Effect of Interaction between Halogenated Fire Suppressants and Inert Gas on Extinction Limit of Premixed Flame

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Abstract

Multiplier effect of halon 1301 and inert gas mixture on fire suppression efficiency was found in the cup burner diffusion flame previously. In order to clarify this effect by removing the diffusion process of fuel and oxidizer, premixed tubular flames of methane-air-halon 1301-nitrogen mixtures are employed in the present study. Halogenated fire suppressants tested in the present study are tetrafluoromethane, HFC-23, HFC-227ea and FC-3-1-10 as well as halon 1301. Concentrations of the mixtures of the suppressants with nitrogen at the extinction limit were measured as a function of mole fraction of nitrogen in the mixtures, and estimated also by using an equation of additive property on flame extinction effect.

Experimentally determined extinction limits of methane-air-tetrafluommethane-nitrogen mixtures agree well with those estimated values. The fact shows that there is no interaction between tetrafluoromethane and nitrogen. This is reasonable because tetrafluoromethane is recognized as an inert agent in hydrocarbon-air flames. Halon 1301-nitrogen mixed agent has shown the maximum multiplier effect at the mole fraction of nitrogen of 0.96, that is identical to the previous finding on the cup burner flame.

In contrast to halon 1301, HFC-23 has no multiplier effect, and HFC-227ea and FC-3-1-10 have exhibited negative multiplier effect in the cases of mixing with nitrogen. These results are also similar to our recent findings by the cup burner study. The present study demonstrates that there exists the positive or negative multiplier effect of halogenated agent-inert gas mixture, independently of the difference in chemical/transport environment between premixed and diffusion flames.

1. Introduction

On January 1, 1994, the production of the halon fire-extinguishing agents was banned to protect the stratospheric ozone layer. Several new agents have been developed as halon replacements, and applied for fire-extinguishing system to date. Almost all of them, however, are not superior to halon 1301 in fire suppression efficiency [1].

On the other hand, to improve the fire suppression effect of existing fire suppressants, some studies about complex usage of agents have been carried out [2, 3], but there was no definite index to indicate the fire suppression efficiency of mixed agents.

To propose an index of fire suppression efficiency of mixed agents, Saito et al. derived an equation of additive property on flame extinction effect of mixed inert-gas agents through consideration of thermodynamics for fire suppression effect under the condition of the constant equivalence ratio, $\phi=\phi_0$ [4].

$$\frac{1}{C}=\sum_{j=1}^{n}\frac{X_j}{C_j} \qquad (1)$$

Here, C is extinguishing concentration of mixed agent, X_j is mole fraction of j th component of the agent, and C_j is extinguishing concentration of j th component of the agent.

They conclude that if each component of mixed agent does not interact with one another and the fire suppression efficiency is proportional to the concentration, the equation (1) can be applicable for all kinds of mixed agents. Therefore, difference between measured efficiency and calculated one suggests that there is an interaction between both agents.

The flame extinguishing concentrations of the mixtures between halon 1301 and inert gases (Ar, N_2, CO_2) for n-heptane diffusion flame were measured by the cup burner apparatus [5, 6, 7].

The result analyzed by using above criterion showed that there is multiplier effect between halon 1301 and inert gases, and they found that the reducing effects of required halon 1301 increase with increasing of the heat capacity of inert gas. That is, the amount of halon 1301 required for extinction of the cup burner flame decreases to 1/2 (Ar) or 1/3 (CO_2) by using the mixed agents of 10% of halon 1301 and 90 % of inert gas. From the interpretation with the calculated adiabatic flame temperature, it was suggested that the inert gases caused decrease in flame temperature, and then the chemical flame inhibition effect of halon 1301 was enhanced by the flame temperature decrease. Furthermore, the experiments of the mixture of other halogenated fire suppressants and inert gases were carried out using the same cup burner, and it was reported that the negative multiplier effects were found out for the mixtures of some halon replacements [8].

In case of the cup burner diffusion flame, however, the flow velocity of the suppressant-air mixture at extinction changes remarkably with variation of the composition of the mixed suppressant, that is caused by the significant difference in the flame extinguishing concentrations between halogenated suppressants and inert gases. This may relate to the observed multiplier effects. In addition, chemical/transport environment such as the equivalence ratio varies spatially in the diffusion flames. Although it is unlikely that such spatial variations relate to the multiplier effects of the mixed suppressants, it is reported that they can fairly affect the inhibition effect of a certain chemical suppressant [9]. The factors mentioned above disturb the clarification of the observed multiplier effects.

