# Effect of Combustible Vapors in Air on Extinction of Cup Burner Flames by HFC and FC Fire Suppressants

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## ABSTRACT

HFC and FC agents were developed as replacements of halon 1301 ($CF_3Br$), however, some fluorohydrocarbons decrease the lower flammability limits of combustible gases and vapors. To use trifluoromethane ($CF_3H$), 1,1,1,2,3,3,3 heptafluoropropane ($CF_3CFHCF_3$), and perfluorobutane ($C_4F_{10}$) as the replacements safely in plants containing combustible vapors, cup-burner flame extinguishing concentrations of the agents, halon 1301, and nitrogen for n-heptane flames were investigated as functions of concentration of methane or methanol vapor in air. The following conclusions have been obtained:

(1) When the air contains a combustible less than the lower flammability limit, blue flame appeared around n-heptane diffusion flame by addition of the HFC and FC agents in air. Such flame did not appear through the addition of $CF_3Br$ and nitrogen.

(2) Methanol vapor in air increased the flame extinguishing concentrations of all agents when increasing the vapor concentration, while methane did not affect the flame extinguishing concentrations of all the agents until the blue flame was formed.

(3) If a combustible vapor is mixed in the air of a space protected by a total flooding fire extinguishing system employing the HFC or FC agent, a design concentration determined by the flame extinguishing concentration is not always sufficient to extinguish fires in the space. An inerting concentration may be desirable for the design concentration in such case.

**KEYWORDS:** halon replacement, fluorocarbon, combustible vapor, extinguishing concentration, flammability limit, design concentration

## INTRODUCTION

A design concentration of a gaseous fire suppressant for a total flooding system is determined by a flame extinguishing concentration [1], that means a suppressant concentration measured by a cup burner for extinguishing a liquid fuel flame in the air [2, 3]. Hence, the flame extinguishing concentration is known as an important performance of the suppressant. Since the production of halon fire extinguishing agents was banned by Montreal Protocol for the protection of the stratospheric ozone layer on January 1, 1994, several new agents with zero ozone depletion effect and low toxicity have been developed and listed as halon replacements in



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the literature [4, 5]. They are tri-fluoromethane ($CF_3H$), 1,1,1,2,3,3,3 heptafluoropropane ($CF_3CFHCF_3$), perfluorobutane ($C_4F_{10}$), and a few inert gas agents.

In 1995, Saito et al [6] reported the flammable ranges of gaseous hydrocarbon / suppressant / air mixtures by a new technique to measure flammability limits. They call the technique a tubular-flame burner method. Similar burners that form premixed tubular flames were already reported by Ishizuka [7] and Kobayashi et al [8]. Saito et al [6] show the limit curves of methane and propane mixtures containing $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$. They found that the lower flammability limit of each mixture decreased with increasing the concentration of the agents. They speculated that the phenomena were attributed to the role of the suppressants as fuel in lean mixtures. At the same time, they also obtained the results that nitrogen and trifluorobromomethane ($CF_3Br$) did not show such effect. Trifluorobromomethane is called halon 1301. Schröder et al [9] studied the explosion range of propane / 1,1,1,2 tetrafluoroethane ($CF_3CFH_2$) / air mixtures by explosion spheres. They reported the same decreasing effect on the lower limit of the propane mixtures as Saito et al reported. They pointed out the risks of $CF_3CFH_2$ on an accidental fire or explosion by the expansion of lower limit of the propane / $CF_3CFH_2$ mixtures used as a refrigerant.

In Japan, there are many important plants equipped with an evaporating process of combustible vapors. They are the plants for painting, coatings of thin magnetic film or photosensitive emulsion, washing electronics circuit, producing plastic foam, and so on. Such plants are usually protected by a total flooding fire extinguishing system. In such case, it is important how to determine an adequate design concentration for the system, because of the reason above mentioned. In the study, the efficiencies of the suppressants are investigated by cup-burner flame extinguishing concentrations when air containing methane and methanol vapor, and by flammability limits of ternary mixtures of the combustibles / air / the suppressants. Then, flame extinction by the suppressants with combustible gases or vapors is discussed to understand appropriate fire / extinguishing systems employing fluorinated suppressants for the spaces containing combustible gases and vapors.

