

EXPERIMENTAL STUDY ON PEAK CONCENTRATIONS OF HALON ALTERNATIVES AT ELEVATED TEMPERATURE

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ABSTRACT

Production of so-called Halon fire extinguishing agents has been prohibited since January 1994 because of their ozone depletion potential. To replace them, several hydrofluorocarbons and fluorocarbons have been developed and utilized. A number of studies on flame extinguishing concentrations and flammability peak concentrations of them have been done. Although there was enough information for practical purpose, more knowledge on fire extinguishing characteristics of them should be attained for efficient use of them. In this study, peak concentrations of methane/air mixtures with gaseous halogenated hydrocarbons were measured at elevated temperature, because the former studies were done at room temperature and temperature of a fire room can be higher than usual. Measurement was done at 200°C, because measuring system could not endure higher temperature. This study revealed that peak concentrations of halogenated hydrocarbons differed little at elevated temperature. The halogenated hydrocarbons have almost the same fire extinguishing ability as Halon 1301.

INTRODUCTION

Fully halogenated hydrocarbons (Halon fire extinguishers) have been used as fire extinguisher widely in computer rooms, communication rooms, parking and so on, because of their high performance as fire extinguisher and their cleanness after fire fighting. However, as Halons cause ozone depletion problem like chlorofluorocarbons (CFCs), production of three types of Halon (Halon 1211: CF_2ClBr , Halon 1301: CF_3Br , and Halon 2402: $\text{C}_2\text{F}_4\text{Br}_2$) was prohibited since January 1994 [1].

New fire extinguishing agents replacing Halons are now under development [2]. Water mist, powder aerosol and inert gases are representative for such new agents, but they have some demerits compared with Halons. Therefore, Halogenated hydrocarbons, which do not contain any chlorine and bromine but contain only fluorine, have also been developed as alternative Halons. They have close characteristics with Halons in nature. HFC-23 (Trifluoromethane, CHF_3), HFC-227ea (1,1,1,2,3,3,3-Heptafluoropropane, $\text{CF}_3\text{CHF}_2\text{CF}_3$), and FC-3-1-10 (Perfluorobutane, C_4F_{10}) are now utilized as alternative Halon extinguishers [3]. They were proved to work as fire extinguishing agents through practical tests, but their fire extinguishing mechanisms have not been understood well.

Then, in this study, fire-extinguishing abilities of the alternative Halons are evaluated quantitatively relative to Halon 1301 at room and elevated temperature, and fire extinguishing mechanisms of the alternative Halons are discussed.

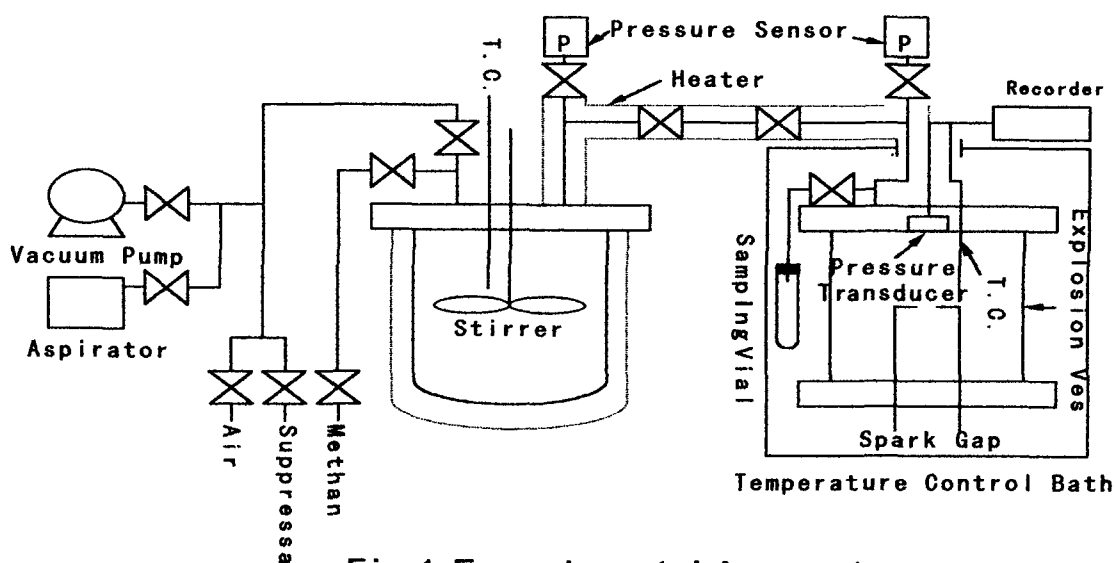


Fig.1 Experimental Apparatus

EXPERIMENTS

Experimental Procedure

Experimental apparatus. Figure 1 illustrates overall view of an experimental apparatus. It consists of an explosion vessel, a dilution vessel, a vacuum pump, a temperature control equipment, and piping.

