

# EXTINGUISHMENT OF LIQUID FUEL FIRES BY WATER MIST WITH ADDITIVES

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## ABSTRACT

The effects of additive type and concentration on the extinguishment of liquid fuel fires are examined in the paper. Tests were conducted using gasoline, diesel and ethanol pool fires, while included NaHCO<sub>3</sub>, AFFF, and a multi-component agent named MC additives. Results show that water mist suppression effectiveness varies greatly depending on fuel type, additive type and concentration. The benefit of adding a small quantity of AFFF to water mist is observed in the suppression of gasoline and diesel pool fires, forming a thin film on the fuel surface by active surfactants. But, too much AFFF additive may decrease the marginal effectiveness due to the saturation effect of surface tension. The AFFF has none effect on ethanol fires because of the fuel erosion. Addition of NaHCO<sub>3</sub> may increase the performance of water mist gradually both for ethanol and hydrocarbon fires, although less effective than the film-forming agent. And there exists upper agent limit for the metallic additive because of the associated limiting vapor pressure of the active metal compound. The multi-component additive shows the combined suppression effect of film-forming agent and metal chemicals. It may effectively extinguish both ethanol and hydrocarbon fires though coupling the physical and chemical fire suppression mechanisms.

**KEYWORDS:** Water mist, Additives, Liquid fuel, Fire suppression effectiveness

## INTRODUCTION

With the phasing out of halogenated agents under the terms of the amended Montreal Protocol, extensive efforts have been made to find alternatives over the last few years. Water mist, which provided efficient fire suppression while minimizing water usage, is considered as a potential alternative to halogen-based agents system due to its superiority in terms of thermal characteristics and low environmental impact<sup>1</sup>. Even with many advantages of water mist systems, there is still room for improvement. Water mist systems have demonstrated effectiveness at suppressing Class B (flammable liquids) fires in compartments. However, an especially challenging fire suppression scenario for water mist systems is the small Class B fire. This scenario is often realized after a large fire has been reduced in size or 'controlled' by water mist. The small fire scenario is challenging because a small fire may not be able to generate enough vaporized water to displace sufficient oxygen for complete extinction. It should also be noted that even if the class B fire is extinguished with a water mist system, re-ignition from the hot surrounding surfaces may occur at any time<sup>2</sup>.

In order to further improve the fire extinguishing effectiveness of water mist, there is consideration of additives adding into water mist. Recent results showed that water mist made with "sea water" (2.5% by weight sodium chloride solution) and the addition of a low percentage of a foam-forming agent (e.g. 0.3% Class A foam concentrate) or a film-forming agent (e.g. 3% AFFF) greatly improved the effectiveness of water mist for suppressing hydrocarbon pool fires<sup>3-5</sup>. Water mist with some kinds of antifreeze chemicals were also proven to be more effective than pure water when applied in the form of mist to suppress small jet fuel pool fires<sup>6,7</sup>. In our previous research, a new multi-component additive named MC also demonstrated superior fire-extinguishing efficiency to plain water mist when injected to liquid pool fires and wood crib fires<sup>8</sup>.

However, up to now, the suppression benefit of adding additive to a water mist was only noted for a few given fuel. There is lack of a match between the fuel and additive. Furthermore, the dominant mechanisms of water mist are well documented as heat extraction, oxygen displacement or dilution and attenuation of radiant heat. In contrast, little is known about the suppression mechanisms and some other aspects of water mist in flames when the additive is added.

The purpose of the present work is to examine the effect of additive on the extinguishment of liquid fuel fires. Tests were conducted using gasoline, diesel and ethanol pool fires in a 3.0 m × 3.0 m × 3.0 m well ventilated compartment. The additives included representative kinds of metal compound, film-forming agent and a multi-component additive. The paper firstly compared the extinguishing effectiveness for different liquid fuels respect to the additive type and then investigated the effect of additive concentration on the suppression performance of water mist. Fire suppression mechanisms of water mist with different types of additive were also briefly discussed in the paper.

