

PROGRESS UNDER THE NEXT-GENERATION FIRE SUPPRESSION TECHNOLOGY PROGRAM (NGP) IN 1999

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INTRODUCTION

Halon 1301 (CF_3Br) has long been the choice for fire extinguishment in most weapon systems and mission-critical facilities. It is also a potent depleter of stratospheric ozone. As part of its effort to eliminate its dependence on Halon 1301, in FY1997 the Department of Defense (DoD) initiated its Next-Generation Fire Suppression Technology Program (NGP). Originally a broad-based effort, the scope of the NGP has recently been narrowed: "to develop and demonstrate, by 2005, technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by Halon 1301 systems in aircraft." Candidate technologies must do well in the following: fire suppression efficiency and reignition quenching, ozone depletion potential, global warming potential, atmospheric lifetime, electrical conductivity, metals non-corrosivity and polymeric materials compatibility, long-term storage stability, low toxicity of the chemical and its combustion and decomposition products, speed of dispersion, safety and occupational health requirements, and compatibility with the host design of the platform.

Support for the NGP comes from DoD funding and cost sharing from the participating laboratories. Most of the DoD support has come from the Strategic Environmental Research and Development Program, with additional support from the Army Tank and Automotive Command.

The NGP has just completed its third year of research. This paper highlights the new knowledge gained from the NGP research and the progress made towards the NGP Goal. Much of the NGP findings have appeared in the current and prior *HOTWC Proceedings*. Additional references appear at the end of this paper and at the NGP website: www.dtic.mil/ngp/.

TECHNICAL PROGRESS

NEW FLAME SUPPRESSION CHEMISTRY

In searching for new chemicals that perform as well as CF_3Br but without the environmental limitation, a comprehensive view of chemical fire suppression has emerged. Catalytic agents, such as CF_3Br and metal compounds, reduce the superequilibrium levels of flame radicals toward equilibrium levels. Adding heat capacity reduces the flame temperature and thus the flame reaction rates below the level needed to sustain combustion. The minimum extinguishing concentrations thus appear to be perhaps on the order of 1%.

There are new findings on several promising suppressant chemicals:

- $\text{H}_3\text{COC}_4\text{F}_9$ (HFE-7100) was shown to be an efficient non-chemically active suppressant. About twice the mole percent of the gas as Halon 1301 vapor is needed to suppress a flame. As an aerosol, only half the Halon 1301 vapor level is needed.

Figure 1. Effect of fluid and fluid flow on droplet size.

Figure 2. Effect of fluid and fluid flow on flame extinction effectiveness.

- Small amounts (ca. 10^{-4} mole percent) of $\text{Fe}(\text{CO})_5$ are near the ideal limit at reducing premixed flame velocities. At higher concentrations the agent becomes less efficient, as the active iron species condense to form relatively inactive particles. Ferrocene is nearly identical, indicating no dependence on the binding of the iron. Manganese-containing compounds behave similarly, but are 5-7 times less efficient at reducing burning velocity.
- Also of interest are tropodegradable bromocarbons. For example, bromoalkenes are expected to have atmospheric lifetimes of a few days. In work jointly supported with the Advanced Agent Working Group, a series of bromofluoroalkenes and bromofluoroamines generally had cup-burner extinguishment values below about 4 mole percent. AAWG data show that rats exposed for 30 min to 5% of four of the compounds (1-bromo-3,3,3-trifluoropropene, 2-bromo-3,3,3-trifluoropropene, 4-bromo-3,3,4,4-tetrafluorobutene, and 2-bromo-3,3,4,4,4-pentafluorobutene) showed no ill effects. The Ames tests were also negative.

Work has begun on developing a set of quantitative structure-activity relationships for compound volatility. These would be used in conjunction with values of agent discharge rates and the known dimensions of and thermal conditions in the fire compartment to determine whether compounds having a specified chemical structure can be expected to put out the fire in the required time frame (e.g., on the order 0.5 s in the case of an engine nacelle fire).

SUPPRESSANT SCREENING TESTS

A set of efficient, accurate screening tests for new suppressant chemicals is near completion.