The explosion vessel was made from a stainless steel cylinder. Its inner diameter was 100mm, and height was 100mm. A couple of tungsten spark plugs were set at ca. 50mm above the bottom of the vessel. Pressure history after ignition was measured by a pressure transducer (range: 0 ~ 10kgf/cm², KYOWA PHS-10KA), and recorded by a digital storage oscilloscope (HITACHI VC-6175).

The dilution vessel was made from a stainless steel cylinder with a semispherical bottom. Its inner diameter was 100mm, and height was 150mm. It had a mixing impeller of 1000-rpm mixing ability at inner top. Composition of tested gas mixtures was determined by partial pressure of each component measured by a pressure sensor.

The explosion vessel was placed in an airflow type-drying oven (ADVANTEC FV-430), the dilution vessel was placed in a mantle heater, and piping between them was covered with flexible heaters. This temperature-controlled area could be heated uniformly up to ca. 200 °C. Temperatures in the explosion and the dilution vessels were measured by 1.6 mm ϕ sheathed K-type thermocouples placed at the center of each vessel. Cooling fans cooled pressure sensors equipped at the vessels.

Experimental procedure. The explosion vessel, the dilution vessel, and piping were vacuumed at first, then methane, suppressant and air were introduced into the dilution vessel as each gas had predetermined partial pressure. Composition of the methane/suppressant/air mixture was determined from partial pressures of each gas. This mixture was stirred in 5 min by a stirrer. Then it was transferred to the explosion vessel as the mixture had atmospheric pressure. The mixture was ignited in the explosion vessel with ignition energy of 300J (15kV, 20mA, 1s) supplied by a neon transformer-type power supply. Pressure history after ignition was recorded by a digital storage oscilloscope. Occurrence of explosion was judged from the pressure history: i.e. the maximum pressure recorded exceeded 0.01 MPa or not.

Above mentioned procedure was conducted at 25 °C for room temperature condition,

and at 200 °C for high temperature condition.

Sample gas. Methane (CH₄) was used as flammable gas because of its wide flammable range that resulted in drastic reduction of the flammable range by fire suppressant.

As sample of fire suppressant, trifluoromethane (HFC-23, CHF₃), heptafluoropropane (HFC-227ea, CF₃CHF₂CF₃), perfluorobutane (FC-3-1-10, C₄F₁₀), perfluoromethane (FC-14, CF₄), perfluoroethane (FC-116, C₂F₆), perfluoropropane (FC-218, C₃F₈), and bromotrifluoromethane (Halon 1301, CF₃Br) were used. Inert gases, argon (Ar), nitrogen (N₂), and carbon dioxide (CO₂) were also used as suppressant for comparative purpose. Air was used as oxidizing gas.

Experimental Results

Flammability areas.

1) At room temperature

Figure 2 shows flammability areas for CF₃Br, CF₄, or CHF₃ mixed with methane and air.

This figure shows the flammability areas for CF₃Br and CF₄ become narrower, i.e. rich limit become smaller and lean limit become larger, as concentrations of the fire suppressant increase. On the other hand, lean limit for CHF₃ becomes smaller as the concentration of CHF₃ increases until the lean limit reaches the minimum value. Then the lean limit becomes larger as the concentration of CHF₃ increases. In the tested fire suppressants, C₃F₈, C₄F₁₀, CH₂F₂ and CF₃CHF₂CF₃ show the same trend with CHF₃. Other fire suppressants, i.e. Ar, N₂, CO₂, CF₃Br, and C₂F₆ show the same trend with CF₃Br and CF₄.

The maximum pressure observed along the line, on which methane concentration was fixed at 5.5 %, will be shown below.

2) At 200°C

All flammability area measured had similar but wider shape as measured at room temperature. Flammability area for CF₃Br was affected most largely in tested fire suppressants (Fig. 3). Variations of flammability limits of methane in air, which are shown on the ordinate, are not so big as shown in Fig. 3. On the other hand, peak concentration of CF₃Br is rather large at 200°C. It becomes more than 50% larger than that at room temperature.