In this study, a premixed flame is employed to further investigate the multiplier effects of halogenated suppressant and inert gas mixtures. The mixed agent concentrations at the extinction limit are measured by a tubularflame burner system [10,11].

The adiabatic flame temperatures of the mixture at the condition of the extinction limits are calculated to interpret the interaction between halogenated agent and inert gas.

2. Experimental

2.1 Apparatus and chemicals

The tubular flame burner system is used for measurement of the extinction limits. Figure 1 is a schematic diagram of the apparatus. The system consists of two parts. One is the tubular flame burner and the other is a gas mixture supply unit. The tubular flame burner is made of porous brass cylinder. The dimensions of the burner are 18 mm in inner diameter, 45 mm in length, 2 mm in thickness, and 5 μm in porosity. To prevent the burner heating by flame, the burner was equipped with water-cooled ends of 25 mm in length, and nitrogen injection parts of 25 mm in length at both sides as shown in Figure 1. A photograph of the tubular flame burner is shown in Figure 2.

Methane with purity of more than 99.9 percent by volume is used as fuel. Dry air is supplied from an air compressor equipped with dryer. Six agents are used as fire suppressant by mixing with nitrogen (N_2). They are halon 1301 (CF_3Br), HFC-23 (CHF_3), HFC-227ea (CF_3CHFCF_3), FC-3-1-10 (C_4F_{10}), tetrafluoromethane (CF_4) and carbon dioxide (CO_2). Methane and the agents are commercial gases. The purity of the agents was checked by gas chromatography. It was more than 99 percent by volume for all the agents. The flow rates of gases are adjusted freely by the precision-type mass flow controllers, then they are mixed.