The Dispersed Liquid Agent Screen (DLAS), based on the Tsuji diffusion burner, is now in use both to obtain suppression efficiency data and as a research tool. Tests with well-characterized droplets of fluids of widely varying density, viscosity, and surface tension (water, 30% and 45% potassium lactate by mass, and 1000 and 2000 mg/L sodium dodecyl sulfate), showed the average droplet diameters of the fluids were within $\pm 15\%$ (Figure 1) and that this variation affected the extinction efficiency by under $\pm 15\%$ (Figure 2), well within useful tolerance for a screen apparatus.

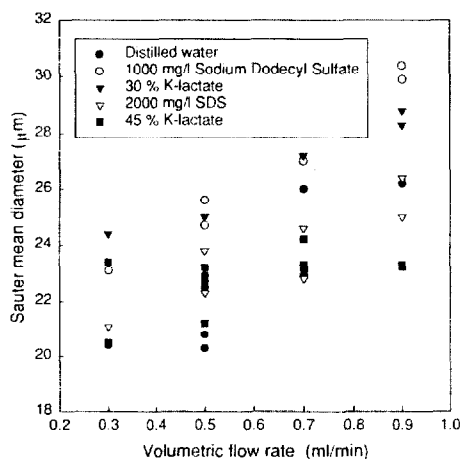


Figure 1. Effect of fluid and fluid flow on droplet size.

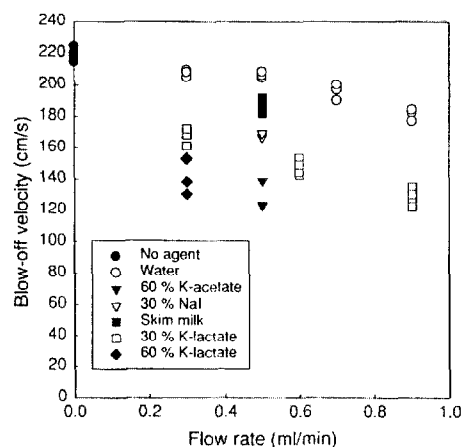


Figure 2. Effect of fluid and fluid flow on flame extinction effectiveness.

The Transient Application, Recirculating Pool Fire apparatus (TARPF), a screening tool for the effectiveness of suppressants that are impulsively discharged, is nearly complete. An injection system for the effluent from solid propellant gas generators has been tested. Direct numerical simulation of the flow over various obstacles in the TARPF has been conducted to help interpret the experimental results and extend them to other conditions.

A tiered screening system for environmental impact, toxicity, and materials compatibility has been developed.

A physiologically based pharmacokinetic (PBPK) model of a human system to describe the short-term inhalation of volatile halogenated hydrocarbons is nearing completion. This model incorporates a breath-by-breath description of respiration and follows the inhaled suppressant to the bloodstream, enabling prediction of safe exposure duration for a given agent used at a known extinguishing concentration. Data have been developed for Halon 1301, CF_3I , HFC-125, HFC-227ea, and HFC-236fa. Extension of the model to other suppressants requires the following:

- Partition coefficients, i.e., solubility of the chemical into blood and other body tissues
- Metabolic rate, the rate at which chemical is broken down by the body
- LOAEL for cardiac sensitization measured in beagle dogs or other endpoint
- Arterial blood concentrations measured in beagle dogs exposed at the LOAEL concentration (without epinephrine challenge). (Data should be collected over a 10-min period, with the 5-min data point being the most critical.)

The NGP research to develop a computational screening tool for a suppressant's atmospheric lifetime and infrared absorption is continuing. Calculated rate constants for the reaction of OH with halomethanes are in good agreement with their experimental counterparts, establishing the viability of *ab initio* calculations as the basis of a screening tool. Calculations for the reactions of OH with several fluoroethanes and the ethers derived from them have reproduced the experimental trends, with predictions in absolute reactivity within a factor of three. Calculations are being extended to ethers with several carbons and containing fluorine along with one or more bromine atoms.

NEW AND IMPROVED AEROSOL SUPPRESSANTS

Nearly all compressed fluid suppressants emerge from storage containers as liquids or powders, along with a gaseous component. The properties of the aerosol determine (a) its transport effectiveness to the fire, (b) the magnitude of its effect on the flames, (c) its ability to quench condensed-phase fuels, and (d) its impact on preventing reignition. The values of the aerosol properties that optimize each of these may be uniform for the four impacts or may be in conflict.

