6th Asia-Oceania Symposium on Fire Science and Technology
17-20, March, 2004, Daegu, Korea

Suppression Effect of Water Vapor on Flammability Limits of Hydrocarbon Fuels
- A Study on Fire Suppression by Water Mist -

Naoshi Saito[1] and Chihong Liao[1]

[1]National Research Institute of Fire and Disaster
14-1, Nakahara 3-chome, Mitaka, Tokyo 181-8633, Japan

Abstract

Since the water is the most famous, non-ozone depleting and effective agent in fire fighting, a water mist is noticed as favorable one of halon alternatives. There are many studies on a fire extinguishing system of the water mist. However, further studies are required on a fire extinguishing effect of the mist for its better application.

Except hydrodynamic properties of the mist in extinguishing fire, it is important to know fire extinguishing efficiency of water vapor that has been assumed to have only thermal effect as a fire suppressant. There is not enough data about such fire extinguishing efficiency of the vapor.

In the study, reducing effect of the vapor for flammable regions of methane and propane was measured at 80°C. The authors used a tubular burner system to measure the limits under well-defined conditions of flame stretch and temperature. The effect was compared with a reducing effect of carbon dioxide at 80°C and 25°C.

Experimental results showed that fire extinguishing effect of the vapor is the same as carbon dioxide for both methane and propane. Since calculated flame temperatures of the mixtures with the vapor are apparently higher than the temperatures of mixtures with carbon dioxide at extinction conditions, the chemical suppression efficiency of the vapor is superior to that of carbon dioxide. This result is attributed to the larger third body effect of water vapor than carbon dioxide in the reaction $H + O_2 + M = HO_2 + M$.

From the result and thermal properties of water, we can estimate required mass per unit volume of water vapor to extinguish n-heptanes flame. The required mass per unit volume is 162 g/m^3, and it is about 0.6 times of required mass per unit volume of halon 1301. The facts show that water mist is a high-performance agent, since the water mist has large latent heat.

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1. Introduction

Production of halons, high performance fire extinguishing agents, was stopped for protection of the stratospheric ozone layer, because the halons have large ozone depletion potential. Today, several alternative agents have been developed and are used for new fire extinguishing equipment.

Since the water is the most famous, non-ozone depleting and effective agent in fire fighting, a water mist is noticed as favorable one of halon alternatives. Recently, there are many studies on the fire extinguishing mechanism [1, 2] and the application [3-7] of water mist or spray. However, further studies are required on a fire extinguishing effect of the mist for its better application. Except hydrodynamic properties of the mist in extinguishing fire, it is important to know fire extinguishing efficiency of water vapor.

The water vapor is one of principal combustion products and inactive species in a flame. Therefore, its fire extinguishing effect is assumed as thermal in origin. Coward and Jones [8] measured flammability limits of methane diluted by water vapor and assumed that the effect is thermal in origin. Lewis and von Elbe [9] also treated that water vapor is a thermal extinguishing agent in the estimation of flammability limit of gasoline/air/vapor ternary mixture. Fuss et al [2] defined "Water is a thermal agent" and discussed its fire "suppression" efficiency.

Nagumo et al [10] studied, however, on the third body effect of argon, nitrogen, oxygen, carbon dioxide and water vapor at the second explosion limit of hydrogen by a shock tube. They found the lager third body effect of water vapor than carbon dioxide. The fact suggests that water vapor may act not only as a thermal agent but a chemical suppressant.

There are hardly data about such fire extinguishing efficiency of water vapor, because quantitative control of higher concentration of water vapor is difficult in the measurement of flammability limits and flame extinguishing concentrations.

In the study, reducing effect of the water vapor for the flammable regions of hydrocarbon fuels was measured at an elevated temperature. To measure the limits, the authors used a tubular burner system that gives reliable data under well-defined conditions on flame stretch rate and temperature. The reduce effect of water vapor was compared with carbon dioxide. The fire extinguishing efficiency of water vapor is also compared and discussed with the efficiency of halon 1301 in the paper.