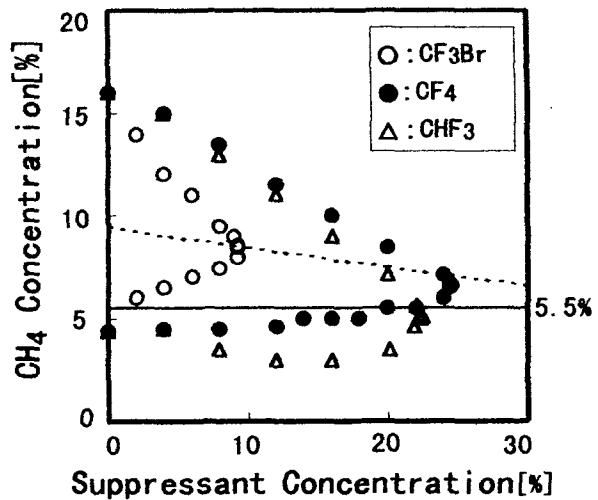


Fig. 2 Flammability Area of Methane/Suppressant/Air Mixture

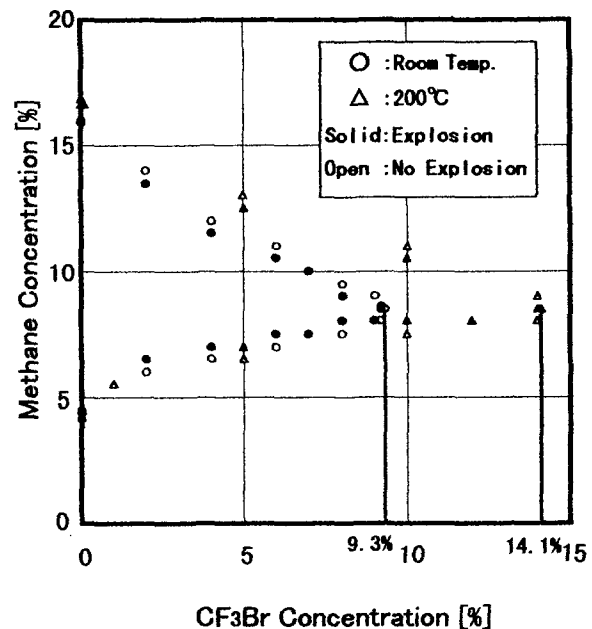


Fig. 3 Flammability Areas of Methane/CF₃Br/Air Mixture at Room and Elevated Temperatures

Maximum explosion pressure.

1) At room temperature

Figure 4 shows variation of the maximum explosion pressure (ΔP_{\max}) with concentration of fire suppressant. As shown in Fig. 2, CHF_3 shows different trend with CF_3Br and CF_4 . Two groups of fire suppressants are also identified from profile of the maximum explosion pressure as identified from the flammability area. In the first group (CHF_3 as representative), the maximum explosion pressure increased once with increase of fire suppressant concentration, reached the peak value, and then decreased with increase of fire suppressant concentration. In the second group (CF_3Br and CF_4 as representatives), the maximum explosion pressure decreased monotonously with increase of fire suppressant concentration.

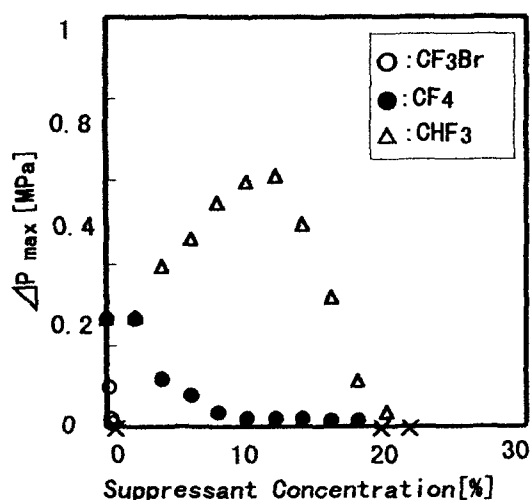


Fig. 4 Variation of ΔP_{\max} with Suppressant Concentration Methane is fixed at 5.5 %.

2) At 200°C

The same groups were identified as those identified at room temperature. But, the peaks became broader at 200°C. Namely, the maximum explosion pressure became smaller as the increase of fire suppressant concentration, but it approached explosion limit slower than that at room temperature.

