

Modeling Study of the Effect of Fine Water Mists on Premixed CH₄/Air Flame Propagation

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The use of fine water mist (less than 200 μm) to suppress and extinguish fires is an emerging technology and is an active area for research and development. Most of the information on the effects of water mist on combustion comes from the study of large scale fire systems developed for specific practical applications. Little fundamental information exists on interaction of a water mist and the propagating flame. It is also known that the systems must generate sufficiently small water droplet size and distribute a "critical concentration" throughout the compartment, however there is no widely accepted "critical concentration". We have studied the water mist interaction with a premixed CH₄/Air flame using the CHEMKIN code. Our mechanism consists of over 200 elementary reactions most of which come from the GRI 2.1 mechanism for methane combustion. Water droplet evaporation rates have been modeled using the *d-square law*. These rates along with the latent heat of vaporization have been incorporated into the mechanism to take into account the transformation of liquid water droplets to the vapor phase. The "critical concentration" of water mist has been inferred from the point at which the computer modeled freely propagating laminar flame fails to propagate. Using above criteria, we have determined the effect of water mist loading and water droplet size on the flame propagating speed and the "critical concentration" of water mist as a function of equivalence ratio of the premixed flame. We have also compared water mist inhibition with Halon 1301 and, have examined the cooling effect (due to water evaporation) and the specific heat effects associated with droplet heating.

INTRODUCTION

Halons are ideal fire suppression agents as they possess excellent fire suppression ability, are non-toxic and have convenient vapor pressure and fluid properties. With halogen-based chemical fire suppression agents such as Halon 1301 (CF₃Br) being banned by the Montreal Protocol, there exists a critical need to find a replacement compound which can fill the void. The niche which replacement agents must fill is quite constrained leading to very difficult challenges to the research community. First and foremost, these agents must fight fires effectively; preferably better than Halons although this may be too stringent a standard. Second, the physical form of the agent must be one which can be delivered to a fire. A liquid with fluid properties (density and viscosity) as well as vapor

pressure similar to Halons would allow for "drop in" replacement but new delivery systems can be designed if required. Third, the replacement agent must be non-toxic in high concentrations and its combustion breakdown products must not be excessively toxic. Fourth, the agent must be such that damage to equipment must be minimal. Finally, the replacement agent must be environmentally acceptable. That is, it must have a low or zero ozone depletion potential (ODP) and a low global warming potential (GWP).

To date, no replacement agent has been identified which can meet all these criteria. One agent which is being deployed, FM-200 (C₃F₇H), is not as effective as Halon 1301 and has a significant GWP (although it does have zero ODP). The fire suppression community is now coming to realize that, in all

likelihood, there will not be a single replacement for Halons. The selection of the replacement will be much more situation specific. The frenzied search for Halon alternative has led to one such situation specific alternative, the water mist technology (fine water spray). The technology has been found to be effective for a wide range of applications such as Class B pool fires [1], shipboard machinery [2-4], aircraft [5,6] and computer and electronics applications [6], to name a few. Recently, NFPA 750 has adopted a standard definition for water mist [7]. The purpose of this standard is to provide a reasonable degree of protection for life and property from fire through standardization of design, installation, maintenance and testing requirements for water based fire suppression systems. NFPA 750 defines water mist as a water spray for which $D_{v0.99}$ at the coarsest part of spray is less than 1000 μm . In simpler words, 99% of spray droplet diameter are less than 1000 μm . More specific classes of water mist are defined in the appendix of NFPA 750 which subdivides water mist into three classes. Class 1 water mist - 10% droplets below 100 μm and 90% below 200 μm . Class 1 represents the finest water mist. Class 2 water mist - 10% droplets below 200 μm and 90% below 400 μm . Class 2 is effective on fires involving ordinary combustibles. Class 3 water mist - 90% droplets greater than 400 μm and 99% droplets less than 1000 μm .