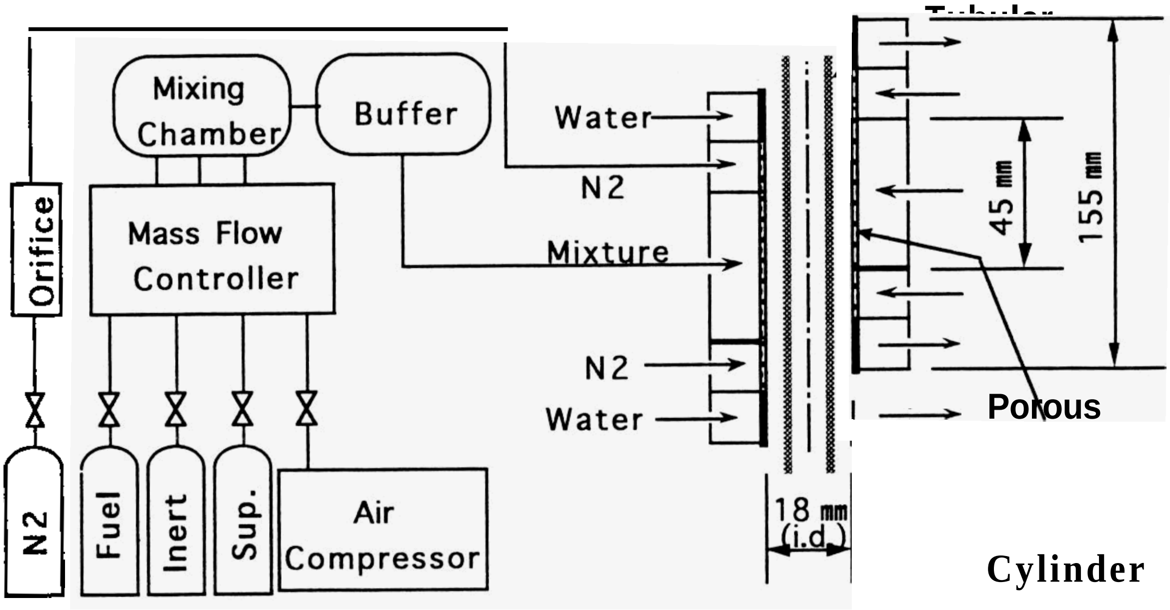

Figure 1 Schematic diagram of the tubular flame burner system

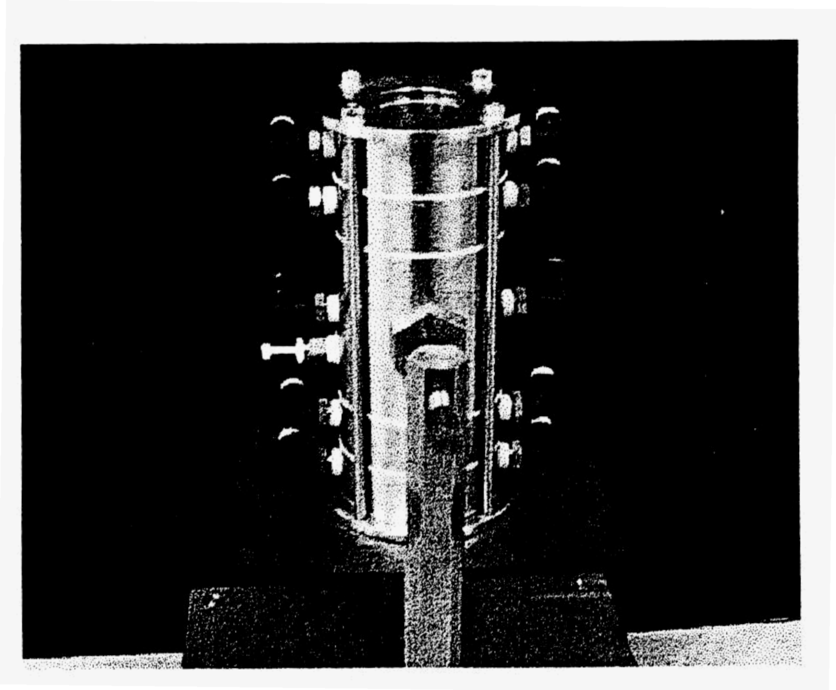

Figure 2 Tubular flame burner

2.2 Measuring conditions

Since a set-up angle of the bumer and injection velocity of the gas mixture affect the extinction limits, such effects were investigated to decide the experimental conditions [11]. Here, the injection velocity stands for average flow velocity at the **porous** cylinder surface of the burner, that was calculated by dividing the mixture flow rate by the area of the surface. To form the symmetrical tubular flame and to facilitate the measurement of the extinction limits, the set-up angle of bumer and the injection velocity of mixture from burner surface are decided **as** vertically and **13.5** cm/s, respectively. Nominal flame stretch rate **(a)**s one of the important factor to determine the extinction limit Under the same stretch rate, the extinction limits measured by various tubular burners with different diameter were agree well each other [12].

Nominal stretch rate (σ) is defined by following equation,

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

Here, V is injection velocity and D **is** burner inner diameter. The stretch rate (σ) is kept at **15.0** s^{-1} in the present study.

The extinction limit concentrations measured by this system include an experimental error of less than **3** percent.

The equivalence ratio of each methane-air-suppressant mixture **is** kept at unity in the present study. Here, oxidation of halogenated suppressant is considered in the definition of the equivalence ratio, that is,

$$xC_{\alpha}H_{\beta} + yC_{\gamma}H_{\delta}X_{\varepsilon} + O_2 \rightarrow \text{Products} \qquad (3)$$

$$\phi = \frac{(4a + \beta)x + (4\gamma + 6 - \varepsilon)y}{4} \qquad (4)$$

where **X** = F, Cl, **Br,** and I

2.3 Adiabatic flame temperature calculation

The adiabatic flame temperatures are calculated on the mixture compositions between methane and **air** containing the mixed agent at the extinction limit The calculations are carried out **taking** dissociation fully into account [7, 13].

3. Results and discussions

3.1 Carbon dioxide-nitrogen and tetrafluoromethane-nitrogen mixed agents

The observed concentrations, Cobs and the calculated concentrations, Ccalc of carbon dioxide-nitrogen and **tetrafluoromethane-nitrogen** mixtures at the extinction limits are shown in Figure **3.** The ordinate represents the concentration by volume of mixed agent, and the abscissa shows nitrogen mole fraction of the mixtures. The observed data **for** the mixed agent containing **carbon** dioxide **is** consistent with calculated concentrations. For the mixed agent containing tetrafluoromethane, calculated concentrations agree well with observed. This is reasonable because tetrafluoromethane is recognized **as** an inert in hydrocarbon-air flames [**14**]. **Figure 4** shows that the ratio of Cobs/Ccalc of mixed agents are almost unity. These results confirm there is no interaction between inert gases.