## EXPERIMENTAL

### Test Set-up and Procedures

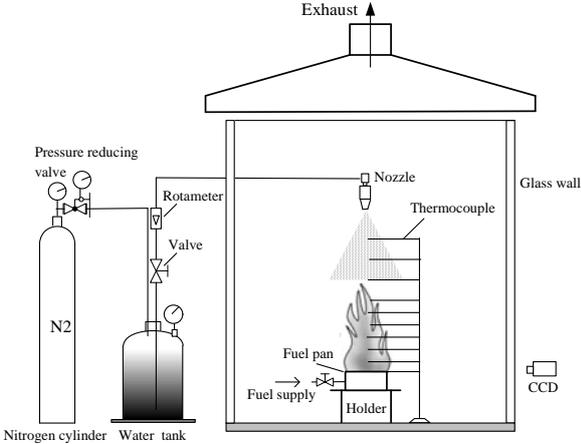
Fire experiments were performed in a 3 m × 3 m × 3 m glass-walled enclosure shown schematically in Fig. 1. A steel square pool pan with the edge of 0.15 m was located 0.65 m above the center of the chamber floor and at a distance of 1.0m below the downward-pointing solid cone spray nozzle. The water flow through the spray nozzle was supplied from a pressurized holding tank and was measured using a calibrated rotameter. The delivery pressure was monitored at the nozzle inlet. An extraction hood was located 10 cm above the chamber and exhausted with the aid of a low-volume fan. A 0.2 m high opening along the bottom of each wall allowed room air to be drawn into the fire, which provided well ventilation during the experiments.

The flames with and without the spray were recorded using a CDD camera with side illumination against a black background. The flame and plume temperatures were measured using a set of type K (chromel-alumel) bare junction stainless steel sheathed thermocouples located between 0.05 m and 0.65 m above the pan. The diameter of the thermocouple wire was 0.5 mm with a time constant of about 0.5 s. The fuel surface temperature was monitored using a rapid-response stainless steel sheathed thermocouple with a time constant of about 0.05 s, which just touched the surface of the fuel at the center of the pool. All data was transferred to disk storage using a PC-controlled data acquisition system.

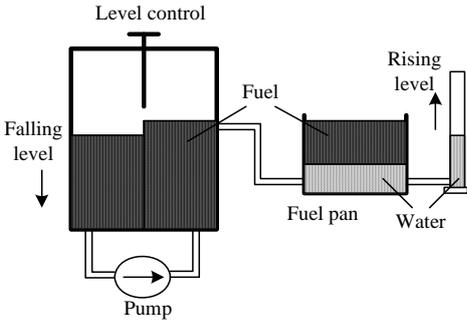
In the pre-tests, the fuel surface temperature was found hard to be accurately measured because the level in the pool pan decreased gradually due to the fuel combustion. Therefore, a simple version of the self-adjusting liquid level apparatus was adopted as shown in Fig. 2, which was described in details in Alexander et al. (1982)<sup>9</sup>. A pool of liquid fuel sited on a layer of water at the bottom of the pan except for ethanol, because the ethanol mixed well with water. As the fuel burnt, the liquid level self-adjusting apparatus supplied fuel from the right tank compartment to the fuel layer in the pan to keep the pool level constant. This resulted in a fall in liquid level in the left tank compartment. When mist was introduced, some of the droplets went through the flame and entered the liquid pool. But the accumulated water would be transferred to the right water jar while keeping the fuel level constant in the pool pan.

In the experiments, the water tank was firstly filled with water adding additives and pressurized. The pan was charged with fuel allowing a lip height of 5-10 mm. This is necessary to avoid fuel flowing over the edge when mist is introduced, since the transfer of water from the pan to the water jar is not instantaneous. Then the fuel was ignited. The water mist was not activated until the fire reached a fully developed stage. For the diesel fires, an about 75 s of pre-burn was allowed to reach a steady burning condition, while for the gasoline and ethanol fires, the pre-burn time was only about 40 s since their flash point are much lower than the diesel. The water mist application would last for five minutes. At

the end of this, the fire (or its remains) was extinguished immediately by covering the pan to eliminate the air supply for combustion. In all the tests, the nozzle pressure was set to 0.6 MPa, functioning as a low pressure system.