The primary flame interaction of an effective Halon replacement should be the one which reduces the peak flame temperature. This can be achieved either through endothermic chemical dissociation reactions, phase change, and/or sensible heat interactions. Water is an effective sensible heat removal agent and has been used as a fire suppression agent for centuries. Water mist technology has emerged as a viable alternative because of the associated advantages such as low cost, non-toxicity, minimal water utilization (a tenth or lower as compared to the sprinklers), and the ability of very small water droplets to move around obstructions (e.g., inside instrument racks) and behave similar to a true flooding agent i.e., diffuse over the volume of interest without appreciable change in droplet mass mean diameter (MMD) and inter droplet distance, emulating gaseous fire suppressant. For the water

mist to be considered a true flooding agent, the droplet MMD has to be below 30 μm . Misting sprays have been suggested to be more effective for deep-seated fires due to higher cooling capacity and penetrating ability of liquid water.

Suggested mechanisms of fire extinguishment include gas phase cooling by inerting, oxygen depletion by steam expansion, wetting and cooling of flamed surfaces and by radiation attenuation. Little fundamental information exists on interaction of water mist with flame. Previous studies have focused on interaction of water sprays with liquid pool fires [8] in terms of extinction time while other investigators have concentrated efforts towards finding adequate flow rate of water [9] for flame quenching [10]. Most of the information on the effects of water mist on combustion comes from the study of large scale fire systems developed for specific practical applications [11]. It is known that the systems must generate sufficiently small water droplet size and distribute a "critical concentration" throughout the compartment [12,13]. Factors that must be considered for system design are drop size distribution, spray flux density, spray angle, spray projection and momentum and mixing characteristics of the spray and geometry of the area [13]. However, at present there is neither a widely accepted "critical concentration" nor a theoretical basis for design parameters and the current state of art is to extrapolate from large-scale test data on a case by case basis.

The work presented herein is an offshoot of the task (currently in progress) of studying the viability of use of water-mist as fire suppressant in spaceships. One of the inherent advantages of water mist in space is the reduced gravity component, which renders bigger droplet (1000 μm) mist as a true flooding agent. The objective of our study is to quantify the critical water mist loading for a premixed laminar flame. The "critical concentration" is inferred from the point at which the computer modeled freely propagating laminar flame fails to propagate. Using the above criteria, we have determined the effect of water mist loading and water droplet size on the flame propagating speed and the "critical concentration" of water mist as a function of equivalence ratio of the premixed flame. We have also compared

water **mist** inhibition with **Halon** 1301 and, have examined the cooling effect (due to water evaporation) and the specific heat **effects** associated with droplet heating.

MODEL

A flame **is** caused by a self-propagating exothermic **reaction** which usually has a luminous reaction **zone** associated with it. Combustion begins in chemistry with a self-supported, exothermic reaction. **The** physical processes involved are those pertaining to transport of material and **energy**. In a propagating combustion wave called a deflagration or flame, reaction is initiated by a spark or other energy **stimulus** [14]. Reaction is then induced in the layer of reactant **mixture ahead** of the flame front by two possible mechanisms, that is by heat conduction or by diffusion of reactive species from the hot burned gas or reaction **zone** behind the flame front. **A** premixed flame propagates **through** a stationary gas at a characteristic velocity termed the burning velocity, or it may **remain** in one place if the reactant gas is forced to move towards the flame front at the same speed. Two important properties of a typical laminar premixed flame are the burning velocity, S_L and the adiabatic flame temperature. The premixed gas composition is usually expressed in terms of an equivalence ratio, ϕ , which is the actual fuel:oxidizer ratio divided by the fuel:oxidizer ratio corresponding to complete combustion to carbon dioxide and water (stoichiometric). The theory of premixed flame is well developed and documented [15,16].

