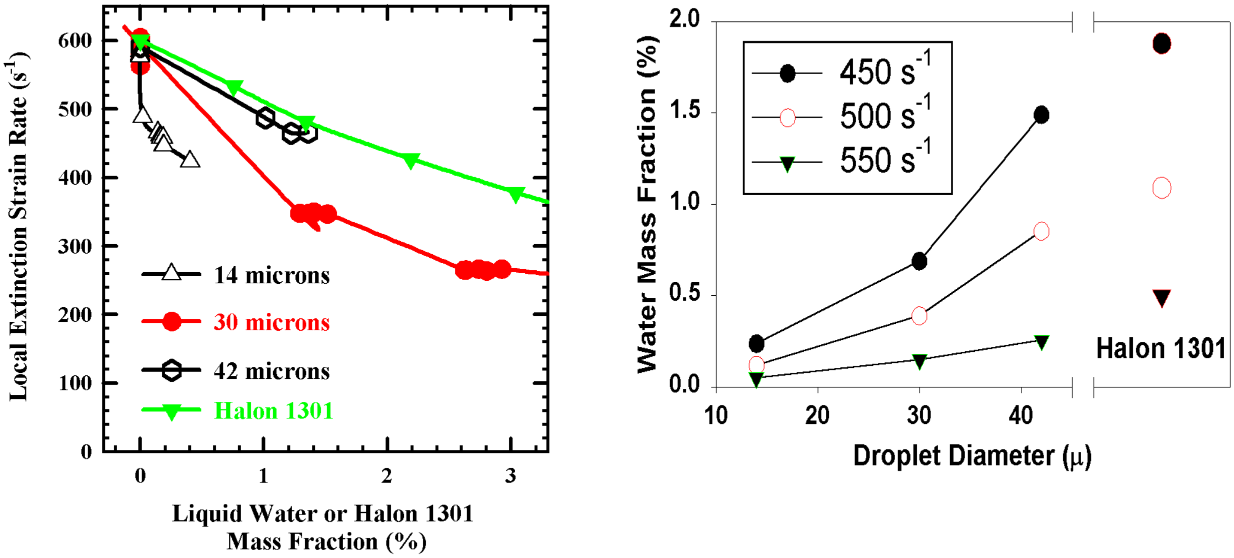
Understanding the inhibited flame structure and drop dynamics provides considerable insight into the mechanisms of flame suppression. The computational model predicts temperature, species concentration, number density, and drop history profiles throughout the flame. These variables represent the underlying factors that control the overall burning velocity. Therefore, detailed measurements of flame structure can be extraordinarily valuable. Unfortunately, both creating the flame and developing the required diagnostics are significant challenges. For these studies, flame structure, burning velocity, and extinction characteristics are modeled as an ideal flat flame. The experiment is a Bunsen-like configuration that allows drops to be introduced through the open tube. The burning velocity in these flames is inferred from analysis of the flame area. In addition, flame profile data can be measured, for example on the centerline. This configuration and modeling approach are valid for sub-micron drops that fully evaporate prior to entering the flame. However, for larger drops or particles, data from such experiments cannot be compared directly to one-dimensional flat-flame models. The gas and particle/drop velocities, for example, are much greater in the Bunsen-like flame. It appears that there are two choices for modeling the inhibition effect of larger particles/drops in premixed flames: configure a “flat” premixed, burner stabilized flame that can be seeded with large water particles/drops, or directly model the three dimensional Bunsen-like flame. The success of uniformly seeding particles/drops into a flat flame is highly unlikely considering the parrticle/drop sizes to be studied. Success seems more likely for alternative modeling approaches. This is area that requires further development.