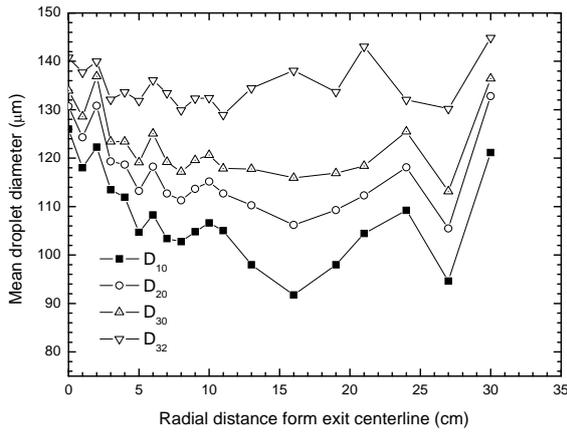
**FIGURE 1.** Schematic of the experimental apparatus



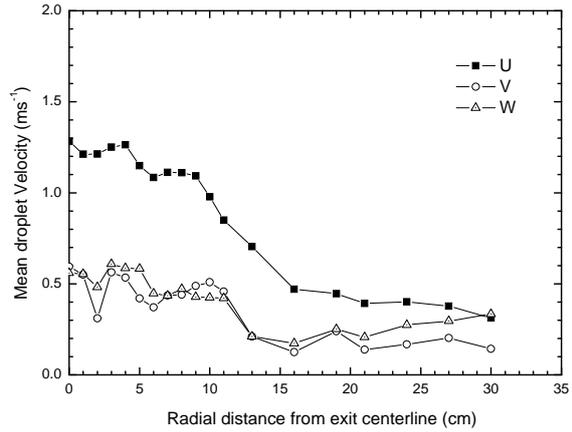
**FIGURE 2.** Schematic of the self-adjusting liquid level apparatus

**Water Mist Characteristics**

Water mist was discharged from a single fluid type nozzle with seven heads made of brass. Only the downward head was used in the experiments. The diameter of the orifice is 0.8 mm. The initial angle of the water spray near the nozzle exit was about 60°. The droplet size and velocity were obtained by a Laser Doppler Velocimetry or Adaptive Phase Doppler Velocimetry (LDV/APV) system at the cross-section 1.0 m away from the nozzle exit. Typical distribution of mean droplet size and mean velocity along the spray radial direction under pressures of 0.6 MPa were shown in Fig. 3. The volume mean diameter was about 135 μm near the spray centerline and 140 μm near the envelope edge. Therefore, it may be classified as Class I water mist following the NFPA 750 Standard<sup>10</sup>. The mean downward velocity, *U*, was about 1.3 ms<sup>-1</sup> at the centerline, and then gradually decreased to 0.3 ms<sup>-1</sup> near the envelope edge because of the drag effect. However, the horizontal velocity kept almost constant along the spray envelope.

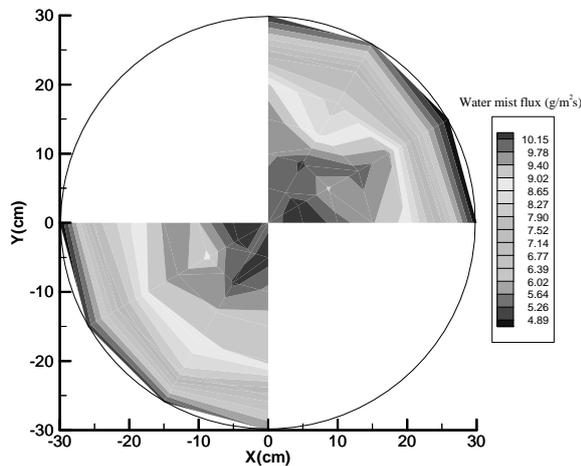


(a) Mean droplet diameter



(b) Mean velocity

**FIGURE 3.** Characteristics of water mist along the radial distance from nozzle centerline. Discharge pressure  $P = 0.6$  MPa, Measurement plane 1.0 m below the nozzle.



**FIGURE 4.** Diagonal distribution of water mist flux in the measurement plane. Discharge pressure:  $P = 0.6$  MPa, Measurement plane 1.0m below the nozzle

The water flux was measured by collecting water with plastic cups placed on the floor 1.0 m away from the nozzle exit. Total 25 sampling cups with a 3.0 cm diameter were placed on the floor starting from the center of spray coverage along the radial and circumferential axis, which occupied one fourth of the coverage area. The distance between the radial cups was 5 cm. The amount of water collected by the cups was weighted after 1-3 min of discharge, depending on the discharge pressure. Diagonal distribution of water mist flux in the measurement plane under pressure of 0.6 MPa was shown in Fig. 4. The Maximum mist flux was obtained at the center of the spray coverage, and then decreased gradually along the radial axis. The mist flux near the coverage edge was less than fifty percent of the central value, which was in accordance with the droplet velocity distribution.