Development of CHEMKIN, a **FORTRAN** computer code and PREMIX module has greatly facilitated the simulation of elementary chemical reactions in a flowing system [17]. In brief, the code solves the mass, **energy** and momentum conservation equations and the numerical solution is obtained by finite difference approximation which reduces the boundary value problem to a set of algebraic equations. We have extensively used CHEMKIN - PREMIX for the purpose of this study.

Our mechanism consists of over 200 elementary **reactions** most of which come from the **GRI** 2.1 mechanism for methane combustion [18]. Water droplet **evaporation** rates have **been** modeled using the **d-square law** model. **These** rates along with the latent heat of vaporization have been incorporated into the mechanism to **account** for the transformation of liquid water droplets to the vapor phase.

Droplet Vaporization Model

In the most notable earlier work **on** droplet vaporization, a quasi-steady spherically symmetric model was used for both liquid and gas phases [19]. **The** droplet temperature **was** assumed to be uniform and remained at its wet-bulb temperature. At the gas-liquid interface, it **was** assumed that the fuel vapor mass fraction **was** a function of the surface temperature given by some equilibrium vapor pressure equation such **as** Clausius-Clapeyron relation. This theory gives the classic **d-square law**. Some of the resulting relationships are give below.

$$m = 4 \pi r \rho_g D \ln (1 + B) \quad (1)$$

$$B = C_{pg} (T_g - T_s) / L = Y_{fs} / (1 - Y_{fs}) \quad (2)$$

where, m is the fuel mass vaporization rate, r is the **radius** of the fuel droplet, ρ_g is the gas density, D is the diffusivity, B is the Spalding transfer number, C_{pg} **is** the specific heat at constant pressure, T_g is the gas phase temperature, T_s is the **fuel** surface temperature, L is the latent heat of vaporization, and Y_{fs} the **fuel** vapor mass fraction at the interface. Subscripts **g** and **s** denote gas phase and droplet surface, respectively.

Note that $Y_{fs} = Y_{fs}(T_s)$ is a function of surface temperature only. For a given ambient condition, T_s and B can be determined by Eq. (2) and subsequent replacement into Eq. (1) followed by algebraic manipulation yields

$$\frac{dr^2}{dt} = K = \text{const} \quad (3)$$

K is also referred to **as** the burning constant and Eq. (3) implies that the radius squared (proportional to the droplet surface area)

decreases linearly in time and hence the model is referred to as *d-square law* model in the literature.

The transfer number B , represents the ratio of an impetus for interphase transfer to a resistance opposing the transfer [15]. From the viewpoint of energetics, the sum of heat released per unit mass of oxidizer consumed and the difference in thermal enthalpy per unit between the ambient gas and the gas at the surface of the droplet comprise the impetus for transfer, while the heat of vaporization L per unit mass of fuel vaporized is the resistance.

Integrating Eq. (3) we get an expression for time for complete burnout (vaporization) of the fuel droplet

$$t = \frac{\rho_l d_{p0}^2}{8\rho_g D \ln(1+B)} \quad (4)$$

where d_p is the initial droplet diameter. Based on Eq. (4), half lives of water droplet (specific diameter) were calculated and then fitted into the modified Arrhenius rate law. The parameters from the rate law were then used in the CHEMKIN/PREMIX code for the following transformation reaction



where H_2O_L is the liquid phase water and H_2O is the vapor phase water. Sample parameters used in the model are shown in Table I. Arrhenius parameter scales inversely with the square of the droplet diameter

Table I. Rate parameters for $H_2O_L \rightarrow H_2O$

d_p μm	A	n	E_a cal/mole
10	4.55×10^7	-1.1	5915
50	1.82×10^6	-1.1	5915
100	4.55×10^5	-1.1	5915
200	1.14×10^5	-1.1	5915
500	1.83×10^4	-1.1	5915

RESULTS

A number of simulations were run to study 1) the effectiveness of water-mist (compared to CF_3Br , Halon 1301) towards flame inhibition (in terms of adiabatic flame speed and flame temperature); 2) the effect of water mist droplet size on the propagation of the premixed flame and; 3) elucidate mechanism of flame inhibition by water mist. All cases studied were further divided into 3 subdivisions based on the fuel-mixture specifics. Representative compositions used were $\phi = 0.7$ (fuel lean), $\phi = 1.0$ (stoichiometric) and, $\phi = 1.3$ (fuel-rich). Table II summarizes the cases along with a brief description of the objective of each exercise.