III E 3. Extinction Strain Rate in Non-Premixed Flames

The effect of water mist on the extinction strain rate of non-premixed propane-air and methane-air counterflow flames was studied. Evaporation behavior of the aerosol drops in these flames was also determined. Experimental details and results are reported in [Zegers, 2000]. The water mass required for extinction of various strain rate flames is plotted in Figure 12. Also plotted is the amount of CF_3Br required for extinction. Water aerosols with a drop size of $\leq \sim 40$ μm are more effective than CF_3Br on a mass basis. Water drops that are 14 μm in diameter are ~ 3 times more effective than CF_3Br at extinguishing these flames. Phase Doppler Particle Anemometry was used to follow the drop size and number density throughout the flow field. We determined that water drops $< \sim 30$ μm diameter completely evaporate in these flames (mid to high strain rates). There is a large increase in effectiveness in going to smaller drop size as seen in Figure 12b. Experimental limitations prevented taking a full complement of data for 20 μm drops. Strain rate extinction concentration measurements that were taken for ~ 20 μm drops were found to be similar to the results for the 14 μm drops, suggesting a limiting drop size for effectiveness between 20 and 30 μm.

Lentati et al., using a multi-phase flame suppression model they developed, predicted that 20 μm is the optimum size for effectiveness of water drops in these flames [Lentati, 1998a]. Our experimental observations are consistent with this prediction. A follow-up study using the same model reported an underprediction of a factor of two for the suppression effectiveness of a 20 μm water mist inhibited methane-air counterflow flame [Lazzarini, 2000]. The difference could not be attributed to the non-monodisperse size distribution of the experimental mist. The counterflow flame model treats the drop trajectories in this flow field. The suppression difference is not likely due to drop residence times as is the case for the premixed flames.

Recent modeling predictions using the same multi-phase model and a validated propane combustion chemical mechanism for water drop suppressed propane-air flames (saturated air stream) are consistent with the results shown in Figure 12 [Chelliah, 2003].



(a) (b)

Figure 12: Water mist effects on the extinction of propane-air non-premixed counterflow flames. (a) Flame extinction strain rate as a function of mass of water or Halon 1301 (CF_3Br) in the air flow [Zegers, 2000]. (b) Mass of water to extinguish propane-air flames as a function of drop size, compared to gas-phase Halon 1301 (CF_3Br).

III F. Drop Evaporation Time Versus Flame Residence Time

III F 1. Drop Evaporation Time

A key component to the suppression effectiveness of liquid (mist) aerosols is the enthalpy provided by the drop evaporation. Several models have been proposed for treating the evaporation of liquid drops, depending on what regimes are relevant and what assumptions are appropriate. One model suitable for the experimental conditions under consideration here is [Turns, 1996]:

$$D^2(t) = D_0^2 - K\,t \qquad (1)$$

where K, the evaporation constant, is given by

$$K = 8\,\lambda / (\rho\, c_p)\ \ln\,[1+(T - T_{boil})(\,c_p / h_{vap})] \qquad (2)$$

The time for complete evaporation to occur can be estimated from:

$$t_{vap} = D_0 / K \tag{3}$$

Equation 1 is referred to as the d-square law for drop evaporation and predicts the drop diameter, D, at any time, t, in terms of the original drop diameter, D_0. The mass transfer is dependent on the temperature, T, and thermal conductivity, λ, of the surrounding gas as well as on the properties of the drop: heat capacity at constant pressure, c_p; density, ρ; enthalpy of evaporation, h_{vap}; and boiling point, T_{boil}. According to Equation 3, the residence time required for the drop to completely evaporate is dependent on the original diameter of the drop.

Evaporation times for water as a function of drop size for temperatures ranging from 1100 to 2200 K are shown in Figure 13. The evaporation time for a 30 μm diameter water drop in an air stream at 2100 K is predicted to be ~ 2.5 ms.

III F 2. Drop Residence Time in the Flame

The degree of evaporation of aerosol drops in a flame depends on the residence time of the aerosol in the high temperature environment. In the flame, the drop evaporation rate and drop size are spatially dependent since the aerosol is moving in a non-uniform temperature field. Solution of the problem requires full consideration of the flow field. However, the evaporation model can be used to estimate a drop size in the two flame configurations for the onset of complete drop evaporation. In the flame temperature field, drops begin to evaporate at the lower temperature and the resulting smaller drop, in traveling into the higher temperature region, will experience a higher evaporation rate and consequently a shorter total evaporation time.