### Additives

Three kinds of additives including a representative kind of metal compound  $\text{NaHCO}_3$ , a film-forming agent AFFF and a new multi-component additive named MC were used to investigate the fire suppression effectiveness of water mist. The main components of the MC additive were:

- (1) Fluorinated surfactant, which produces a low surface tension in the solution;
- (2) Viscosity modifier, which improves the blanketing and runoff properties of water;

- (3) Fire retardant salt, which produces active radicals during extinguishing the fires;
- (4) Thermal compound, which absorbs heat from flame and generates a great amount of inert gases by decomposition;
- (5) Solvent, which acts as anti-freeze and dissolves all the components.

The detailed formulation of the MC additive is presented in Table 1, where the mass percentage of each compound is given.

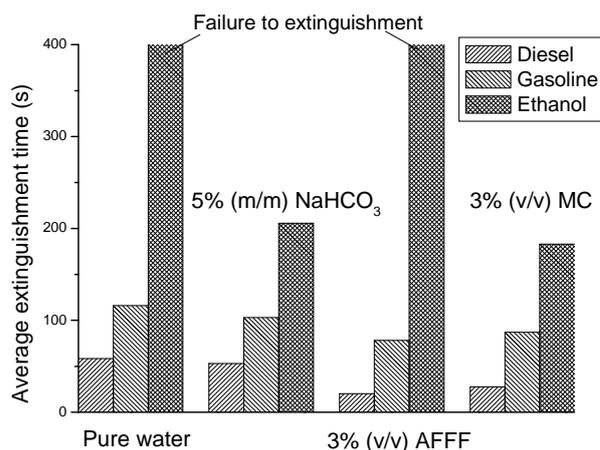
**TABLE 1.** Formulation of the MC additive

Compositions	Role	Mass percent (%)
N,N-DimethylFormamide	Co-solvent, Anti-freeze	15.0
$C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$	Viscosity modifier	3.0
$(C_2F_5)_2C(CF_3)=C(CF_3)-OC_6H_4SO_3Na$	Fluorinated surfactant	6.0
Sodium acetate	Fire retardant salt	1.5
Carbamide	Thermal compound	6.5
Dematerialized water		68.0

## RESULTS AND DISCUSSIONS

### Suppression Effectiveness versus Additive Type

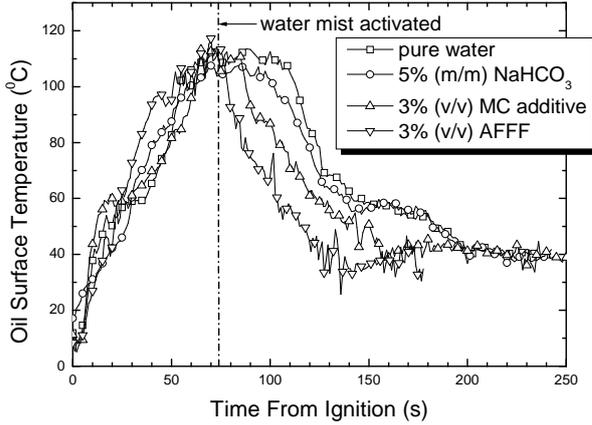
Fig. 5 presents, in graphical form, a comparison of the average extinguishing time of liquid pool fires suppressed by water mist with different additives. It can be easily found that while some of the additives are significantly more effective than water, other solutions are less effective. Furthermore the fuel type has a great effect on the suppression effectiveness of the additives. 3% (v/v) AFFF is the best performing of solutions for diesel and gasoline fires, while it has none effect on the suppression of ethanol fire. On the other hand, 3% (v/v) MC additive seems to be effective for all the three fuels. The differences may be caused by the suppression mechanisms and some other aspects of water mist in flames when the additive is added.



**FIGURE 5.** Comparison of average extinguishing time of liquid pool fires suppressed by water mist with additives. The discharge pressure is 0.6 MPa.

