A literature survey on water additives has been conducted. Many water additives have been examined. Potassium lactate was found to be the current most effective water additive. The polymeric additives tested by the Army Research Laboratory are currently available in minute quantities, which will impose a constraint in testing. In addition, the rheological properties of these fluids pose a technical challenge in their dispersion in fire suppression applications. A qualitative assessment of the potential applicability of a liquid agent in several fire scenarios has been provided based on several time scales in the suppression processes.
TECHNICAL SUPPORT FOR THE STUDY OF DROPLET INTERACTIONS
WITH HOT SURFACES

FINAL TECHNICAL REPORT

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PROJECT OBJECTIVE:

The main objective is to provide technical support (literature review on water additives, fluid property and possibly droplet impact data) for the study of the dynamics of droplet/surface and droplet/flame interaction and its effect on burning cessation to be conducted by other investigators in two other projects, also funded by SERDP.

TECHNICAL APPROACH:

There are two major projects in this research area. The first is being conducted at the Naval Research Laboratory (NRL), and the second at Purdue University.

The NRL project addresses what happens when aerosol droplets or particles approach and enter a flame. Specifically, it will provide an understanding of the interactions of liquid aerosols and particles with flames, identify key parameters (e.g., aerosol properties including droplet or particle size, velocity, and chemical composition) that govern the flame suppression processes, and identify what aerosol sizes will penetrate the flames.

The Purdue study examines what happens when aerosols and particles penetrate through the flame and reach the burning surface. The project will provide experimental data for four key physical phenomena involved in the interaction of droplets with burning surfaces: (1) the effect of buoyancy on the trajectory of a single droplet, (2) the effect of evaporation on the trajectory of a single droplet, (3) the cessation of reaction and reduction in flame spread caused by the droplets on flaming surface combustion, and (4) the reduction in surface temperature caused by the effect of droplet impingement, spreading, and evaporation on surface combustion.

The role of the National Institute of Standards and Technology (NIST) is to work with the Principal Investigators of the two projects to identify, through literature search, potential fluids for their experiments and models and to cull from the published and product literature the thermochemical properties of these fluids, as needed. If the appropriate data are not available, NIST is to estimate these properties. In addition, NIST will visit laboratories as appropriate to identify further data needs, and if needed, perform single droplet/surface interaction experiments, determining droplet impact dynamics using a single-shot flash photographic technique or high-speed movie camera to facilitate the interpretation of results from the Purdue project which involves the use of a spray to study droplets/burning surface interaction. NIST is responsible for
coordinating the overall project, monitoring progress, maintaining communication among all parties through e-mails, phones, faxes to assure the overall project is on track, and visiting sites as necessary.

Figure 1 is a flowchart showing an overall engineering approach of assimilating the results from these research elements to improve liquid agent delivery systems.

Figure 1. A flowchart showing an overall approach to improve liquid delivery systems.
LITERATURE REVIEW ON WATER ADDITIVES

The principle function of water additives is to alter the thermophysical properties of neat water. An example is to lower the normal freezing point of water so that it can be used at sub-zero temperatures. If the additives act as a fire suppressant, additional benefit will result; this was the original impetus for examining water additives in fire suppression applications.

Monson et al. [1,2] investigated various water additives for fire fighting. Several formulations were identified, which included the following solutions:

- 24% (mass fraction) LiCl and 76% H₂O
- 5% LiCl, 26% CaCl₂, 69% H₂O
- 10% Ca(NO₃)₂, 27% CaCl₂, 63% H₂O
- 5% FeCl₃, 29% CaCl₂, 66% H₂O

Only the first formulation listed above was tested for fire suppression applications using a spray nozzle and a wood crib fire and was found to be approximately 1.4 times better than water in terms of extinguishment time.

In a series of reports, Grove and co-workers [3,4,5,6,7,8,9,10,11] evaluated the effect of the addition of a viscosity modifier, a surfactant, and/or an opacifier to water on improving the fire suppression effectiveness of water (applied in the form of a spray). The purpose of using a viscosity modifier was to improve the blanketing and runoff properties of water. The opacifier additives were used to mitigate the radiative feedback from the fire to the burning fuel surface. The surfactant was used to facilitate the dispersion of opacifiers in water. Based on the experimental results of their scaled model Class-A fires, it was concluded that:

- Viscous water produced more rapid initial control of the fires than neat water.
- The rate of extinguishment of the fires is more rapid with viscous water; the extinguishment time decreased as the viscosity of water was increased.
- The danger of re-ignition was reduced when the fires were extinguished with viscous water as a result of less water runoff.
- Reduced runoff of viscous water provided better water utilization for fire control and minimized collateral water damage.
- The major contribution to the improvement of the fire suppression effectiveness was attributed to the viscosity modifier. The addition of an opacifier to viscous water
further improved the fire fighting properties of water; however, the surfactants used in the study had very little effect on the improvement of the extinguishing properties of water.