2. Experimental

2.1 Tubular flame burner system for addition of dense water vapor

In the study, a tubular flame burner system [11] was employed to measure the flammability limits of methane and propane. It is known that flammability limits measured by burner system are affected by physical conditions such as flame stretch rate and temperature of mixture. However, the tubular burner system has some merits that are clear limits, clear physical conditions and excellent reproducibility [12].

A schematic diagram of the tubular flame burner system is shown in Figure 1. The burner is made of a bronze cylindrical filter. The dimensions are 30mm inner diameter, 40mm outer diameter, 80mm length, and 5μm porosity, respectively. The cylindrical filter puts center axis together in a cylindrical casing. A mixture of gases flows toward a center axis of the burner from outside of the cylindrical filter and formed a stretch flow. When the mixture is ignited, a tubular flame is formed along the

Corresponding Author- Tel.: +81-422-44-8331;
Fax: +81-422-42-7719
E-mail address: saito@fri.go.jp

center axis of the burner. In the study, the burner was installed horizontally.

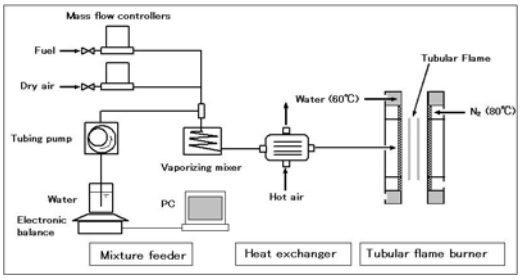

Figure 1. Tubular flame burner system to measure the effect of water vapor on flammability limits.

Electric tape-heaters heated the burner and the piping of the system. The temperature of mixture was kept at 80± 2.5°C at the burner. Since the vapor pressure of water is more than 40kPa around 80°C, the concentration of water vapor becomes up to 40% and more in a mixture. To avoid accidental explosion, the mixtures were heated by a heat exchanger with a hot air generator. The all sample mixtures were heated up to maximum 140°C.

The water vapor was supplied and controlled by a water vapor generator composed by an electronic balance, a tubing pump and a vaporizing mixer. Electronic mass flow controllers were employed to control the flows of fuels and air. The relative error of each flow control system is ±2% for water vapor and ±1% for the other gaseous chemicals.

2.2 Chemicals

Methane (99.99% purity) and propane (99.9% purity) were used as the fuels. The dry air was supplied an oil-free compressor with a dryer. The dew point of the air was lower than -10°C, thus the concentration of water vapor containing in the dry air was less than 3000ppm. Distilled water for medical use was evaporated and supplied as water vapor. Carbon dioxide is commercial liquefied carbon dioxide in a cylinder.

2.3 Experimental procedure

Following procedure was employed for measuring flammability limits. At first, the tubular burner system was heated with flowing dry air through the burner system. The flow rate of dry air was 25 liters per minute at 25°C. Then, the temperature of a vaporizing mixer was increased and kept at 140°C in an oiling bath. The burner and piping were also heated. The air temperature was controlled at 80±2.5°C in the burner. After the air temperature was controlled, methane or propane was added gradually in the hot air stream until a mixture was able to be ignited by a pilot flame.

When a tubular flame was formed in the burner, a fuel/air ratio and a flow velocity of mixture were adjusted according to the experimental conditions. Then, keeping the fuel/air ratio and the total flow rate of mixture constant, water was supplied into the vaporizing mixer. The flow rate of water was increased gradually until flame extinction occurred. The vapor concentration in the mixture was calculated by the mass rate of supplied water. The composition at the flame extinction point becomes the composition of mixture on a flammability limit of the fuel/air/water vapor mixture. In the experiment at 85±2.5°C, the flame stretch rate was controlled at $5.9s^{-1}$.

Here, nominal stretch rate σ is defined by following equation.

$$\sigma = 2V/D \qquad (1)$$

In Equation (1), V and D are a mean flow velocity of a mixture at the inside surface and the inner diameter of the tubular burner, respectively.