Fuel surface cooling is considered as the main suppression mechanism for the hydrocarbon fuels especially for the high boiling fuels such as diesel <sup>11</sup>. Fig. 6 compares the results of fuel surface temperature before and after the application of water mist with additives for the diesel pool fire. One

can see that with the additives, the fuel surface temperature decreases more quickly than that with pure water, especially for AFFF and MC additives. Furthermore, the relative suppression time scales are also changed as listed in Table 2. The extinction time is the time from the start of water mist application until complete flame disappearance, and the fuel cooling time indicates the time until the fuel surface cooling below flash point. It is shown that for the pure water and water with NaHCO<sub>3</sub>, the flame extinction time is a little longer than the fuel cooling time; while for the AFFF and MC additives, the flame extinction time is much shorter, which imply that the fuel surface temperature is still well above the flash point even when the flame is put out. This maybe results from the additional suppression effect of the additives.

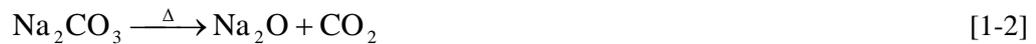


**FIGURE 6.** Comparison of fuel surface temperature before and after the application of water mist with additives for diesel pool fire. The discharge pressure is 0.6 MPa.

**TABLE 3.** Comparison of suppression time scales by water mist with additive for diesel fire

	Flame extinction time (s)	Time of fuel surface cooling below flash point (s)
Pure water	67	63
5% (m/m) NaHCO <sub>3</sub>	59	57
3% (v/v) AFFF	18	32
3% (v/v) MC additive	23	47

When water mist with NaHCO<sub>3</sub> is injected into the flame, the evaporation of water from the salt-containing solution will lead to the formation of solid particles in the flame zone<sup>12</sup>. These particles serve as surfaces capable of quenching flames through chemical effect. For NaHCO<sub>3</sub>, the following reactions are considered to scavenge the key OH and H radicals which are critical for the flame combustion<sup>13</sup>. However, because chemical effects primarily take place in the gas phase of the flame, they have indirect influence on the fuel surface cooling as expected in Fig. 6.

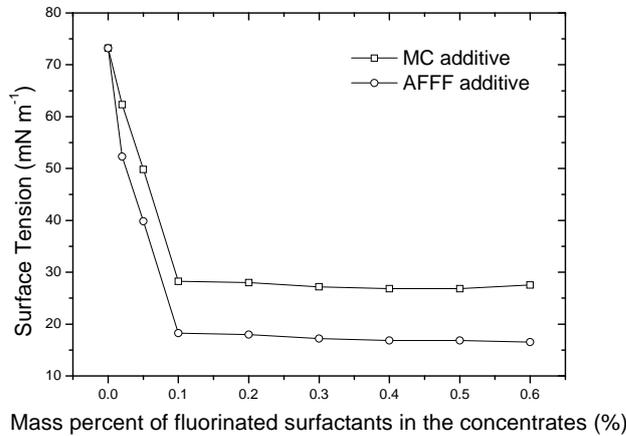




While in case of the AFFF and MC additives, the surfactants of the additives may decrease the surface tension of water greatly. It is generally known that many physical-chemical properties correspond with surface tension. Therefore, when water with surfactants is injected into the flame, the droplets which reach the pool surface may spread and form a thin layer of film on the fuel surface, which improve the oxygen and fuel isolation and reduce the radiant heat that is absorbed by the fuel. The film spreading rate is decided by the spreading coefficient  $S$ <sup>13</sup>,