It is important to know the properties of fine droplet sprays that promote suppression of the fireballs experienced in aircraft dry bays. NGP studies of water droplets injected into propane/air and methane/air counterflow non-premixed flames have shown that extinction effectiveness correlates with the degree of evaporation. If all of the water droplets can evaporate in or near the flame, which happens for diameters $0 \leq 30 \mu\text{m}$, water is as effective as Halon 1301 on a mass basis. Calculations for fine sprays (diameters $< 50 \mu\text{m}$) indicate nominally complete evaporation near the flame front, consistent with the experimental results above. For these small droplets, other parameters such as the droplet transport time to the fireball must be considered.

It is possible to encapsulate a practical mass of a suppressant onto an inert host for transport to the fire. A large mass fraction of $\text{Fe}(\text{CO})_5$ can be absorbed into zeolites (33%) and aerogels (up to 200%). Further, thermogravimetric analysis showed that at 250 °C a large fraction of the $\text{Fe}(\text{CO})_5$ is desorbed. Flame tests will allow assessment of whether the agent can be liberated in the time available in a flame. It was found that sometimes matrix materials (i.e., zeolites) can exacerbate the pyrophoricity of $\text{Fe}(\text{CO})_5$, likely due to reaction with residual absorbed water. However, ferrocene has been shown to be as effective as $\text{Fe}(\text{CO})_5$ (Figure 3) and is less toxic and pyrophoric. Combining iron compounds with HFCs is not an effective combination because stable iron-halogen species act as sinks for active gas-phase iron compounds.

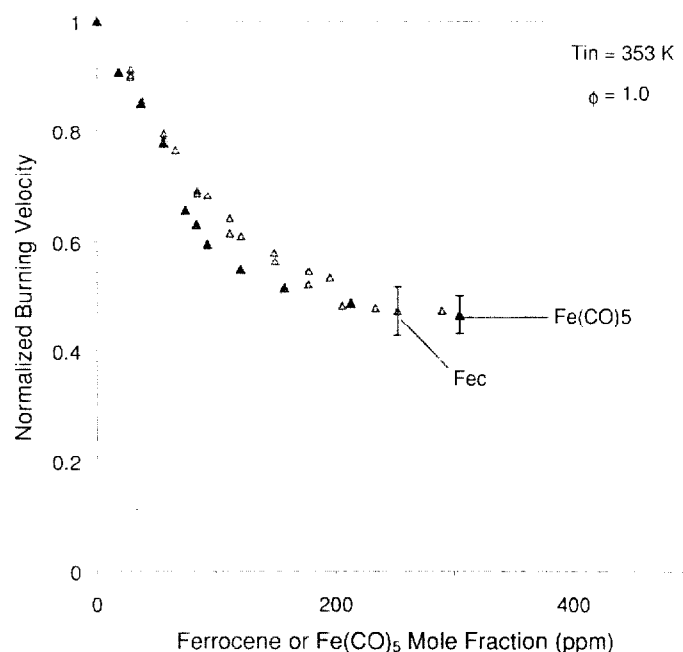


Figure 3. Comparison of premixed $\text{CH}_4/\text{O}_2/\text{N}_2$ flame inhibited by ferrocene and $\text{Fe}(\text{CO})_5$.

IMPROVED SUPPRESSANT DELIVERY

The complement to identifying new suppressants is improving the efficiency of getting the suppressant to the site of the fire. This comprises storage and discharge technology, transport through any distribution piping and dispersion throughout the compartment.

Replacement fluids must function within the existing distribution plumbing. Replacing the piping is a major cost in retrofit and is to be avoided. Therefore one has to know how a new, multiphase chemical will behave in a long run of bent pipe.