Similar measurements were carried out on the mixtures containing carbon dioxide at 80±2.5°C and 25°C. In the cases, a calibrated mass flow controller was used for carbon dioxide. The nominal stretch rates of the flames were controlled at $5.9s^{-1}$ at 80±2.5°C and $3.3s^{-1}$ at 25°C.

3. Results

Figure 2 and Figure 3 show the effect of water vapor on flammability limits of methane and propane, respectively. The figures show also the data on the effect of carbon dioxide measured at the same conditions of temperature 80±2.5°C and stretch rate σ=5.9s^{-1}. On the mixtures with carbon dioxide, the flammability limits measured under another conditions of temperature 25°C and stretch rate σ=3.3s^{-1} were showed in the same figures. The vertical axis of each figure shows fuel concentration in mixtures, and horizontal axis shows concentrations of water vapor or carbon dioxide.

Both Figure 2 and Figure 3 show that increase of water vapor concentration decreases the flammability regions for methane and propane as effective as carbon dioxide.

On the mixtures diluted with carbon dioxide, the conditions of temperature and stretch rate did not affect apparently the flammability limits in the study. These limit curves seem to agree with each other as seen in Figures 2 and 3.

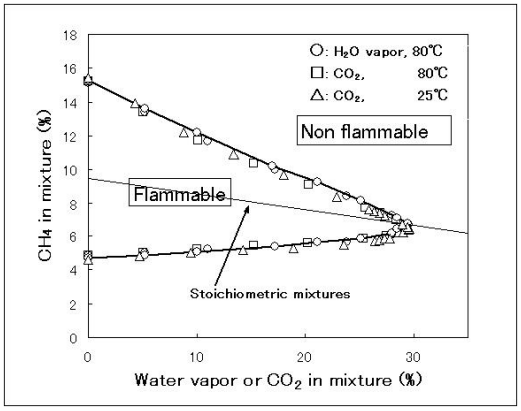

Figure 2. Flammability limits of methane in air diluted with water vapor at (80±2.5°C, σ=5.9s^{-1}) and carbon dioxide at (80±2.5°C, σ=5.9s^{-1}) and (25°C, σ=3.3s^{-1}).

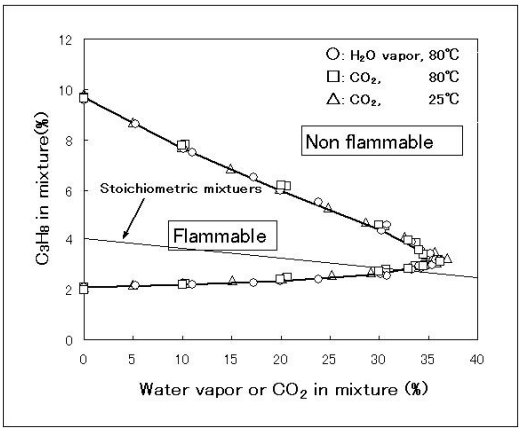

Figure 3. Flammability limits of propane in air diluted with water vapor at (80±2.5°C, σ=5.9s^{-1}) and carbon dioxide at (80±2.5°C, σ=5.9s^{-1}) and (25°C, σ=3.3s^{-1}).

Adiabatic flame temperatures of the near stoichiometric mixtures of the limits were calculated and compared with each other of the mixtures on each fuel. The results are showed in Table 1. For each fuel, the adiabatic flame temperatures of the limit mixtures with water vapor are about 100°C higher than the mixtures with carbon dioxide, respectively.

Fuel	methane	methane	propane	propane	Remarks
Fuel concentration	6.7	6.9	2.9	2.9	vol.%
Water vapor concentration	29.4	0	34.0	0	vol.%
Carbon dioxide concentration	0	28.4	0	34.5	vol.%
Stoichimetric ratio	1.01	1.02	1.11	1.11	
Mixture Temperature	80	80	80	80	℃
Calclated flame temperature	1489	1401	1417	1285	℃

Table 1. Composition of the near stoichiometric mixtures diluted water vapor or carbon dioxide and the adiabatic flame temperatures.