$$S = \gamma_o - \gamma_w - \gamma_{o/w} \quad [2]$$

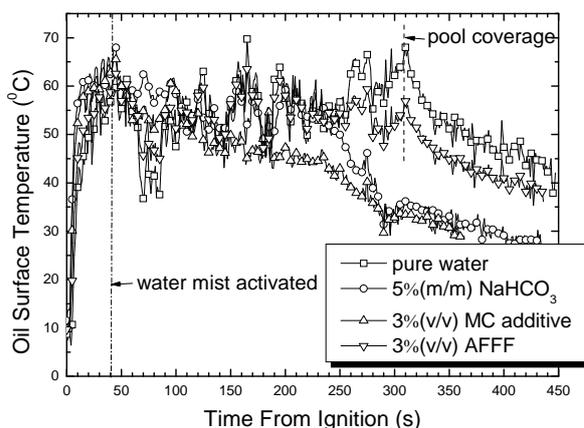
where  $\gamma_o$  is the surface tension of the fuel, and for most hydrocarbon fuel is about 20dyn/cm;  $\gamma_w$  is the surface tension of the solution; and  $\gamma_{o/w}$  is the interfacial tension between the fuel and the solution. When  $S > 0$ , the solution may spread over the fuel, which is much faster than the fuel surface cooling rate. Therefore, in the tests the flame was put out while the surface temperature may keep well above the fire point. Furthermore, The rate of interfacial and surface tension reduction drives the film spreading. Fig. 7 shows the comparison of the surface tension versus the mass concentration of the active fluorinated surfactants for the solutions. It is shown that the AFFF decreases the surface tension of the solution more quickly than the MC additive, which results in the faster spreading rate of AFFF solution over the fuel surface. Therefore the extinguishing time of AFFF additive is shorter than that of the MC additive for hydrocarbon fuels in the tests.



**FIGURE 7.** Surface tension versus the mass concentration of the active fluorinated surfactants for the water with MC and AFFF additives

However, the above relationship between the suppression effectiveness and additive type may make a difference from that of ethanol fires. Fig. 8 shows the comparison of surface temperature of ethanol fires before and after the water mist application with different additives. For the ethanol fire, the MC additive and  $\text{NaHCO}_3$  are more effective than AFFF, because ethanol, as one of polar liquids, may destroy the classical AFFF foam films on contact by dehydration<sup>13</sup>. Therefore, the main contribution of the additive is the chemical effect produced by metal salts. The nature of salt is very important in this case. In tests, both Sodium Acetate in MC additive and  $\text{NaHCO}_3$  belong to the sodium salts family, resulting in a similar chemical suppression. However, other components such as Carbamide in MC additive may produce additional thermal effect on the fire suppression compared to  $\text{NaHCO}_3$ .

Therefore, the extinguishing time of MC additive is shorter than that of  $\text{NaHCO}_3$  for ethanol fires.



**FIGURE 8.** Comparison of oil surface temperature before and after the application of water mist with additives for ethanol pool fire. The discharge pressure is 0.6MPa.

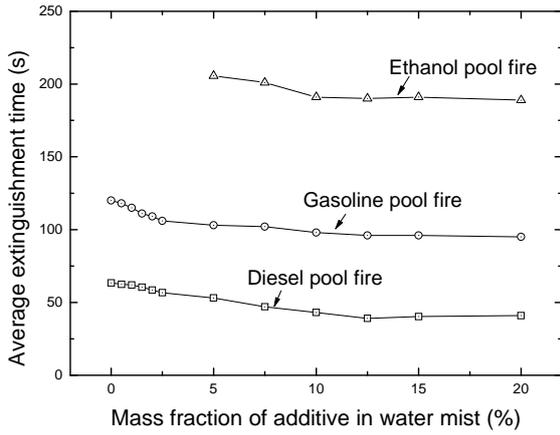
### Suppression Effectiveness versus Concentration of Additive

In order to see the relationships between additive concentration and the suppression effectiveness of water mist, the extinguishing time as a function of the additive concentration was measured for diesel, gasoline and ethanol fires respectively (see Fig. 9).

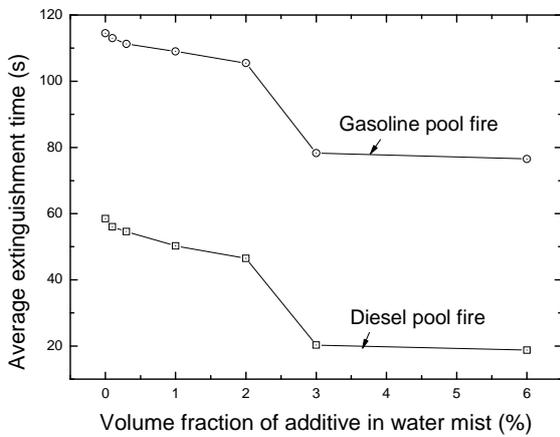
As shown in Fig. 9, the extinguishing time for  $\text{NaHCO}_3$  firstly decreases linearly with the agent, and then become constant above a certain concentration, which imply that when the mass fraction of  $\text{NaHCO}_3$  in water is above a limit, not any improvement in the fire suppression ability of solution would yield with the additive increasing. The existence of upper limit may be because of the associated limiting vapor pressure of the active metal compound as discussed by Linteris et al.<sup>14</sup>

