Chemical Fire Suppressants: How Can We Replace Halon?

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INTRODUCTION

Halons, halogenated hydrocarbons containing bromine, appeared on the scene for fire suppression in the late 1940's following a U.S. Army study to identify effective agents. Halon 1301, bromotrifluoromethane, with its low boiling point is extremely effective in total flooding applications, which rely on the agent completely filling the space to be protected. Halons that exhibit good fire suppression properties but have boiling points closer to room temperature (Halon 1211, bromochlorodifluoromethane, and Halon 2402, dibromotetrafluoroethane) are more suitable for streaming agents which can be directed toward the fire threat as a liquid stream, typically from hand-held units. Interestingly, Halon 1301 was not the most effective total flooding compound on the list. However, Halon 1301 provides a near optimum combination of good fire suppression effectiveness, low toxicity, suitably low boiling point, and a reasonably low density and molecular weight. The combined effectiveness and desirable properties quickly accelerated the use of halons to a wide range of fire suppression applications, including movable platforms such as ships and planes. Dependence on halons increased as more and more fire suppression systems were engineered around these compounds.

In 1974, Rowland and Molina called the world community's attention to the fact that chlorofluorocarbons (CFCs), although very unreactive at ground level, have the potential to catalytically destroy stratospheric ozone once the chlorine is released through uv photolysis. Subsequent research including work done at NRL in 1976 showed that bromine containing halons are more deleterious to ozone than CFCs. When released in the stratosphere, bromine catalytically destroys O_3 : $Br + O_3 \rightarrow BrO + O_2$; $BrO + O_3 \rightarrow BrO_2 + O_2 \rightarrow Br$. CF_3Br is very stable to attack by OH and uv wavelengths present at ground level, the primary removal mechanisms of compounds in the troposphere. Thus, Halon 1301 has an undesirably long atmospheric lifetime that allows transport of the problematic bromine into the stratosphere.

The search for environmentally acceptable fire suppression halon replacements requires identifying compounds that have: good suppression efficiencies compared to Halon 1301, very low potential for destroying the stratospheric ozone, minimal impact on global warming, low human toxicity, and desirable boiling points. Significant efforts are underway to find halons replacements to protect both new construction as well as retrofitting current systems [1]. Different applications require different criteria. Suppression system weight and space constraints on retrofitting current systems make replacement particularly challenging. The search for acceptable replacements must be more than a random walk through an extremely large number of possibilities. Replacement choices demand compromises and systematic methodologies for

identifying suitable replacements based on fire suppression mechanistic understanding. An understanding of the suppression mechanism can effectively guide the search in promising directions. Modeling predictions are valuable for providing insight. Models must be validated against experimental data for a range of conditions and for a number of compounds. This paper covers current and past activities related to our efforts in halon replacement in a variety of flame environments. Some of the projects presented are part of the current Department of Defense's Next-Generation Fire Suppression Technology Program which seeks retrofit halon replacements for military applications [2].

PHYSICAL SUPPRESSION

Flame suppression agents can be generally categorized into chemical agents, such as those containing bromine or iodine, and physical agents such as nitrogen. However, an agent can only be a purely physical agent if it suffers no degradation in the flame, either via chemical attack or thermal decomposition. Molecular nitrogen and other physical agents are effective at flame suppression through heat extraction and dilution of oxygen. The amount of N_2 required for adequate protection is very costly in terms of total system volume and weight, including storage containers and dispersal hardware. Both volume and weight are critical parameters in movable platforms such as vehicles, ships, and planes. Although CO_2 can be used in some applications, the concentration required for flame suppression exceeds the human toxicity levels. In occupied spaces, the potential of accidental release is a very serious threat to human safety.

In terms of sensible enthalpy per unit mass, liquid water is the best physical agent. A key issue is how to take advantage of the latent heat of vaporization (> 40% of the sensible enthalpy) in an actual fire suppression application, including dissemination and distribution of the optimum droplet size. If the drops are too small they will not make it to the fire; droplets which are too large will not completely evaporate. Water spray typically discharged from overhead water sprinklers is characterized by very large (> 500 μ diameter) water drops. Although water spray can control a fire, smaller droplets (< 200 μ diameter) characteristic of water mist, are much more effective at heat abstraction due to their higher evaporation. The increased evaporation rate of water mist also leads to higher oxygen dilution in the air stream.

Lentati and Chelliah [3] predicted that ~ 25 μ water droplets should be near the optimum size to extract the greatest amount of heat yet large enough to just survive traveling through a low strain rate counterflow diffusion methane/air flame when seeded from the air side. Studies at NRL on water mist suppressed propane/air flames are consistent with these predictions and are reported at this meeting [4]. In these studies, water droplets are monitored throughout the flowfield using phase Doppler anemometry to determine the optimum droplet size as well as the quantity of mist required to extinguish the counterflow diffusion flames. Recent results also presented at this meeting on the flame speed inhibition by very fine water mist, nominal 0.3 μ diameter droplets, show that the theoretical heat extraction potential of water can be achieved [5]. The combination of the heat extraction by fine water mist and a chemical suppression component by an additive has the potential to impact a significant chemical suppression component to the overall flame extinction mechanism. Our laboratory is currently assessing the effectiveness of water additives for suppressing both counterflow diffusion flames and premixed

Bunsen flames.