Consideration of the burning velocity and flame thickness of the methane-air premixed flames studied here suggests that the water drops should experience a residence time in the range of 1-2 ms. Consideration of the temperature field and the results of Figure 13 indicate a drop size limit for complete evaporation (and the corresponding onset of water drop limiting effectiveness) at ~ 15 μm in premixed flames. This upper limit estimate is consistent with the water drop size profiles observed in the premixed flame and with predictions of the multiphase model [Fuss, 2002].

For counterflow flames, transit time in the flame can be estimated from the inverse of the strain rate [Lentati, 1998]. For a strain rate of 450 s^{-1} (high strain rate for methane, mid strain rate for propane) the residence time is ~ 2.2 ms. The drop size for the onset of complete evaporation predicted from Figure 11 is ~ 25 μm. This value agrees with the experimental water drop size survival properties in propane-air flames [Zegers, 2002] and is consistent with the modeling predictions for methane-air flames [Lentati, 1998a].

The transition diameter from very effective small drops to larger, less effective drops depends on the evaporation rate of the aerosol. In general, evaporation times are shorter at higher temperatures. However, for premixed flames, higher flame temperatures mean higher burning velocities and shorter residence times. For counterflow flames, predicting drop evaporation for long residence times and large drops is complicated by several competing factors related to the inability of larger drops to follow the gas streamlines. For co-flow flames (e.g. in a cup burner) residence times are > 20 ms. In each of these flames there is a tradeoff between flame temperature, flow field, residence time and drop evaporation. Quantifying the inhibition effects of large drops is experimentally challenging since independent control of the two phases is difficult to accomplish. The interrelated effects of drop size and flame conditions on drop evaporation explain why seemingly contradictory suppression results have appeared in the literature quantifying the effectiveness of aerosols in differing flame systems.

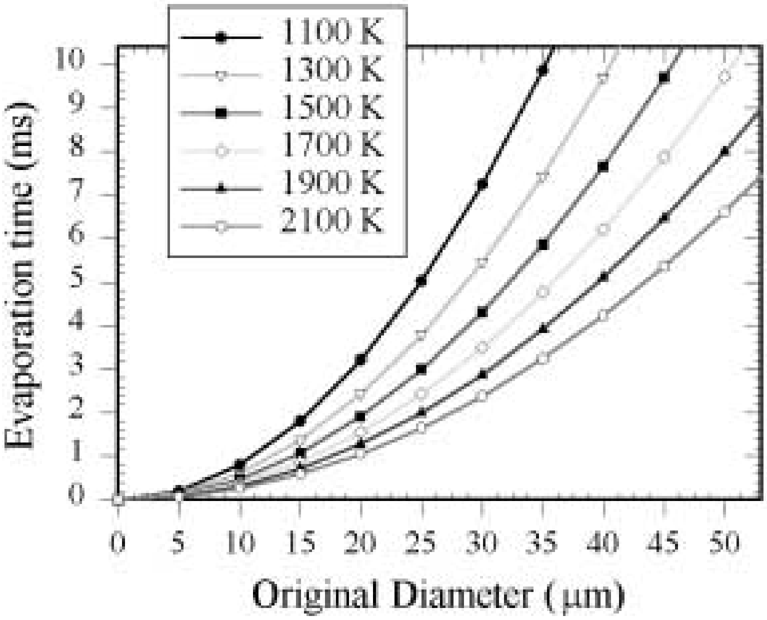


Figure 13: Predicted evaporation times using Equations 1-3 for water drops in air at the indicated temperature as a function of initial drop diameter. The thermal conductivity data for air is from [Kays and Crawford, 1980].

III G. Combining Chemical and Physical Agents

Water mist, a physical agent, can be as or more effective than CF_3Br, consistent with the maximum sensible enthalpy that this condensed phase agent can provide to the flame though evaporation. There is the possibility of increasing the physical effectiveness of water through the use of a chemical additive. For the chemical additives, enhanced effectiveness is accomplished through the catalytic removal of H, OH, or O flame propagation radicals by the additive inhibitor species. Most of the potential additive compounds exist as liquids or solids at room temperature and many are water soluble to some extent. The effect of additional water on flames is almost entirely thermal [Seshadri, 1978] and water is already present in the flames as a combustion product. Thus water is unlikely to interfere with the chemical activity of these additives. In addition to the thermal benefit to fire suppression, water may be useful as a delivery method for non-volatile chemical fire suppressants

The enhanced suppression for water and additives comes about due to the synergistic effect of combining a chemical catalytic agent with water that acts through physical means. By lowering the flame temperature, water also lowers the concentration of the key flame propagation radicals, H, OH, and O. More importantly, the lower flame temperature results in an *increase* in the ratio of the concentration of these radicals to their thermal equilibrium concentration values, thereby making the catalytic cycles more favorable for further reducing the flame radicals.