## EXPERIMENTAL

### FRI cup burner apparatus

A cup burner apparatus gives reproducible flame extinguishing concentrations [10]. However, the extinguishing concentrations depend on sizes of the apparatus, especially on a cup diameter and a chimney diameter, even if the other conditions are fixed [11]. The fact is shown in the "Cup-Burner Heptane Flame Extinguishing Data" in the literature [1, 5]. FRI cup burner was employed and fixed to measure the effect of the mixed combustible gas or vapor on the extinguishing concentrations, because the authors understand well the characteristics of the burner.

A schematic diagram of FRI cup burner system is shown in FIGURE 1. The system has been developed by National Research Institute of Fire and Disaster in Japan. Its main parts are composed by a cup burner, a fuel feeder with a fuel level controller, a gaseous agent supplier, and a liquid vaporizer. The cup burner system has a 30 mm outer diameter cup and an 85 mm inner diameter chimney. The cup is installed in the chimney with coaxial arrangement. They are made of "Pyrex" glass. Keeping a fuel surface in a constant level, the liquid fuel was supplied from a fuel feeder to the cup. The feeder has an overflow tank, a reservoir, and a tube pump as seen in FIGURE 1. The fuel level in the cup is controlled by the overflow tank height. Flow rates of the gaseous agents were regulated by mass flow controllers that were calibrated by wet-type gas meters. Relative errors of the mass flow controllers are less than 1 % of each regulated flow rate. A special vaporizer was developed to evaporate methanol and to mix the vapor into air. The vaporizer was equipped with a special pump system to supply precisely quantity of methanol into an air heater where the vapor and the air were mixed. In the study, the variation of the methanol flow rate was less than 2 % of each regulated value.

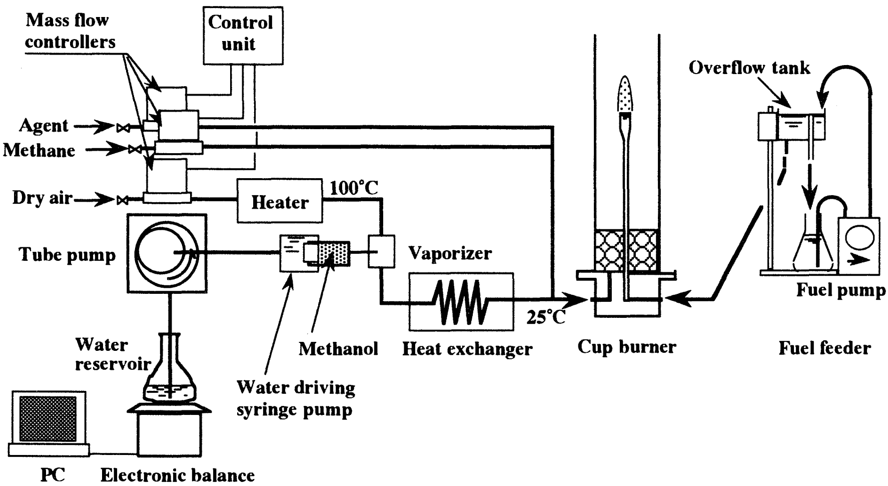


FIGURE 1 Schematic diagram of FRI cup burner system

## Flame extinguishing concentration measurement

Flame extinguishing concentrations ($C$) of the fire suppressants were measured at 25 °C and the atmospheric pressure. The air flow rate $Q_a$ was fixed at 40.0 l/min in accordance with the literature [2, 3, 5, 10, 12]. Before every flame extinction experiment, n-heptane in the cup was preburned for 8 minutes without any agents to make the same experimental condition. After the preburning treatment, the agent was mixed into air at a certain flow rate. Then, the flow rate of the agent was increased stepwise every 10 seconds until the flame went out. Air and all the additives were supplied to the burner through a glass beads layer for mixing. Methane and methanol vapor were mixed in the air flow from 6 minutes after ignition, when flame extinguishing concentrations were measured in air containing the combustibles. A flame extinguishing concentration $C$ (%) of the fire suppressants was calculated by the following equation:

$$C = 100Q_i / (Q_a + Q_f + Q_i) \quad (1)$$

Here, $Q_f$ and $Q_i$ are flow rates of both the agent and the combustible mixed into the air stream at flame extinction, respectively.

## Flammability limit measurement of combustibles with suppressants

Flammability limits of methane and methanol vapor with suppressants were measured by a tubular flame burner reported elsewhere [13]. The burner, made of a porous bronze cylinder of 30 mm inner diameter ($D_i$) and its cylindrical casing, was set horizontally for its axis. A combustible mixture flowed from the porous cylinder surface to the axis and formed a stagnation flow. Average flow velocity $V_i$ (mm/s) of the mixture at the inner surface of the burner was calculated by devising a total flow rate by the surface area. The flow velocity was fixed at 50 mm/s in every limit measurement. Since the nominal stretch rate ( $\sigma$) defined by the following equation for the tubular flame after the literature [14]

$$\sigma = 2V_i/D_i, \qquad (2)$$

the stretch rate $\sigma$= 3.3 $s^{-1}$ was obtained in the case. The flammable area was determined by the compositions where tubular flames were maintained for more than 1 minute. Since methanol vapor pressure is about $1.6 \cdot 10^{-2}$ MPa at 25 °C, upper limits of the methanol vapor were not measured.

## Chemicals

N-heptane and methanol were grade guarantee commercialized chemicals and used no further purification in the experiments. Purity of methane and nitrogen was more than 99.9 %. The purity of $CF_3Br$, $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$ was 99 % or more by GC analysis.

# RESULTS

## Flame behavior in air containing combustibles

Methane and methanol vapor in air increased only flame height of n-heptane diffusion flame. When nitrogen and $CF_3Br$ were applied as suppressants to the cup burner flame, any drastic changes did not observe in the flame extinction phenomena. However, by the addition of $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$ in the air, a blue flame appeared around the n-heptane diffusion flame on the cup as seen in FIGURE 2.

With increasing the concentration of the agents, the blue flame expanded from the cup edge to the inside surface of the chimney like a trumpet, then both flames lifted from the top of the cup and spread over a cross section of the chimney. In the study, the minimum agent concentration that causes a flame lifting is called a flame lifting concentration. In the cases of $CF_3H$ and $CF_3CFHCF_3$, the higher concentration of the agents shifted the lifting flame at the higher position of the chimney, and then the flame went out from the top of the chimney. The lifting flame apart from the cup was bluish and looked like a premixed flame. In the case of $C_4F_{10}$, however, both n-heptane flame and the blue flames became unstable when increasing the concentration, and they disappeared at the beginning of their lifting up form the cup.

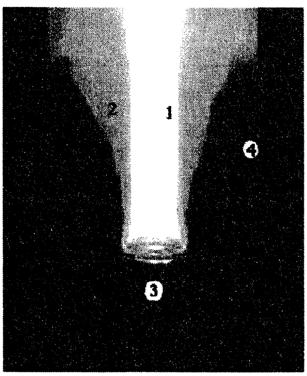


FIGURE 2 Blue flame in air stream including 4.8 % methanol vapor formed by addition of $CF_3CFHCF_3$
1: n-heptane diffusion flame 2: blue flame
3: cup 4: chimney

## Extinguishing concentrations in air containing combustibles

### (a) Methane

FIGURE 3 shows the flame extinction results as functions of methane concentration in the air stream. Measurement of the extinguishing concentration was repeated at least three times under the same conditions. The average values were plotted as a function of methane concentration for all the suppressants in the figure, where white circles represent flame extinguishing concentration or flame lifting concentration, and black circles mean that the flames went through the top of chimney. The flame extinguishing concentrations did not increase with increasing the methane concentration, except the case to appear a lifting flame by CF3H. The flame lifting concentrations were smaller than the extinguishing concentrations.