CHEMICAL SUPPRESSION

All agents have a physical component to suppression. In addition, they can have a chemical component that significantly increases effectiveness. Halon 1301 is effective at fire suppression because the bromine can chemically combine H radicals and remove them from the flame: $H + Br \rightarrow HBr$, $HBr + H \rightarrow H_2 + Br$. Catalytic removal is possible because the H, OH, and O radicals controlling the flame chemistry are at superequilibrium concentrations in the flame front. Designing bromine containing molecules that do not make it to the stratosphere (e.g. tropodegradable compounds) is one area of current study. Inclusion of chemical structures that promote oxidation or photolysis leads to compounds with higher boiling points, toxicity concerns, and less suitability as "drop-in" Halon 1301 replacements. Iodine containing compounds are also tropodegradable and have good chemical suppression efficiency but also suffer from the problem of toxicity and low volatility concerns. Although these compounds are less likely to be used as total flooding agents, many of them have potential for use in other applications.

In the mid 1970's Sheinson and others at NRL began studies on the extinction of small liquid pool fires in a cup burner [6]. Extinction concentration data provided suppression effectiveness ranking for a large number of compounds (exclusively gases). Real scale tests show that the cup burner extinction concentration (plus a small margin) is usually adequate to extinguish most fires due to the very stable cup burner flame. Cup burner data have been used to derive recommended agent concentrations for suppression systems. However, realistic scale results are still needed to evaluate non-scaling effects such as agent mixing, by-product formation, and fire extinguishment times.

From the large number of compounds measured in the NRL Cup Burner, Sheinson derived a suppression predictive capability based on physical and chemical properties [7]. These studies also provide a great deal of understanding concerning the interplay of chemical and physical properties of various compounds [8]. They reported the enhanced suppression effect of combining chemically acting and physically acting agents [9] which has been further explored by Saso et al. [10]. The source for this enhancement results from the impact of the agent on the temperature field and the flame radical concentrations.

An outgrowth of the NRL Cup Burner studies on hydrofluorocarbon compounds (HFCs) was the recognition that there was an increased chemical contribution to suppression if the fluorines are arranged on the hydrocarbon in CF_3-groups [7]. The increased effectiveness observed was significantly greater than that predicted based on the heat capacity of the CF_3-group. This observation led to the commercialization of CF_3CHFCF_3 (HFC-227ea, heptafluoropropane noted here as HFP). In addition, of the HFCs that have multiple isomeric forms, those that have been commercialized as fire suppression agents have the fluorines and hydrogens arranged to maximize the number of CF_3-groups. NRL suppression testing and full scale evaluation of HFP resulted in the implementation of HFP by the U.S. Navy as one of the replacements for Halon 1301 in the next class of ships to be constructed [11].

NRL extinction strain rate studies in counterflow diffusion flames showed that the

distribution of fluorine atoms on the HFC that maximizes the number of CF_3-groups leads to better suppression across a range of strain rates [12]. Extinction strain rate curves for hydrofluorocarbon agents cluster into groupings corresponding to the number of CF_3-groups on the molecules. The similarity of the thermochemical properties of these compounds suggests that the higher extinction effectiveness associated with the CF_3-groups might be due to differences in chemical kinetics.

Our laboratory has investigated the chemical kinetic pathways relevant to inhibition by HFCs in low pressure flat flames [13]. Flame structure information using laser induced fluorescence was compared to flame modeling calculations; a kinetic sub-model was used for HFP that was developed by Hynes et al [14]. Reaction pathway analysis points to a combination of events rather than one specific source to explain the CF_3-group enhanced effectiveness. For HFP there is a strong suppression dependence on agent decomposition, whether thermal or via flame radical attack. Regardless of the initiation step, the thermodynamically favored by-product for HFP or any partially fluorinated hydrocarbon will be HF. The human health hazard HF presents is cause for concern when using fluorine containing agents in occupied spaces or ones that must be entered after application of the agent.

A method to reduce the amount of HF has been patented by NRL [15] and combines the use of water spray with the fluorinated agent. Large reductions in HF can be achieved, resulting from the significantly lower temperature and oxygen dilution due to the water spray, which greatly weakens the flame and thus reduces the HFP decomposition.