DISCUSSION

The peak concentrations of fire suppressants against Methane/Air mixture at room temperature and 200°C are summarized in Table 1. Heat capacity of each fire suppressant is also shown in the table. The peak concentration means the maximum

Table 1 Peak Concentrations for fire suppressants.

Suppressant	Heat Capacity ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	Peak Concentration		200°C/Room Temp.
		Room Temp.	200°C	
CF_3Br	69.5	9.3	14.1	1.52
CF_4	61.09	24.5	26.0	1.06
C_2F_6	105.85	13.2	14.6	1.11
C_3F_8	144.68	11.1	14.2	1.28
C_4F_{10}	183.51	11.0	14.1	1.28
CF_3CHF_2	136.24	13.5	15.2	1.13
CHF_3	51.04	22.5	25.5	1.13
Ar	20.786	50.5	53.3	1.06
N_2	29.124	41.0	46.3	1.13
CO_2	36.99	27.5	32.1	1.17

concentration of fire suppressant in the flammability area as shown in Fig. 3. Over the peak concentration, the mixture cannot be flammable for any methane and air composition. CF_3Br has the smallest peak concentration at room and elevated temperatures. It is considered to come from powerful fire suppression effect of bromine, i.e. chemical effect. Fluorine does not have fire suppression effect by itself. On the other hand, if fire suppressant had only physical effect, i.e. heat-sink effect, peak concentration of the fire suppressant depends on its heat capacity. In the case, peak concentration should decrease as heat capacity of fire suppressant increases. This table shows there should be chemical effect among the halogenated fire suppressants.

Effect of Carbon Atom Number

Comparing peak concentrations of perfluorocarbons (CF_4 , C_2F_6 , C_3F_8 , C_4F_{10}) at room temperature, the peak concentration becomes smaller as heat capacity becomes larger (Fig. 5). However, three perfluorocarbons except CF_4 have comparable peak concentrations (11-13%). It means that their fire suppression mechanism is affected not only by heat-sink effect but also by other, maybe chemical, effect. Radical scavenging of CF_3 radical is considered to be the main chemical fire suppression effect for fluorohydrocarbons [4]. These three perfluorocarbons have 2 CF_3 groups each in one molecule, so they have almost the same fire suppression ability except difference in heat sink effect. As seen in Fig. 5, in the case of C_3F_8 and C_4F_{10} , their flammability areas are widened toward fuel lean area and they had peaks in profile of the maximum explosion pressure as their concentrations increase. These show they are a little flammable. They release carbon atoms when they decompose, so released carbon atoms show flammability.

Effect of Hydrogen Atom Number

Comparing flammability areas of fluoromethanes CF_4 , CHF_3 and CH_2F_2 (Fig. 6), CHF_3 is easier to decompose because it has a hydrogen atom in it. It emits CF_3 radical easier than CF_4 . Consequently, it has smaller peak concentration, nevertheless it has smaller heat capacity. CHF_3 is a little flammable because it has hydrogen atom in it. It is known that CH_2F_2 , which has two hydrogen atoms, is