A new computer code for prediction of transient two-phase fire suppressant flows during discharge is now complete. The user can select water, Halon 1301, CO_2 , HFC-227ea or HFC-125 as the suppressant. The software tracks both the fluid and nitrogen as a pressurizing gas. Figure 4 compares the vessel pressure calculations with published data (Elliott et al., *Flow of Nitrogen-Pressurized Halon 1301 in Fire Extinguishing Systems*, JPL Publication 84-62, 1984). New data have also been generated using a unique test facility with the capability to measure the instantaneous (a) mass flow of fluid during transient discharge from the source vessel, (b) fluid temperatures along the discharge pipe, (c) local pressure at five different locations in the system,

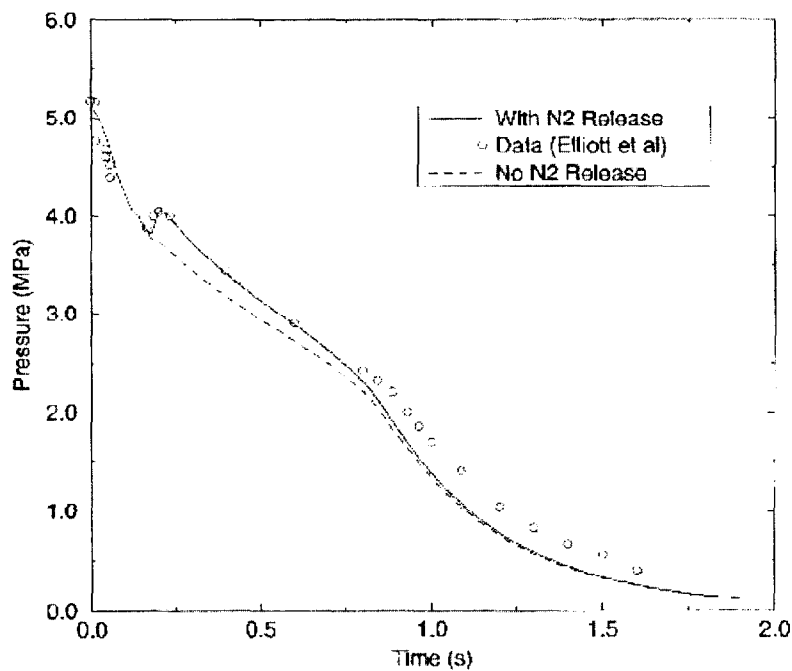


Figure 4. Comparison of calculated supply vessel pressure with experimental data.

(d) void fraction at the end of the pipe, and (e) mass flow from the discharge vessel. The code is portable to a variety of commonly used operating systems.

A principal reason for the historic overdesign of Halon 1301 systems was to overwhelm the impedance of distribution by the extensive clutter. NGP engineers have quantified these penalties for different fuels (methane, ethane, JP-8), fire suppressants (Halon 1301, HFC-125, nitrogen), and bluff body shapes (step, baffle, J-flange). These results will both quantify the potential gains from redesigned distribution systems and assist in screening for the effectiveness of candidate suppressants.

An NGP model based on a well-stirred reactor relates the agent concentration and injection period to the concentration needed for extinguishment and a characteristic mixing time for agent entrainment into the recirculation zone. Figure 5 shows that this model captures the normalized agent mole fraction at extinction as a function of agent injection period for a range of flow conditions, agents, and clutter shapes.

Based on these results, a fire suppression system should be designed to provide a critical concentration of agent for a period at least three or four times the characteristic mixing time of the system.

NGP research is developing new types of solid propellant gas generators (SPGG) that have high flame suppression efficiency with reduced SPGG combustion temperatures. One approach directs a rapid gas generator discharge of additive-enhanced propellant formulation into a flame zone. A second approach directs the hot gas generator discharge from an "inert" solid propellant across an "activated" agent bed, entrains a chemically active additive into the gas stream, and carries it to the flame zone.