ULTRA-HIGH EFFICIENCY AGENTS

Compounds containing elements other than the halogens have shown potential for chemical fire suppression many times greater than bromine. Babushok points out the very high flame speed reduction potential for a number of compounds, including iron and alkali metals [16]. Recent studies at NIST show that iron pentacarbonyl, $Fe(CO)_5$, is some 70 times more effective than Halon 1301 in reducing the flame speed of a methane/air flame by 25% [17]. The mechanism responsible is postulated to be a catalytic removal of both H and O atoms. Unfortunately, above ~ 200 ppm of added Fe (in the form of $Fe(CO)_5$) there is a leveling off of effectiveness with increased Fe addition. This diminished effectiveness comes at much lower concentrations than the expected slowdown for catalytic agents [18] due to the flame H, O, and OH radical concentrations approaching their equilibrium values. Early onset of decreased effectiveness has been attributed to the condensation of gas phase iron atoms at the higher concentrations [19]. It is likely that other iron compounds will be impacted by the thermodynamic limit of the gas phase Fe or FeO concentration.

The effectiveness of sodium and potassium bicarbonate powders was measured in counterflow diffusion flames [20]; Hamins reported results for sodium bicarbonate in a cup burner [21]. Potassium bicarbonate powders are at least twice as effective as sodium bicarbonate for similar particle sizes and flame strain rate; small particles of both compounds are more effective than Halon 1301. Determining the mechanism for particle suppression requires particle size and surface area information. Although these studies confirmed the enhanced effectiveness as particle size decreases, quantifying the effectiveness as a function of particle size is difficult

for powder samples. Although a nominal particle size can be determined by sieving, obtaining an *in situ* particle size or surface area is not possible. Optical techniques assume a spherical particle (phase Doppler Anemometry measures the local radius of curvature) or provide a generalized shape (diffraction-based or imaging methods). The assumption that an off-line size determination is the size delivered to the flame is questionable, especially for very small particles where several factors including humidity and static charges can affect the particle size distribution. Despite this limitation, results on sodium and potassium bicarbonate flame extinction effectiveness based on sieving size show that effectiveness is controlled by particle size [22]. These studies suggest that there is a limiting small size below which there is no increase in effectiveness based on mass of the alkali metal compounds. It should be possible to quantify the chemical effects of various powders if sufficiently small particle samples are studied.

Studies are underway in our lab to assess the mechanistic reasons for the higher effectiveness observed for potassium over sodium and the generally observed increase in effectiveness as one goes down the row of alkali metals (Li < Na < K < Rb). Preliminary flame speed calculations have been carried out for sodium inhibited flames [23]. Only the sodium chemistry currently has a sufficient number of reported reaction rate coefficients. In general alkali metal atoms and metal hydroxide molecules can combine H and OH flame radicals according to

$$M + OH \rightarrow MOH \tag{1}$$
$$MOH + H \rightarrow M + H_2O \tag{2}$$
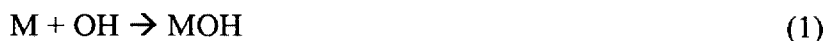
where M represents an alkali metal atom. Calculations assuming similar chemistry and kinetics for lithium suggest that thermochemistry alone does not account for the higher effectiveness of potassium relative to sodium. However, thermodynamics does limit the amount of Li relative to LiOH which in turn greatly diminishes the effectiveness of the Li + OH + M $\rightarrow$ LiOH / LiOH + H $\rightarrow$ Li + H$_2$O catalytic cycle.

Flame speed versus added sodium plots show the typical limiting behavior at high agent concentration characteristic of very efficient catalytic agents. Calculations predict that methane/air flames inhibited with an "ideal" agent, one which causes the H + OH recombination rate to equal the collision rate with no added thermal mass, can reduce the flame speed from ~ 39 cm/s to ~ 8 cm/s. This is not enough to extinguish the flame in the absence of any other heat losses. For agent addition beyond the chemical saturation point, even an ultra-high efficient chemical agent begins to act more like a physical agent, essentially only adding thermal mass. The resulting heat loss is more effectively accomplished using an efficient physical agent such as water mist.

CONCLUSIONS

Finding a true, drop-in replacement for Halon 1301 with identical properties yet environmentally acceptable is not likely. However, there are environmentally acceptable compounds that hold real promise as potential retrofitable replacements. Exactly what chemical form is best and how to get it to or in the flame are key issues. As we decide on halon

replacement options, there will also be the need for more critical assessment of the areas requiring protection and other means of minimizing fire damage. It is apparent that future choices of which agent to use will be based as much on the fire protection requirements and the area to be protected as on the agent itself. Choices will obviously result in tradeoffs and engineering compromises.

Combining a highly efficient chemically acting agent with a physically acting agent holds the greatest promise for future systems. This might be done in a single designer molecule or perhaps in a dual system. Combining the superior chemical suppression capability of additives such as iron or potassium at low concentrations with the large heat extraction capabilities of fine water mist is a combination worthy of further study. Such systems will present storage and delivery issues and engineering challenges to meet both reliability requirements and weight and volume restrictions. The need for environmentally acceptable replacements for halons will continue to drive the creativity and ingenuity of both chemists and engineers to meet these challenges.

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