3.2 Halon 1301-nitrogen mixed agent

Figure 5 shows the concentrations of mixed agent of halon **1301** and nitrogen **at** the extinction limits. Filled symbols and dashed line are the observed concentrations and the calculated concentrations represented by the equation (1), respectively. For all range of

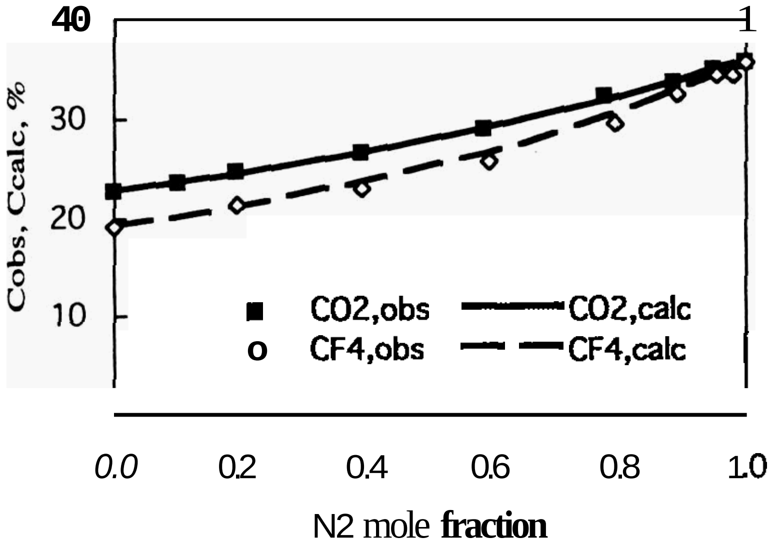

Figure 3 Concentrations of CO_2-N_2 and CF_4-N_2 mixed agents at the extinction limit

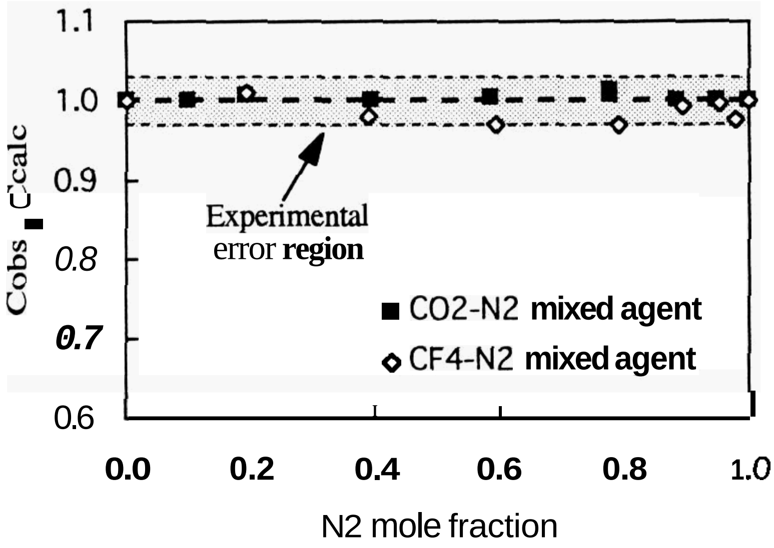

Figure 4 Ratio of Cobs/Ccalc of CO_2-N_2 and CF_4-N_2 mixed agents at the extinction limit