Table 11. Description and objective of various simulations. Note all cases were run for $\phi = 0.7, 1.0, \text{ and } 1.3$.

Case	Additive	Objective
A	None	Base Case
B1-5	H_2O_L $d_p = 10, 50, 100,$ $200, 500 \mu\text{m}$.	Effect of droplet size
C	CF_3Br	Comparison of Halon 1301 with water mist.
D	H_2O (vapor)	Cooling effect from vaporization
E	H_2O_L present but no transformation to H_2O (vapor).	Specific heat effects

Case A. Base Case

Base case simulations were run with CH_4 -air mixtures (no additive) to provide with a standard against which the other scenarios can be compared. Table III shows the adiabatic flame speeds and the flame temperature for this case. For stoichiometric inlet CH_4 -air (Case A2) the adiabatic flame speed obtained from the model is

40.21 cm/s which compares favorably with the experiments.

Table III. Base case simulation results.

Case	ϕ	S_L (cm/s)	Flame Temperature (K)
A1	0.7	20.50	1837
A2	1.0	40.21	2230
A3	1.3	26.50	2059

Case B. Droplet Size

To ascertain the effects of water droplet size on flame inhibition, water was added to the flame simulation in mole fractions ranging from 0% to 15%. Figure 1 shows the effect of addition of water (droplet size = 10 μm) to flame inhibition in terms of S_L (adiabatic flame speed) and the adiabatic flame temperature. S_L shows a monotonic decrease with initial steep gradient with the addition of water. The flame temperature shows a linear decrease with water addition.

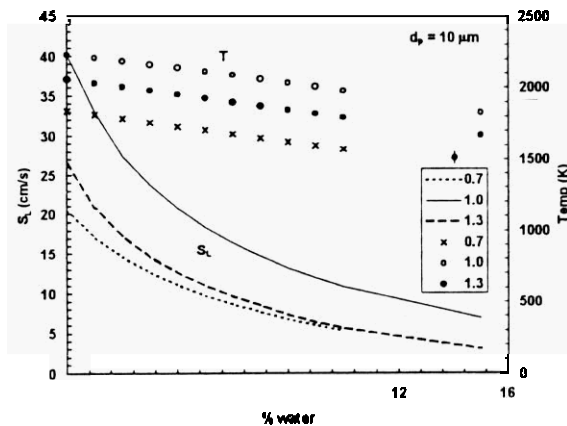


Figure 1. Effect of water addition ($d_p = 10 \mu\text{m}$) on S_L (adiabatic flame speed) and adiabatic flame temperature.

Simulations were also run for droplet sizes ranging from 10 μm to 500 μm . Figure 2 shows

the effect of droplet size on flame speed for the same water loading.

Larger droplet sizes are found to be more effective for flame inhibition as opposed to smaller droplet sizes for the same water loading. The result has been experimentally verified for flame propagation in liquid aerosols [20]. From the experimental work, researchers have speculated that momentum of bigger droplet improves the ability of the droplet to break through the flame and reach the fuel surface where they provide cooling effect and dilute the oxygen being delivered to the fire. Current model setup does not take into account the momentum of the water droplets and hence, the above reasoning is invalid for our case. The actual reason (based on the model) is that bigger drops take longer to vaporize. Heat, which comes from the flame is required to raise the temperature of the droplet, thus causing a reduction in adiabatic flame temperature resulting in slowdown of the flame chemistry. It is then possible that the droplet size effects are due to unevaporated water droplets existing at high temperatures, in equilibrium with the flame. Before we can experimentally validate, this modeling result must be treated with caution as experimental runs with water mist have shown on the contrary, that droplets lesser than 100 μm are more efficient in extinguishing fires.