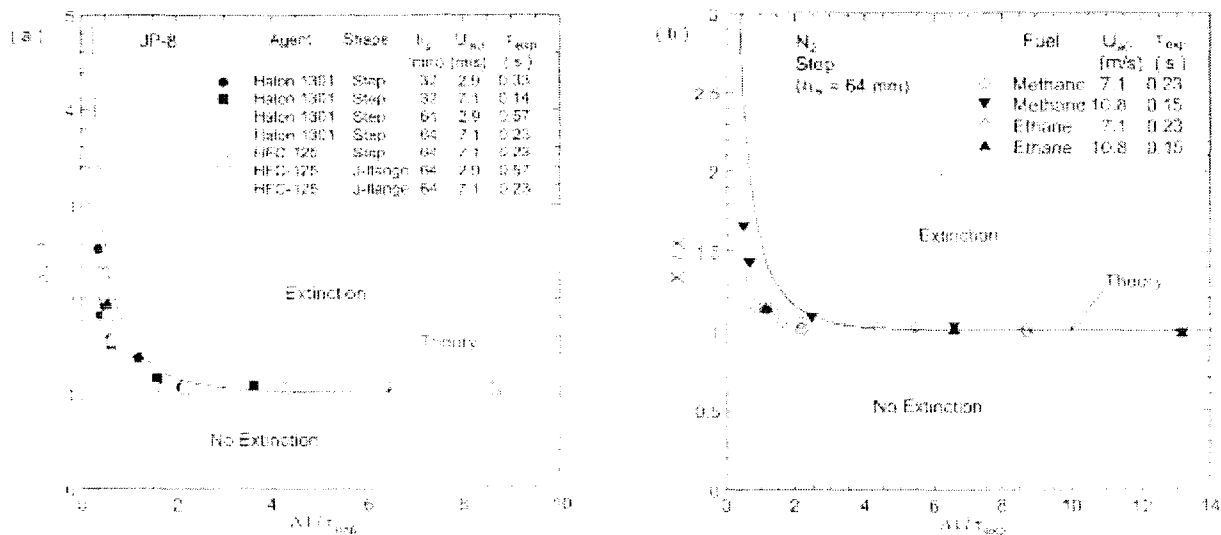


Figure 5. Calculated and measured normalized extinction concentrations as a function of normalized agent residence time.

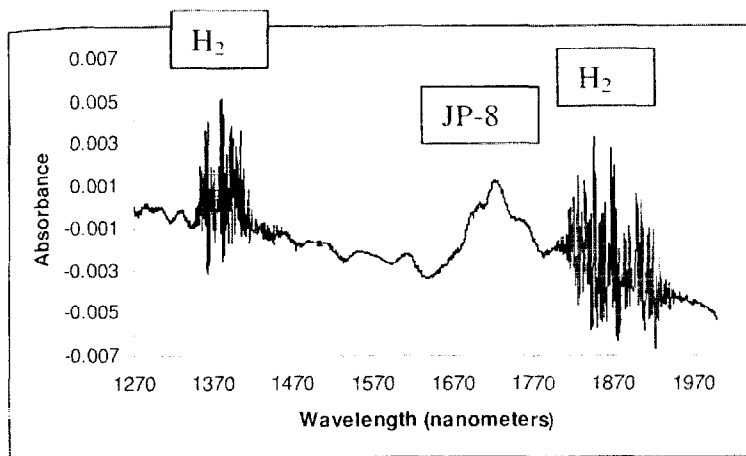
VIABILITY OF NEW SUPPRESSANT TECHNOLOGIES

The success of new NGP technologies requires that (1) the laboratory research replicate the suppression phenomena in real-scale fires and (2) the NGP be able to demonstrate that candidate fire suppression methods are quenching flames as they would under the threats experienced in the field. Meeting both of these needs entails improved instrumentation in the test articles already owned by the military department laboratories.

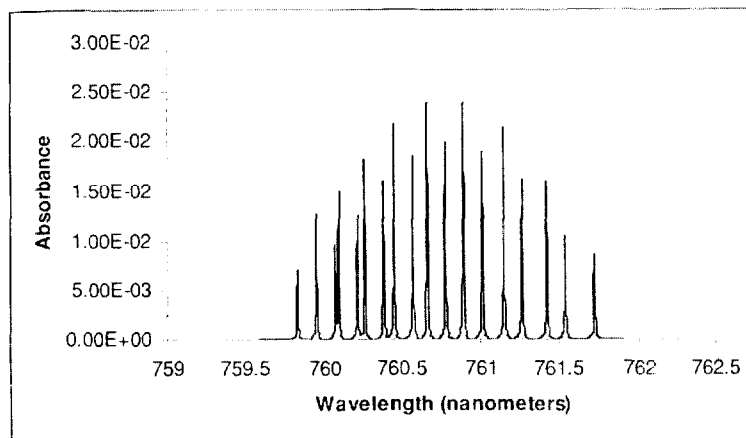
NGP researchers are complementing prior instrumentation advances by developing a time-resolved (10 ms), multipoint, fieldable, fiber-coupled, near-infrared tunable diode laser-based sensor for measurement and detection of combustible mixtures of oxygen and hydrocarbon fuels (heptane and JP-8) before, during, and after the fire suppression event of 250 ms duration. Detection of fuel and oxygen concentration is especially important after the suppression event in order to predict the possibility of reignition. Two separate lasers, one to detect each species, are combined to produce the probe beam. Initial tests of this system have shown that detection of fuel and oxygen at the anticipated levels is feasible (Figure 6).