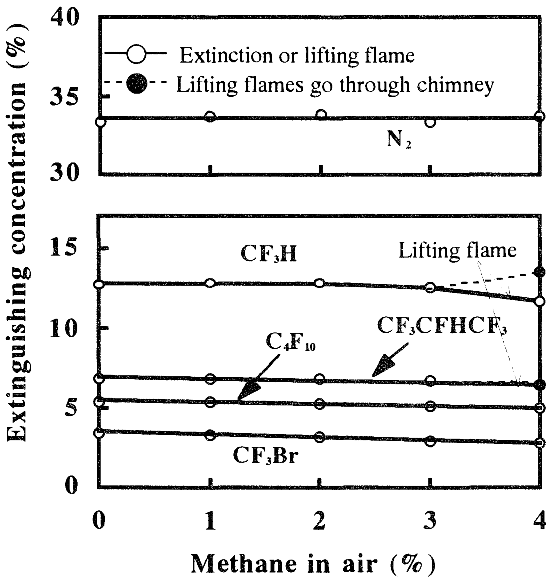


FIGURE 3 Variation of flame extinguishing concentrations with methane concentration in air

### (b) Methanol vapor

FIGURE 4 shows the flame extinction results of all the fire suppressants as functions of concentration of methanol vapor in the air stream. In this case, measurement was only once at each condition, but the concentration of the vapor was changed little by little to provide many different conditions. In FIGURE 4, white circles also show extinction or flame lifting, and black circles mean that lifting flames went through the chimney. The extinguishing concentrations of all the suppressants increased with increasing the concentration of methanol vapor. Similar to the case of the air containing methane, the addition of CF3H and CF3CFHCF3 caused the lifting flames in the chimney for more than 3.5 % and 4 % vapor concentrations, respectively. The lifting flames formed by the addition of methanol vapor seemed to be more stable than by methane. The flame lifting concentrations decreased with increasing the methanol vapor concentration.

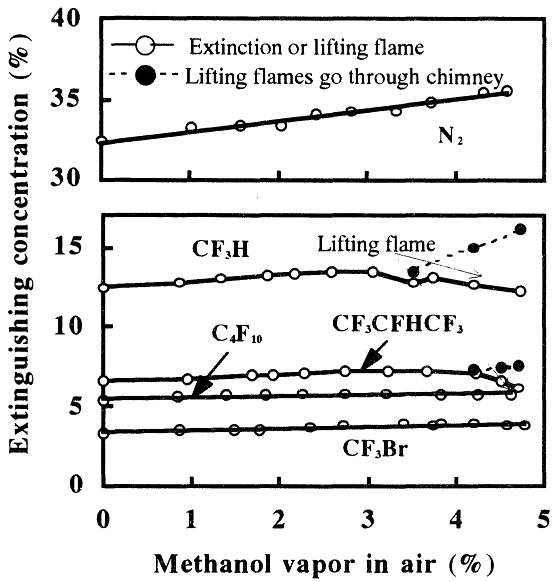


FIGURE 4 Variation of flame extinguishing concentrations with methanol vapor concentration in air

**Effect of suppressants on lower limits of methane and methanol vapor**

FIGURES 5 and 6 show the flammability limit curves of methane and methanol vapor with the suppressants, respectively. However, the limit data on $CF_3Br$ is not in FIGURE 6, because of the lack of measurement about the limit of methanol vapor / $CF_3Br$ / air mixture. Since vapor pressure of methanol at 25 °C is insufficient to measure the upper limit of methanol, the limit curves are not showed in FIGURE 6. Dashed lines in FIGURES 5 and 6 mean the combustible concentration of the ternary mixture. They show 4 % for methane and 4.8 % for methanol vapor in the binary mixtures between the air and a combustible, e.g., no-agent containing mixtures, respectively. The symbols on the combustible concentration lines in FIGURES 5 and 6 indicate compositions of a combustible and an agent contained in the air stream on the flame extinguishing experiments by the cup burner.