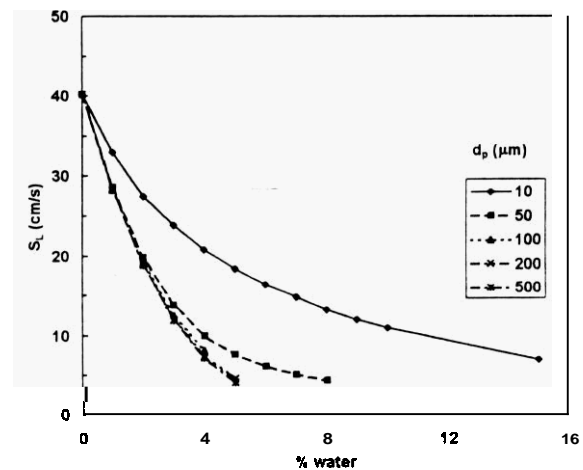


Figure 2. Effect of droplet size on S_L (adiabatic flame speed).

Critical Concentration

We define “critical concentration” of the inhibitor (water **mist** in this case) **as** the mole-fraction of the inhibitor which **results** in an adiabatic flame speed of **4 cm/s** which **is** considered the lower limit value for stable flame propagation. This is a working **definition** of the “critical concentration”. It is assumed **that** further addition **of** inhibitor would result in lowering the adiabatic flame velocity below the lower limit value resulting in unstable flame propagation leading to extinguishment of the flame.

Table IV lists the critical concentrations of water mist for various droplet sizes for the stoichiometric case, $\phi = 1.0$. **Data** shows that there exists an optimum water **mist** droplet size for flame extinguishment.

Table IV. Critical concentrations (water mist), $\phi = 1.0$.

Case	d_p (μm)	Critical concentration (% mole fraction)
B1	10	16.43
B2	50	8.25
B3	100	4.69
B4	200	4.92
B5	500	5.02

Case C. Comparison of Halon with Water Mist

Potency of any new fire suppressant must be compared with Halon 1301, the industry standard for decades. Critical concentrations of Halon 1301 are shown in Table V. Comparison of critical concentration of Halon 1301 for stoichiometric flame condition (Case D2) with 100 μm droplet size for the same flame condition (Case **B3**) shows that Halon 1301 is 2.6 times more effective than water mist (100 μm). However, for fuel lean conditions, Halon 1301 was found to be 18 times more effective.

Predominant mechanisms of Halon 1301 include consumption of **free** radicals H and HO₂ and reduced rate of heat release due to endothermic reactions [21].

Table V. Critical concentrations of Halon 1301 for CH₄/air flame extinguishment.

Case	ϕ	Critical concentration Halon 1301 (% mole fraction)
D1	0.7	0.64
D2	1.0	1.80
D3	1.3	2.18

Figure 3 **shows** the flame inhibition resulting from Halon 1301 and the adiabatic flame temperature.

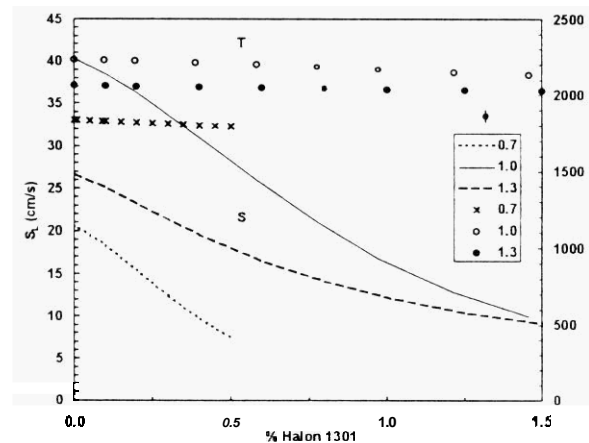


Figure 3. Effect of Halon 1301 addition on S_L (adiabatic flame speed) and adiabatic flame temperature.