Research is also continuing on developing an instrument for measuring agent concentration with a 10-ms time response for quantification of the transient agent concentration during suppression of the fastest fires involving military systems. Tests of a second-generation version of the Differential Infrared Agent Concentration Sensor (DIRRACS-2) showed that the device is able to follow HFC-125 discharges with acceptable signal-to-noise ratio and time response. The next stage in the development of the DIRRACS-2 will be the assembly of two portable units to be deployed in the field.

Numerous contributing factors are to be considered when making a decision to retrofit a fire suppression system (or not). These include objective cost factors and subjective value factors.



JP-8 vapor, 10 cm path length
355K, 4cm⁻¹ resolution,
256 scans.



O₂, 1 m path length,
296K, calculated using
HITRAN database.

Figure 6. Measured near-infrared absorbance in the region near JP-8 vapor at 355 K, and the calculated absorbance spectrum of O₂.

Thus, the NGP is developing a methodology to quantify a fire suppression technology by its total, life-cycle cost and to enable superimposing on this a subjective value system.

The data gathering for and formation of the baseline (Halon 1301) case has been completed, as has the structuring of the cost benefit analysis process. The latter provides a framework for evaluating a range of weapons systems, taking financial and technical variables into consideration. Figure 7 displays a framework for qualifying benefits. Expert Choice will be the methodology for evaluating benefits.

IMPROVED FUEL TANK INERTION

Research in this area has been limited. Two aircraft use CF₃Br to inert fuel tanks when entering combat—the F-16 and the F-117. Should the Air Force's current consideration of CF₃I for this application be positive, then fuel tank inerting will not be an NGP task. Meanwhile, NGP staff have begun a project to assess the current status of alternate systems that had in prior decades shown promise for fuel tank inerting. Tasks underway include assessment of in-flight fuel tank operating environments and identification of whom to consult in gathering information about these alternate systems.

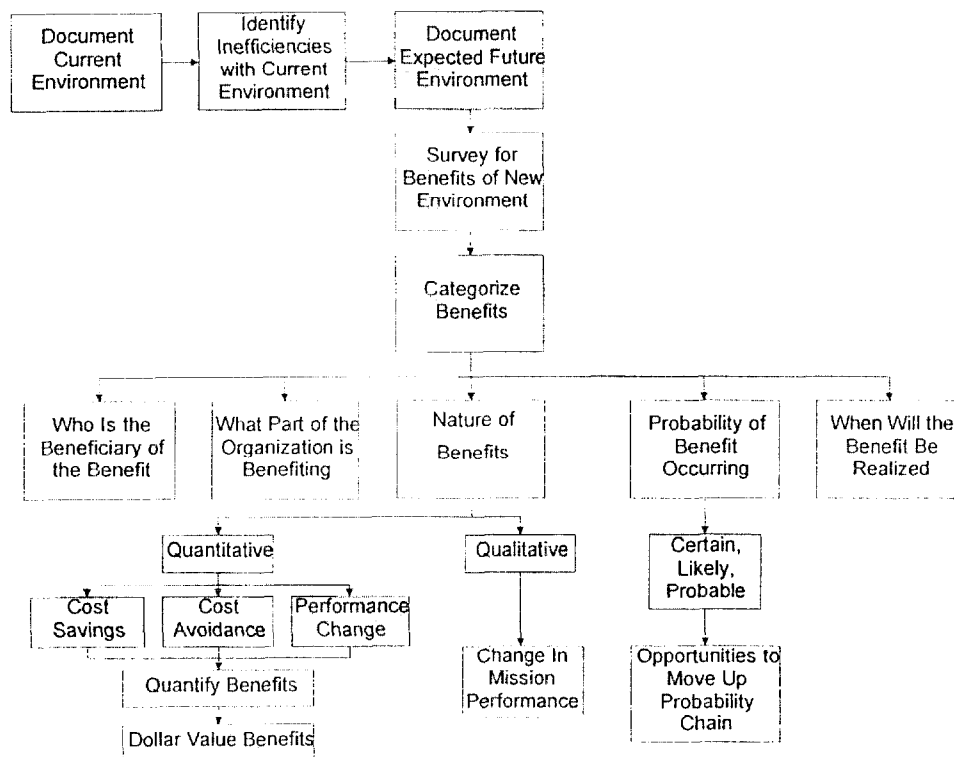


Figure 7. Framework for quantifying benefits.