While, in the case of AFFF, the extinguishing time decreases non-linearly with the agent. When the AFFF concentration is below 1.0% volume fraction in water mist, the extinguishing time decreases less than five percent of that required for pure water mist. But, one may observe a sharp reduction once the concentration of AFFF passes through 2.0% to 3.0%. After then, the extinction time becomes saturated till to 6.0% volume fraction in the water mist. In fact, the trends of suppression effectiveness for AFFF reflect the solution surface tension change with the additive increasing. In the tests, with 3.0% AFFF added, the solution would reach the CMC (Critical Micelle Concentration) of active surfactants, which result in the most rapid rate of the film spreading on the fuel surface. Therefore, a break of the fire suppression effectiveness occurs at this CMC. Furthermore, the “saturation extinction time” lies at a higher concentration with respect to CMC. This saturation concentration depends on the type of fires. For the hydrocarbon fuel, the saturation concentration is almost twice of CMC.

On the other hand, the extinguishing time versus concentration of MC additive shows two linear relationships. When the concentration of MC is less than 3.0% (v/v), the extinguishing time decreases gradually like the metal salts. But a transition also occurs at the CMC of MC additive (3.0% (v/v)). However, compared with the AFFF agent, the transition shows gentler for the MC additive, which imply that the MC additive may stand much more tolerance of the suppression concentration through coupling the physical and chemical fire suppression mechanisms<sup>8</sup>.

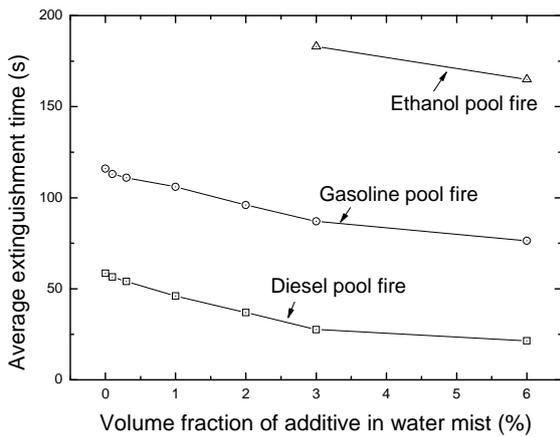


(a) Water mist with  $\text{NaHCO}_3$  additive



NOTES:  
Ethanol pool fires were failure to extinguishment with AFFF additive

(b) Water mist with AFFF additive



(c) Water mist with MC additive

**FIGURE 9.** Comparison of the relation curve between additive concentration and the extinguishing time of liquid pool fires. The discharge pressure is 0.6 MPa.

## CONCLUSIONS

This paper has presented the results of an experimental study of the effects of additive type and concentration on the extinguishment of liquid fuel fires. The experiments were conducted using gasoline, diesel and ethanol pool fires in a 3.0 m × 3.0 m × 3.0 m well ventilated compartment. The additives included NaHCO<sub>3</sub>, AFFF, and a multi-component agent named MC additive. Analysis of the results led to the following conclusions.

Water mist suppression performance varies greatly depending on fuel type, additive type and concentration. The benefit of adding a small quantity of AFFF to water mist is observed in the suppression of gasoline and diesel pool fires, forming a thin film layer by active fluorinated surfactants on the fuel surface. But too much AFFF additive may decrease the marginal extinguishing effectiveness due to the saturation effects of surfactants. Besides, the AFFF additive has none effect on improving the performance of water mist for ethanol fires because of the fuel erosion.

Addition of metal compound such as NaHCO<sub>3</sub> may increase the performance of water mist gradually both for ethanol and hydrocarbon fuel fires, although less effective compared to the film-forming agent. There also exists upper agent limit for the metallic additive because of the associated limiting vapor pressure of the active metal compound.

The multi-component additive, MC shows a combined suppression effect of film-forming agent and metal chemicals. It may effectively extinguish both ethanol and hydrocarbon fires though coupling the physical and chemical fire suppression mechanisms. Therefore, the multi-component additive seems superior to the conventional water additives and worth for further exploration.

## ACKNOWLEDGEMENTS

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