Case D. H₂O vapor as Flame Inhibitor

To study the cooling effect associated with evaporation of droplets, H₂O **was** added in the flame **as** vapor and not as a liquid. Figure 4 shows the flame inhibition and adiabatic flame temperatures for this case.

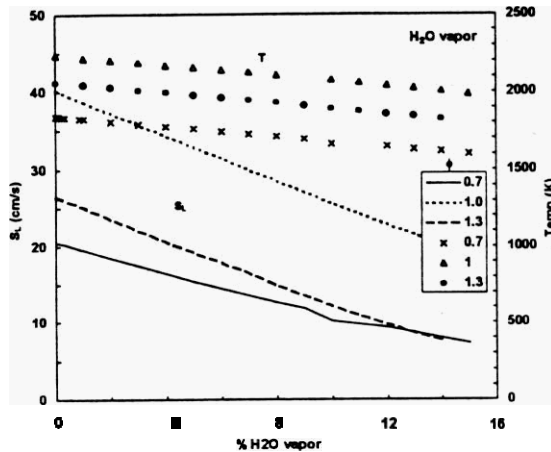


Figure 4. Effect of H₂O vapor addition on S_L (adiabatic flame speed) and adiabatic flame temperature.

Table VI shows the critical concentration of H₂O vapor, (Case D2) required for flame extinguishment. Comparison of critical concentration for H₂O vapor (Case D2) with water mist of 100 μm diameter (Case B3) shows that cooling effect from droplet vaporization is a much more significant mechanism than oxygen dilution with water vapor for flame inhibition by water mist.

Table VI. Critical concentrations of H₂O vapor for CH₄/air flame extinguishment.

Case	ϕ	Critical concentration H ₂ O vapor (% mole fraction)
D1	0.7	20.80
D2	1.0	26.80
D3	1.3	17.24

Case E. Specific Heat Effect

Specific heat effect results from the heat required to equilibrate the unburned water droplet temperature to that of the surrounding flame. This was accomplished by forcing the water droplet not to vaporize in the model. Although, the results in this case are exaggerated as lesser heat

would be required to raise the temperature of the un-vaporized liquid droplet, preliminary results show that specific heat effects are predominant in flame suppression for bigger droplet diameters ($d_p > 150 \mu\text{m}$).

CONCLUSIONS

Following conclusions can be drawn from the modeling and simulation of water mist interaction with a premixed CH₄/air flame:

- CHEMKIN/Premix code can be used for coupled chemical-physical interactions such as water mist and flame.
- Water mist can be an effective fire suppressant in spaceship as the bigger droplet mist ($d_p > 2000 \mu\text{m}$) will act as a true flooding agent in absence of gravity/inertial forces.
- Based on the working definition of critical concentration, comparison of Halon 1301 with water mist shows that Halon 1301 is 2-25 times more effective than water mist depending on the fuel oxidizer stoichiometry and water droplet size.
- Cooling effect from droplet vaporization plays an important role in flame inhibition.
- Specific heat effects become predominant for bigger droplets ($d_p > 150 \mu\text{m}$) which take longer to evaporate as compared to 10 μm droplets.

Besides experimental validation, future tasks include modification of the model to account for the following:

- Water droplet does not attain thermal equilibrium with the flame and as such its temperature lags behind that of the flame.
- Momentum effects of the water mist spray leading to forced convection and higher vaporization rates in the preheat zone resulting in most of the liquid water being converted to vapor before the reaction zone of the flame.

- Radiation effects which change square diameter dependency of the droplet vaporization rate (*d-square law* model) to a linear droplet diameter dependency.
- Water droplet distribution, preferably in the form of a 2 parameter fit such as Rosin-Rammler distribution.

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