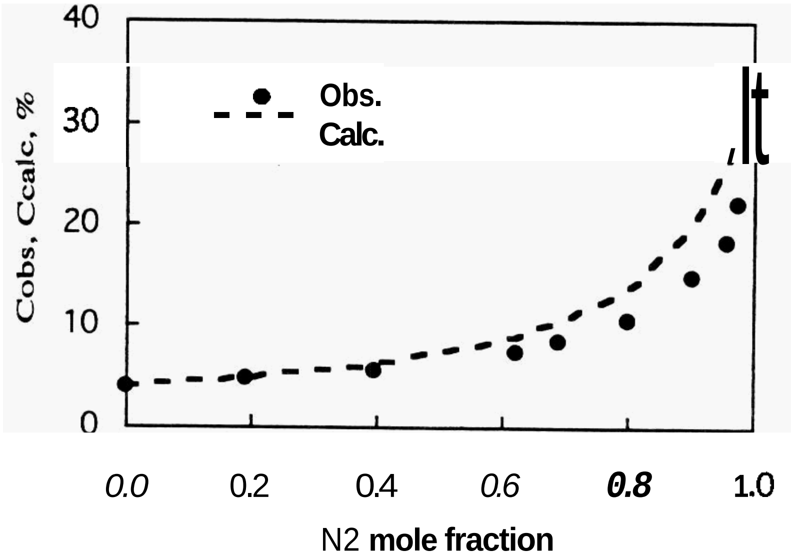

Figure 5 Concentrations of halon 1301-N_2 mixed agent at the extinction limit

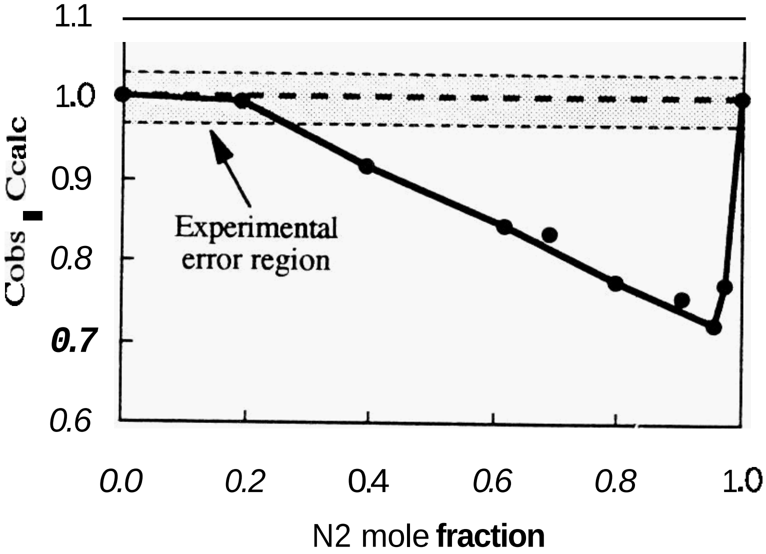

Figure 6 Ratio of Cobs/Ccalc of halon 1301-N_2 mixed agent at the extinction limit

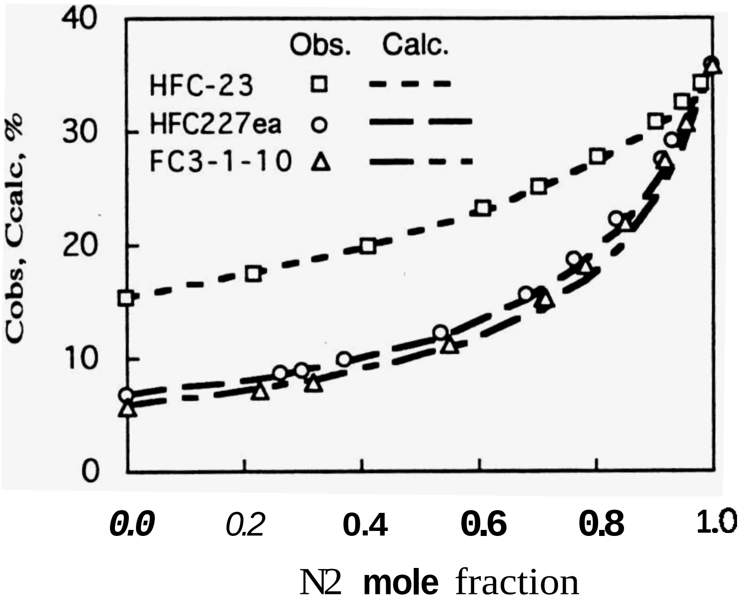

Figure 7 **Concentrations of halon replacements-N_2 mixed agents at the extinction limit**