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- Small amounts (ca. 10^{-4} mole percent) of $\text{Fe}(\text{CO})_5$ are near the ideal limit at reducing premixed flame velocities. At higher concentrations the agent becomes less efficient, as the active iron species condense to form relatively inactive particles. Ferrocene is nearly identical, indicating no dependence on the binding of the iron. Manganese-containing compounds behave similarly, but are 5-7 times less efficient at reducing burning velocity.
- Also of interest are tropodegradable bromocarbons. For example, bromoalkenes are expected to have atmospheric lifetimes of a few days. In work jointly supported with the Advanced Agent Working Group, a series of bromofluoroalkenes and bromofluoroamines generally had cup-burner extinguishment values below about 4 mole percent. AAWG data show that rats exposed for 30 min to 5% of four of the compounds (1-bromo-3,3,3-trifluoropropene, 2-bromo-3,3,3-trifluoropropene, 4-bromo-3,3,4,4-tetrafluorobutene, and 2-bromo-3,3,4,4,4-pentafluorobutene) showed no ill effects. The Ames tests were also negative.

Work has begun on developing a set of quantitative structure-activity relationships for compound volatility. These would be used in conjunction with values of agent discharge rates and the known dimensions of and thermal conditions in the fire compartment to determine whether compounds having a specified chemical structure can be expected to put out the fire in the required time frame (e.g., on the order 0.5 s in the case of an engine nacelle fire).

SUPPRESSANT SCREENING TESTS

A set of efficient, accurate screening tests for new suppressant chemicals is near completion.

The Dispersed Liquid Agent Screen (DLAS), based on the Tsuji diffusion burner, is now in use both to obtain suppression efficiency data and as a research tool. Tests with well-characterized droplets of fluids of widely varying density, viscosity, and surface tension (water, 30% and 45% potassium lactate by mass, and 1000 and 2000 mg/L sodium dodecyl sulfate), showed the average droplet diameters of the fluids were within $\pm 15\%$ (Figure 1) and that this variation affected the extinction efficiency by under $\pm 15\%$ (Figure 2), well within useful tolerance for a screen apparatus.

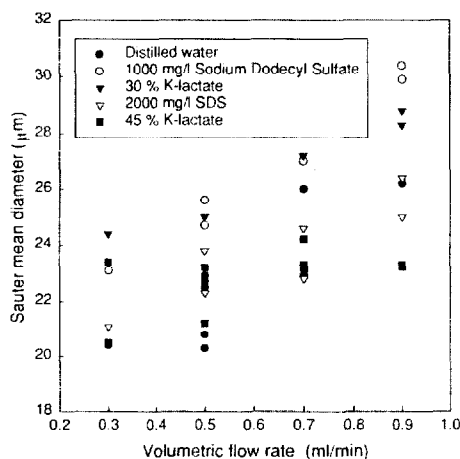


Figure 1. Effect of fluid and fluid flow on droplet size.

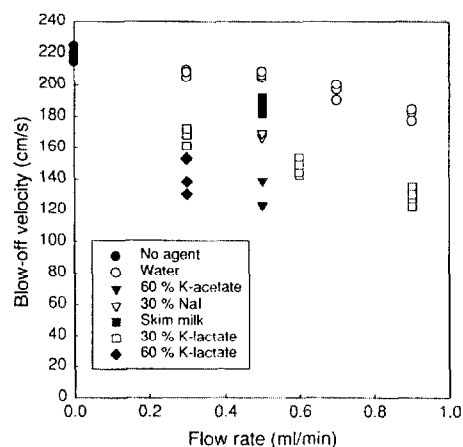


Figure 2. Effect of fluid and fluid flow on flame extinction effectiveness.