The addition of nitrogen kept the lower limit almost constant as seen in the flammability diagrams of FIGURES 5 and 6. $CF_3Br$ increased remarkably the lower limit of methane as seen in FIGURE 5. However, $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$ decreased the lower limit of both methane and methanol vapor. The limit results were obtained under the constant nominal stretch rate, $\sigma = 3.3\ s^{-1}$ for all the ternary mixtures.

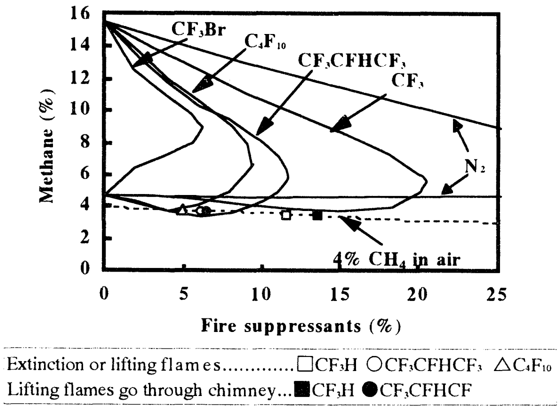


FIGURE 5 Flammability limit curves of methane / fire suppressant / air mixtures and compositions of the air at the moment of flame extinction, lifting flame, and going-out flame of the chimney

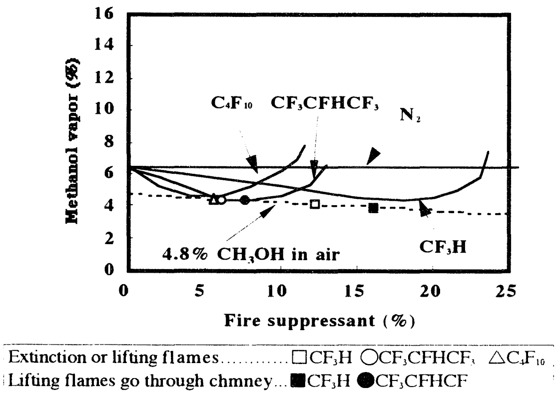


FIGURE 6 Flammability limit curves of methanol vapor / fire suppressant / air mixtures and compositions of the air at the moment of flame extinction, lifting flame, and going-out flame of the chimney

## DISCUSSION

### Flame extinguishing concentrations in air containing combustibles

On the cup burner experiments, addition of methane in air did not increase any flame extinguishing concentrations of all the suppressants but methanol vapor increased in lower concentration of the combustibles where no lifting flames of n-heptane occur.

Extinction of a diffusion flame on the cup is affected by stabilization at the flame base where both flow velocity and the burning velocity of stoichiometric mixture are locally balanced through the same magnitude in the opposite directions of each other. In a flame of a cup burner, a stoichiometric mixture formed by mutual diffusion effect between air and a fuel vapor at certain parts on the cup. Hence, the combustible mixed in the air stream of the cup burner should affect to shift the flame base to the air side, where the flow velocity becomes larger. Consequently the diffusion flame becomes less stable than the case where the air contains no combustibles. Therefore, combustibles in a air stream of a cup burner brings smaller flame extinguishing concentrations.