Water mist additives that have been investigated include alkali metal and phosphorus compounds. Zheng et al. reported the effect of 14 to 25 μm diameter aqueous NaOH drops on the burning velocity of premixed flames [Zheng, 1997]. We studied the burning velocity reduction in premixed methane-air flames by sub-micron size aqueous NaOH drops. Results for the extinction strain rate lowering in non-premixed methane-air counterflow flames by ~ 20 μm diameter aqueous NaOH drops were reported [Lazzarini, 2000]. The ~ 20 μm drops in the non-premixed counterflow flames demonstrated an effectiveness for the combined effect of water and sodium consistent with predictions of evaporation time and flame residence time of the aerosol drops as well as the chemical contribution of the sodium. On the other hand, results in premixed flames point to the much shorted residence times for these flames compared to the counterflow flames. In the premixed flames, the drop residence time in the flame are comparable to the required evaporation times of the aerosols. In this case, e*ither* essentially no effect for the water/additive aerosol above that of pure water is observed or there is abrupt flame extinguishment.

The alkali metal-water aerosol results are consistent with the characteristic residence times provided by the different flame configurations investigated and the drop size dictated evaporation times for water as discussed earlier. These studies point out that aerosol drop evaporation time (water plus additive) is even more important for the effectiveness of water mists with additives than for pure water aerosols. For additives with boiling points above ~ 100 ^{o}C, more time is required over the water evaporation time to allow the subsequent evaporation/decomposition of the residual particles and create the key chemical catalytic player(s) that will participate in the chemical suppression cycle. Water drops that are only small enough to completely evaporate just as they leave the flame zone will likely be too large to be able to release the chemical additive in time to participate optimally in the suppression process. Quantitative determination of the suppression effectiveness of water mists with additives must be deconvoluted from the properties of the aerosol introduced into the flame, including size and thermodynamic properties (e.g. boiling/decomposition temperature and heat capacity), and the properties of the flame (including temperature field and flow field configuration).

One benefit of the presence of additives to water mist may lie in the creation of solid particle residue. Extinction strain rate lowering of methane-air non-premixed counterflow flames by aqueous aerosols of both liquid and solid phosphorus compounds have been recently reported [Jayaweera, 2003]. They observed that additives that left a particle residue were slightly more effective than phosphorus compounds that left no residue. Differences in the chemical composition of the additive compounds were considered and may play a small role. However, the increased effectiveness may be due to the presence of the particles themselves. In addition to the increase in the total sensible enthalpy due to the decomposition or evaporation of the particles, the particles could also increase the heat loss from the flame via radiation or increased heat conduction. These mechanisms have been predicted for inert particles in flames [Ju, 2000; Blouquin, 1998]. The experimental studies show that although the physical effect of residual particles formed from the aerosols on the flame leads to an enhanced suppression effectiveness, participation of phosphorus in the gas-phase chemistry is the primary suppression mechanism. The reaction mechanism for phosphorus inhibition requires more work before the role of the particles can be fully explored.

IV. UNRESOLVED TECHNICAL ISSUES

Generating, controlling, and measuring aerosols are challenging but necessary tasks for studying these systems. However, the most challenging aspect of working with aerosols is quantification. Although standards exist for gases, there is no such aerosol standard. Development of a system that can reproducibly produce a known quantity of a given aerosol would be extremely useful.