In an attempt to improve the effectiveness of water to control and suppress forest fires, Davis et al. [12,13] used several viscosity modifiers in plain water. The experimental results from their controlled field and laboratory fire tests also indicated that fire suppression effectiveness was related to the viscosity of water.

Fine spray solutions of sodium and potassium carbonates and bicarbonates were studied by Friedrich [14] to evaluate the effectiveness of these aqueous solutions in suppressing liquid pool fires. Concentrations ranging from a mass fraction of 0.01 to 0.1 were used in the study, which involved the application of the solution from a spray nozzle located at a fixed distance from the liquid pool. The salt solutions with the highest concentration exhibited the highest effectiveness; however, no improvement in the effectiveness was observed when the concentration was less than a mass fraction of 0.05. No comparison of the fire suppression effectiveness among various salt solutions was given in the cited reference. The author attributed the increase in fire suppression effectiveness of these aqueous solutions to the chemical inhibition ability of the salts and suggested that other compounds such as the oxalates would probably be more effective than the carbonates (albeit low solubility in water and toxicity are potential issues).

The use of anti-freeze (ethylene glycol) in water for fire suppression was studied by Elkins [15]. At a volume fraction of 0.3, the ethylene glycol/water solution was found to be approximately three to four times less effective (in terms of extinguishment time) than pure water. The author recommended that the concentration of ethylene glycol (used as an anti-freeze for water) should not exceed a volume fraction of 0.3; otherwise, the solution would lose its fire fighting capability.

The fire suppression effectiveness of aqueous solutions of KBr, KCl, NH₄Cl, Na₂CO₃, NaHCO₃, K₂CO₃, KHCO₃, and HCOOK of various concentrations were examined by Kida [16]. The solutions were sprayed vertically downward to a small hexane pool fire, and the extinction times were measured. Despite large scatter in the data, a 20 % KHCO₃ solution was found, on
the average, to be at least twice as effective (in terms of the extinction times) as pure water; however, the performance of the other aqueous solutions was not reported in the cited reference.

In a United Kingdom Patent by Ball et al. [17], potential water additives such as phosphates, carbonates, amino compounds, citrates, anti-freeze agents, and surfactants were suggested to increase the solubility of CO₂ in water for fire suppression applications.

Finnerty et al. [18] evaluated the fire suppression effectiveness of thirteen water additives using an airless paint sprayer and a small JP-8 pan fire. Potassium lactate (60 %, mass fraction) and 60 % potassium acetate were found to be superior to the other additives and at least four times more effective than pure water in term of extinguishment time. The superior performance of the potassium lactate and acetate solutions was further demonstrated using the dispersed liquid agent fire screen apparatus developed by NIST [19] under the auspices of SERDP.

Recently, Beck Tan et al. [20] of the Army Research Laboratory (ARL) assessed the applicability of dendritic polymeric additives in water for fire suppression using the NIST dispersed liquid agent screen apparatus and liquid pool fires at ARL. Although limited test data were promising for some additives, further research is needed to better characterize their fire suppression performance.

The use of proprietary wetting agents and aqueous film forming foam (AFFF) and film forming fluoro protein (FFFP) as additives in water to improve its fire suppression effectiveness for shipboard machinery spaces is currently being evaluated by the Royal Navy in Great Britain [21]. The preliminary test results indicted that these additives showed improvement in fire suppression effectiveness over neat water.

Finally, a brief, general discussion on the uses of water additives for fire fighting can also be found in Wahl [22].

In summary, based on the test results reported in the literature, the current most promising additive is 60 % potassium lactate. Although 60 % potassium acetate has the same overall fire suppression efficiency as the lactate [18], it has a higher normal freezing point than the lactate [18], which will render it undesirable for low-temperature applications.
ASSESSMENT OF POTENTIAL APPLICATIONS OF LIQUID AGENTS

Although the projects carried out at NRL and Purdue University will identify the optimum droplet size required to extinguish a flame in a controlled setting, an overall engineering evaluation has to be made to determine the applicability of a particular agent (delivered in droplets) in a particular fire scenario. An order-of-magnitude analysis of various time scales in the suppression processes may be used to provide such an assessment. However, quantitative evaluations of these time-scales are beyond the scope of this work.