However, methane has no decreasing effect on the flame extinguishing concentrations in spite of the above simple consideration as seen in FIGURE 3. Moreover, in FIGURE 4, the increasing concentration of methanol vapor yields larger flame extinguishing concentrations for the all agents. Methanol vapor seems to have the stabilizing effect of the diffusion. The facts suggest that the effect of the combustibles in air is more complicate than the above simple explanation. The further studies must be required to explain the effect.

## Appearance of blue flames

When flame extinguishing experiments were conducted in the air containing the combustible vapors of near their lower limits, blue flames formed around the n-heptane diffusion flame by the addition of $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$, but not nitrogen and $CF_3Br$. The appearance of the flame is apparently attributed to the decrease of lower limits by $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$. The reason is as follows;

In FIGURES 5 and 6, all the limits concerned with a constant burning velocity, because the limits were measured at the same stretch rate even if it is nominal. On the concentration lines of 4 % of methane and 4.8 % of methanol vapor in the figures, there are the symbols indicating the extinction behaviors of the cup burner flames. The white symbols denote the minimum suppressant concentrations at flame extinction or lifting flames by addition of $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$ in the air stream, and the black symbols mean the minimum concentrations where the lifting flames go out of the chimney. Since the lower flammability limits of both methane and methanol vapor decreased by $CF_3H$, $CF_3CFHCF_3$, and $C_4F_{10}$, both the concentration lines of the combustibles can run parallel near to the lower limits or pass through the lean flammable areas in FIGURES 5 and 6. Therefore, the mixtures containing less concentration of a combustible than its lower limit, can burn if adequate amount of the fluorinated suppressants is mixed. However, $CF_3Br$ and nitrogen do not have such effect clearly, because they never decrease the lower limits of hydrocarbon fuels. The facts are very important for use of the new fluorinated suppressants for avoiding fire accidents.

## Appearance of lifting flames and their extinction

In the air containing either methane or methanol vapor, $CF_3H$ gave the most stable lifting flames in the chimney. The next is $CF_3CFHCF_3$, but $C_4F_{10}$ could not stabilize any lifting flames. From the order of the lifting flame stabilization and FIGURES 5 and 6, it is easily understandable that there is a good relation between the stabilizing effect and an extension of the suppressant concentration decreasing the lower limit. At the same time, the relation means that the more effective suppressant is also more effective for the extinction of the lifting flames.

## Design concentration of fluorocarbon suppressants

The study revealed that the fluorocarbon suppressants as replacements of halon 1301 may produce new problems on fires in air containing combustible gases and vapors. The problems are that the fluorocarbons decrease the lower limits of hydrocarbon fuel and that they may change the mixtures of nonflammable composition to "flammable". The facts mean that design concentrations of a fire extinguishing system have to be determined by the concentration to extinguish the combustion of air-combustible vapor-fluorocarbon suppressants mixtures. It seems to be similar to inerting the combustible vapors. Therefore, inerting concentrations are required as the design concentrations to extinguish fires in the spaces evaporating combustible vapors, if a total flooding fire extinguishing system is employed to prevent the fires of plants of hazardous materials.

## CONCLUSIONS

It is known that fluorocarbon fire suppressants as replacements of halon 1301 decrease the lower flammability limits of hydrocarbon fuels. Such effect of the suppressants was studied by measuring the flame extinguishing concentrations in the air including methane and methanol vapor in less concentration than the lower limits of flammability. The following conclusions are obtained:

(1) Methane in the air does not increase the flame extinguishing concentrations, but methanol vapor increases the flame extinguishing concentrations of all types of fire suppressant.

(2) The air containing a combustible in less concentration than the lower limit of flammability burns with addition of adequate amount of fluorocarbon suppressants, but $CF_3Br$ and nitrogen never show such effect.

(3) Design concentrations determined by the usual flame extinguishing concentrations are not always sufficient to extinguish fires of spaces where the air contains combustible gases or vapors in less concentration than the lower limits of flammability.

(4) It is desirable to determine design concentrations for plants of hazardous materials by inerting concentrations.

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