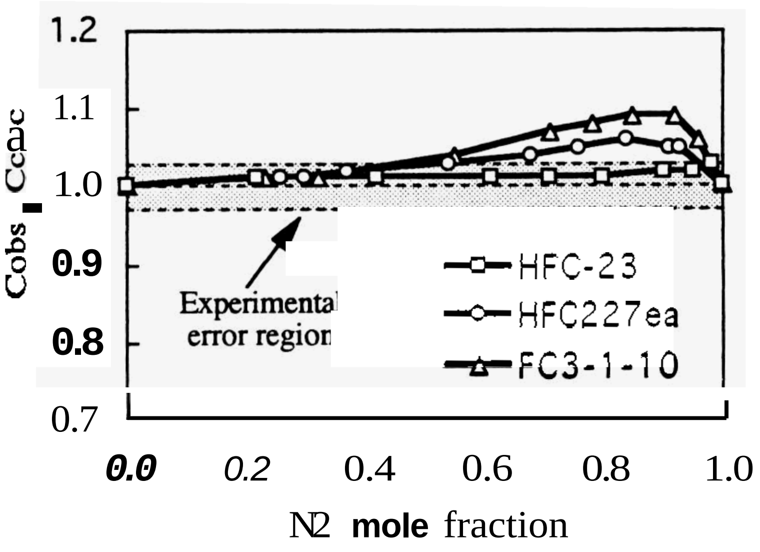

Figure 8 **Ratio of Cobs/Ccalc of halon replacements-N_2 mixed agents at the extinction limit**

nitrogen mole fraction except 0 or 1, Cobs is smaller than Ccalc. This discrepancy between Cobs and Ccalc increase with increasing of nitrogen mole fraction until 0.96.

Figure 6 shows the ratio of observed concentrations to calculated concentration of Won-nitrogen mixed agents at the extinction limit The Cobs/Ccalc is lower than unity, and the lowest ratio is 0.72 at 0.% of nitrogen mole fraction in the mixed agent It suggests that there exists a multiplier effect between halon 1301 and nitrogen, and required amount of mixed agent is reduced as compared with estimate by the equation (1). This results of multiplier effect of halon 1301 and inert gas mixture are similar to the cup burner results in n-heptane diffusion flame [7].

3.3 Halon replacements-nitrogen mixed agents

Figure 7 shows the concentrations of mixed agents of the Won replacements and nitrogen as a function of nitrogen mole fraction. In the case of HFC-23-nitrogen mixture, Cobs are almost consistent with Ccalc. For HFC-227ea and FC-3-1-10, however, Cobs are larger than Ccalc.

Figure 8 shows the ratio of observed concentrations to calculated concentrations of the halon replacements-nitrogen mixed agents. For HFC-23, the ratio is slightly larger than unity, but the difference from unity is smaller than the experimental error. However, it is obvious that the discrepancy between Cobs and Ccalc for HFC-227ea-nitrogen mixed agent is larger than the experimental error in this study. The largest ratio is 1.06 at near 0.8 of nitrogen mole fraction in the mixed agent For FC-3-1-10-nitrogen mixed agent, the discrepancy between Cobs and Ccalc is larger than that for HFC-227ea. The largest ratio is 1.09 at 0.9 of nitrogen fraction. For mixing use of some halon replacements and nitrogen, the results suggest that more amount of mixed agent will be required than estimated. It indicates that there is negative multiplier effect between nitrogen and HFC-227ea or FC-3-1-10, These results are also similar to the cup burner results [8].

3.4 Calculated adiabatic flame temperature at the extinction limit

To interpret the interaction for mixed agents, adiabatic flame temperatures at the extinction limits are calculated. The results are shown in Figure 9 as a function of mole fraction of nitrogen. The ordinate is the calculated adiabatic flame temperature at the extinction limit. For halon 1301, the adiabatic flame temperature decreases from 2130 K with increasing of nitrogen mole fraction, which is corresponding to the ratio of Cobs to Ccalc decreases as shown in Figure 6. Thus, the positive multiplier effect dominates along with decreasing of the flame temperature.

The calculated adiabatic flame temperatures of the mixtures containing halon replacements are near 1950 K at zero mole fraction of nitrogen. Because these flame temperatures are higher than that of methane-air-nitrogen mixture at the extinction limit (1750 K), it suggests that these halogenated agents have some chemical suppression effects. For HFC-23-nitrogen mixed agent, it suggests that fire suppression effect has no relation to the calculated adiabatic flame temperature through the comparison with Figure 8 and Figure 9.