In principle, there are six time scales to be considered: (1) \( t_{\text{det}} \), the detection time of the fire, (2) \( t_{\text{transport}} \), the transport time of the droplet to the fire, (3) \( t_{\text{preheat}} \), the preheat time of the liquid droplet to its wet-bulb temperature, (4) \( t_{\text{evap}} \), the evaporation time of the droplet, (5) \( t_{\text{res}} \), the residence time of the evaporating droplet in the fire, and (6) \( t_{\text{burnout}} \), the burnout time of the fire. The scenario that is relevant to the evaluation of the effectiveness of a fire suppressant is:

\[
t_{\text{burnout}} > t_{\text{det}} + t_{\text{transport}} + t_{\text{res}}
\]  

For liquid droplet suppressant, two additional constraints may have to be considered. To ensure that the droplet is transported to the fire without being completely vaporized,

\[
t_{\text{preheat}} + t_{\text{evap}} > t_{\text{transport}}
\]  

For a liquid droplet to exert its optimal fire suppression performance in the flame zone,

\[
t_{\text{res}} > t_{\text{preheat}} + t_{\text{evap}}
\]

The underlying assumption in writing Eqs. (2) and (3) is that the suppression action of the liquid agent is primarily physical via heat extraction from the flame zone.

In Eq. (1), the burnout time can, in principle, be estimated based on the average burning rate and the amount of combustibles. For a pool fire, numerous empirical correlations [e.g., 23,24] and global burning rate models [e.g., 25,26] can be used to obtain an estimate of the burning rate. In the specific case of a fireball, the burnout time (in seconds) is given as [27,28,29,30]

\[
t_{\text{burnout}} = 0.684 W_b^{1/6}
\]  

where \( W_b \) (kg) is the mass of fuel and air in the fireball (assuming a stoichiometric mixture). Equation (4) was obtained by correlating the fireball data of liquefied gases.
The droplet transport time to the fire is one of the primary governing factors (the other being the droplet residence time in the flame) in determining if a liquid agent can be effectively used to suppress a fire. It depends on the location of the agent release relative to the fire, the geometry of the protected space, the flow conditions in the protected space, the fire size, and the thermophysical properties of the agent; therefore, it is not straightforward to obtain a good estimate of this time. In this regard, computational fluid dynamics can be a useful tool [e.g., 31]. If the droplets cannot reach the fire (i.e., $t_{\text{transport}} \rightarrow \infty$), the fire cannot be suppressed, irrespective of how effective the agent is.

The detection time of a fire is also dependent on the fire scenario. For a dry-bay fire, the detection time is relatively short compared to the fireball burnout time (i.e., $t_{\text{burnout}} > t_{\text{detect}}$); however, for other applications (e.g., machinery spaces), there are instances when $t_{\text{burnout}} \approx t_{\text{detect}}$ (e.g., a hidden fire), depending on the location of the fire detector. If $t_{\text{burnout}} < t_{\text{detect}}$ (e.g., malfunction of the detector), the effectiveness of the liquid fire suppression is immaterial, and potential catastrophe can happen.

For a pool fire, a zero-order estimate of the droplet residence time can be made if the droplet velocity and the flame characteristics are known. For a fire stabilized behind a bluff body, if the droplet is small enough to follow the air stream, $t_{\text{res}}$ is on the order of $(L/V_f)$, where $L$ and $V_f$ are a characteristic length of the recirculation zone behind the bluff body and the free stream velocity respectively [32,33]. The characteristic length $L$ depends on the geometry of the bluff-body, the fire size, and the free stream velocity. The residence time should also include the retention time of the liquid droplets on the fuel surface since surface cooling is part of the suppression mechanism.

The droplet preheating time, $t_{\text{preheat}}$, can be calculated approximately using a lumped-capacitance model with an appropriate heat transfer coefficient [34]. For a given stagnant ambiance, $t_{\text{preheat}}$ is proportional to the square of the droplet diameter.

Droplet evaporation time, $t_{\text{evap}}$, can be estimated using the classical $d^2$-Law [35] with corrections for the convective flow environment [36]. The $d^2$-Law states that $t_{\text{evap}}$ varies quadratically with the initial droplet diameter.
IMPORTANT FINDINGS:

A literature survey on water additives has been conducted. Potassium lactate was found to be the current most effective water additive. A qualitative assessment of the potential applicability of a liquid agent in several fire scenarios has been provided based on several time scales in the agent transport and suppression processes.

SIGNIFICANT HARDWARE DEVELOPMENTS

None.

IMPLICATIONS FOR FURTHER RESEARCH:

One fluid, which has been suggested by ARL to be more effective than water, is 60 % (mass fraction) potassium lactate solution. This fluid is relatively inexpensive and is available in bulk quantities. Potassium lactate solution merits further research using the respective experimental set-ups in the other two projects, if funding permits.

Although the interaction of a water mist with a burning solid surface is examined in the Purdue project, there is no information on droplet interaction with a burning liquid fuel surface (a pool fire). When liquid droplets with high momentum impact on such a surface, splashing of the fuel will likely occur. The splashing may generate small satellite burning/non-burning fuel droplets, which may create additional, potential fire hazard. Experiments using liquid fuels should be performed.

REFERENCES