The largest deficiency in the current study of the interaction of aerosols with flames is the lack of generally available computer codes to model the experimental observations and predict other behavior. The complexity of the flow and the non-trivial treatment of the interdependent gas and aerosol properties demand such models. Multi-phase models do exist for the one-dimensional premixed flame. However, this is not an experimental configuration that can be duplicated in the lab. Further development is required for treating aerosols in more typical Bunsen-type premixed flames. A multi-phase model does exist for the counterflow configuration and was used (via collaboration) to model data in this project. General availability of such validated codes is needed.

V. RECOMMENDATIONS FOR ADDITIONAL RESEARCH

How do we use what we have learned? This project has contributed experimental data and understanding of the interaction of aerosols with certain flames. Applying this understanding to a greater range of conditions and for more varied systems can only be done by utilizing validated multi-phase aerosol/flame models. Further development is needed before these codes are generally available.

It would be very worthwhile to study the behavior of aerosol suppression agents in the more realistic cup burner flame. The counterflow flame flowfield studied in this project is well characterized while the cup burner flame flowfield is more complex. Because of this complexity, understanding the aerosol/flame interaction in cup burner flames is currently very challenging. Characterization of the cup burner flowfield and development of suitable flame models should be pursued in order to make this experimental platform more tractable for key, informative research in this flame configuration.

VI. CONCLUSIONS

This project has addressed the relationship of aerosol particle/drop size and physical and chemical properties to the aerosol suppression effects in both premixed and non-premixed flames. Aqueous and non-aqueous aerosols (thermal suppression agents) investigated including water, perfluoro n-hexane, and HFE-7100. Powder aerosols investigated (chemical suppression agents) included the alkali metal bicarbonates and several phosphorus compounds. Aerosol properties were monitored using optical diagnostic techniques in both premixed flames and non-premixed counterflow flames. For each of the aerosols studied, the decomposition/evaporation behavior of individual particles/drops was found to correlate with the measured suppression effectiveness (flame burning velocity reduction or extinction strain rate lowering).

Water mist under certain conditions was found to be as or more effective than CF_3Br on a mass basis at inhibiting or extinguishing the flames. Results for water are consistent with an evaluation of the thermodynamic properties including evaporation of the liquid indicating that the total thermal capacity of liquid water in comparison with gaseous thermal agents can be achieved, given suitable conditions. The effect of water mist on burning velocity reduction and extinction strain rate lowering can be predicted by multiphase models incorporating detailed combustion chemistry and multicomponent molecular transport. The other liquids investigated had much higher molar heat capacities and also much higher room temperature vapor pressures. Evaporation of these agents was so rapid that all of the agent reaching the flames was in the gas phase. Drop size effect studies on these systems were not possible.

Alkali metal powder aerosols with particle diameters < ~50 μm were more effective than Halon 1301 in extinguishing counterflow non-premixed flames. Participation of the powders in the flame chemistry is responsible for the higher effectiveness. The higher effectiveness of potassium over sodium can also be attributed to differences in the chemical kinetics of the two metals.

In general for liquid or powder aerosols, the amount of aerosol to effect suppression decreases with decreasing particle/drop size, reaching a limit at small size, below which there is no further suppression advantage based on added mass. The particle/drop size limit that assures complete decomposition/evaporation provides the maximum suppression effectiveness per mass of added aerosol. Drop residence time in the elevated temperature of the flame flow field is key to the suppression performance as it controls the extent of decomposition/evaporation. For combined agents (solid chemical agent dissolved in liquid thermal agent) the drop residence time is even more critical. Here, the liquid drop must evaporate in time for the chemical agent to decompose/evaporate and release its chemical player(s) before exiting the flame.

VII. ACKNOWLEDGMENTS

Significant contributions to this project by Dr. Bradley Williams (NRL) are acknowledged as are key contributions by Eric Zegers (NRL/NRC Postdoc), Paul Fuss (NRL/ASEE Postdoc), Derek Dye (UMd-Baltimore County Intern at NRL), Mark Reed (WPI Intern at NRL), and Ezra Chen (UMd Intern at NRL). We thank Jiann Yang (NIST) for many useful conversations and assistance with aerosol generation issues. The Department of Defense Next-Generation Fire Suppression Technology Program funded by the DoD Strategic Environmental Research and Development Program supported this project. Partial funding was also received from the Office of Naval Research through the Naval Research Laboratory.

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