On the other hand, for HFC-227ea and FC-3-1-10, the calculated flame temperatures at the extinction limits decrease, but the ratios of Cobs to Ccalc of the mixed agents are exceed unity with increasing of nitrogen mole fraction from zero. This relation means the negative multiplier effect increases in lower temperature. It suggests that the decreased temperature weaken fire suppression effect of HFC-227ea and FC-3-1-10.

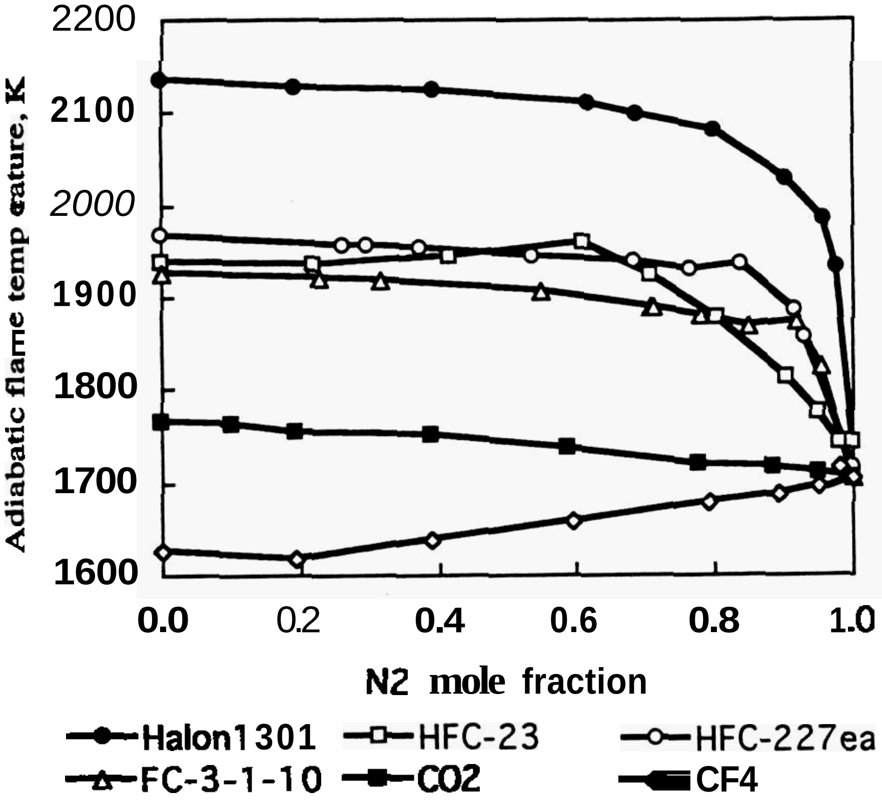

Figure 9 Calculated adiabatic flame temperatures at the extinction limit

4. Conclusions

To investigate the effect of the interaction between halogenated fire suppressants and nitrogen on fire suppression efficiency, concentrations of the mixtures of the suppressants with nitrogen at the extinction limit were measured as a function of mole fraction of nitrogen in the mixtures, and estimated also by using an equation of additive property on flame extinction effect.

For tetrafluommethane-nitrogen mixed agent, there is no multiplier effect similar to carbon dioxide-nitrogen mixed agent The result means that tetrafluoromethane affects as an inert gas in the flame.

Halon 1301-nitrogen mixed agent has the positive multiplier effect Through the interpretation of the calculated adiabatic flame temperature, the multiplier effect of halon 1301 mixture dominates with increasing of nitrogen mole fraction. It is suggested that the inert gases caused decrease in flame temperature, and then the chemical flame inhibition effect of halon 1301 is enhanced by the flame temperature decrease.

There is no interaction between nitrogen and HFC-23. It indicates that the chemical suppression effect of HFC-23 is not related to the change of the flame temperature in this study.

For HFC-227ea-nitrogen or FC-3-1-10-nitrogen mixed agents, the negative multiplier effects are observed, and the effects increase with increasing of nitrogen mole fraction. It suggests that decreased temperature weaken fire suppression effect of HFC-227ea and FC-3-1-10.

These results of positive or negative multiplier effect between agents and nitrogen show the same tendency of the cup burner experiment. Therefore, the multiplier effect of mixed agent exists independently of the difference in chemical/transport environment between premixed and diffusion flames.

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