4. Discussions

Water vapor and carbon dioxide showed the same reducing effect on the flammability regions of methane and propane measured under the same physical conditions. The fact means that water vapor has the same flame extinguishing effect as carbon dioxide on mole basis under the experiment conditions. Although the molar heat capacity of water vapor is smaller than carbon dioxide, the flames diluted with water vapor went out at higher flame temperature than carbon dioxide on the same stoichiometric mixtures. If the origin of the fire extinguishing effect of water vapor is thermal, the flame temperatures at a flammability limit have to be as same as the flames with carbon dioxide at the limit. Therefore, the fact shows that water vapor has larger chemical suppression effect than carbon dioxide. The report by Nagumo et al [10] suggests that the lager chemical suppression effect of water vapor appears through the lager rate of the following reaction than carbon dioxide. Here, M means the third body in Equation (2).

$$H + O_2 + M = HO_2 + M \qquad (2)$$

In the mixtures with carbon dioxide, change of the conditions of temperature and stretch rate did not affect the flammability limits apparently in the experiment. It is because (1) the effects of parameter are small in the experiment [13, 14], and (2) the increasing effect with increasing temperature was compensated by decreasing effect with increasing stretch rate for the flammable region [13].

Water vapor has the same fire extinguishing effect as carbon dioxide and about 0.4 times of molecular weight of carbon dioxide on mole basis. On mass basis, therefore, the fire extinguishing effect of water vapor becomes 2.5 times better than carbon dioxide.

The authors reported parallel relation between peak (inerting) concentrations for a combustible mixture and flame extinguishing concentrations of a cup burner [15]. In Table 2, the flame extinguishing efficiencies of water vapor, carbon dioxide and halon 1301 on mass basis are compared on the flame extinguishing concentrations measured by n-heptane cup burner flame. Here, it is assumed that the flame extinguishing concentration of water vapor at 25°C is equal to carbon dioxide for n-heptane flame.

Table 2 shows that on mass basis water vapor is 2.5 times more effective fire extinguishing agent than carbon dioxide and 1.5 times mere effective fire extinguishing agent than halon 1301.

Agent	water vapor	carbon dioxide	halon 1301	Remarks
Formula	H_2O	CO_2	CF_3Br	
Molecular weight	18	44	149	
Flame extinguishing concentration	22	22	3.4	vol.% at 25℃
Required mass	162	396	226	kg/m^3 at 25℃
Extinguishing efficiency	1	0.4	0.7	water vapor: 1

Table 2. Comparison of fire extinguishing efficiency of water vapor, carbon dioxide and halon 1301.

Since the water has large latent heat, it is easy to understand that water mists as dispersed water possess larger effective fire extinguishing efficiency than water vapor. Therefore, water mist is a higher performance agent than halon 1301.

However, water mist is composed by liquid water particles and affected by the gravity. This causes to decrease intrinsic fire extinguishing efficiency of water mist. On the other hand, water vapor condenses to droplets, and it is affected consequently by the gravity. This effect decreases the fire

extinguishing efficiency of water vapor and also water mist.

It is the most important issue to solve in the fire extinguishment by water mist how the water particles supply into flames with high efficiency.

5. Conclusion

The water vapor has the same fire extinguishing efficiency as carbon dioxide on mole basis.

Since the molar heat capacity of water vapor is smaller than carbon dioxide, water vapor has larger chemical inhibition effect on combustion than carbon dioxide.

Lager chemical inhibition effect of water vapor may derive from the lager third body effect in the reaction

$$H + O_2 + M = HO_2 + M.$$

On mass basis, the fire extinguishing efficiency of water vapor is 1.5 times lager than halon 1301.

Water mist is a group of droplets and it is affected by the gravity. Such gravity effect decreases the efficiency of water mist.

It is the most important issue to solve in the fire extinguishment by water mist that the water particles supply into flames with high efficiency.

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