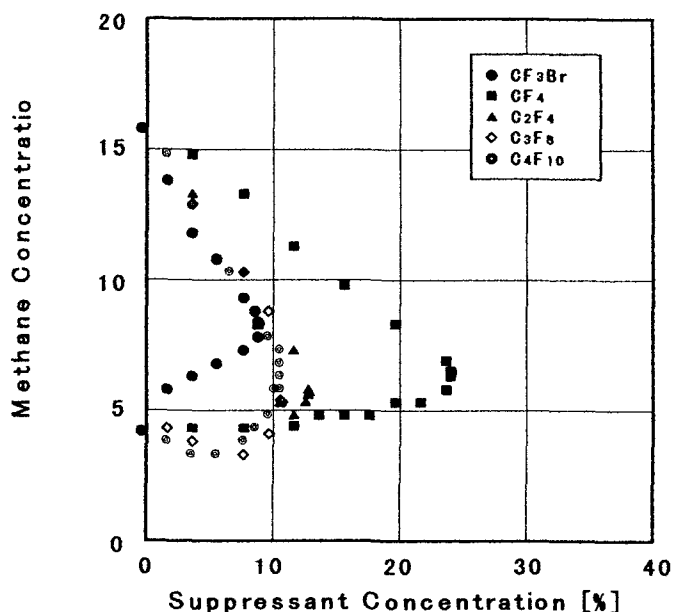


Fig 5. Effect of Carbon Number

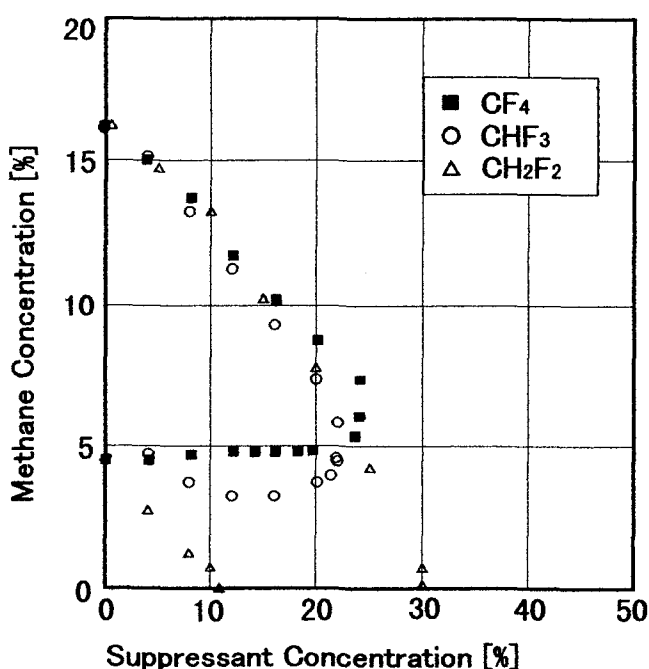


Fig 6. Effect of Hydrogen Number

flammable.

Effect of Environmental Temperature

For all fire suppressants, peak concentration became larger at 200°C than at room temperature. Especially, peak concentration of CF₃Br was affected most strongly, it became 1.52 fold larger at 200°C than at room temperature. Consequently, CF₃Br, C₂F₆, C₃F₈, C₄F₁₀ and CF₃CHF₃ had almost identical peak concentrations, ca. 14%, at 200°C. It means that fire suppression ability of bromine atom is more affected by environmental temperature than CF₃ radical. Bromine atom seems to have quantitatively same fire suppression effect as CF₃ radical at 200°C. At higher temperature, CF₃Br may have larger peak concentration than C₂F₆, C₃F₈, C₄F₁₀ or CF₃CHF₃. In real fire situation, fire suppressant is used at higher temperature, so C₂F₆, C₃F₈, C₄F₁₀, and CHF₃ may have more powerful fire suppression ability than CF₃Br.

Moreover, CF₄ and CHF₃, which has one CF₃ group, has almost same peak concentration, 26%, at 200°C. Ratio of peak concentration for them over remaining methane and air concentration is almost twice the ratio for the fire suppressants mentioned above, which have two CF₃ groups or one bromine atom and one CF₃ group. It means fire suppression ability of fluorohydrocarbon depends strongly on number of CF₃ group at 200°C.

CONCLUSION

The following results were derived from this study.

- 1) Fire suppression ability of CF₃Br is affected largely by environmental temperature compared with fluorohydrocarbons tested in this study.
- 2) At 200°C, the peak concentrations of CF₃Br, C₂F₆, C₃F₈ and C₄F₁₀ were all about 14%.
- 3) The peak concentration of fluorohydrocarbon depends on number of CF₃ groups in molecule.
- 4) Some fluorohydrocarbon, which have a hydrogen atom or have more than 2 carbon atoms, shows a little flammability.

These findings suggests that fluorohydrocarbon has stronger fire suppression ability as it has larger number of CF₃ groups and no hydrogen and no excess carbon atom in it.

REFERENCE

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- [2] Gann, R.G., Ed., Fire Suppression System Performance of Alternative Agents in Aircraft Engine and Dry Bay Laboratory Simulations, NIST SP 890, November, 1995
- [3] Saito, N., Saso, Y., Liao, C., Ogawa, Y., and Inoue, Y., ACS Symposium Series No.611, Halon Replacements: Technology and Science, 243-257, 1995.
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APPENDIX

COMBUSTION PRODUCTS OF CH₄/HALOGENATED FIRE SUPPRESSANT /AIR MIXTURE

Combustion products of the gas mixtures were also studied for not only academic but also practical purpose. To use the fire suppressants as an alternative Halon extinguisher, their combustion products should not harm human [A-1,A-2].

Burned gas was vacuumed from the explosion vessel, and bubbled in water. Fluorine compounds or bromine compounds, if existed, were soluble in water, so they were measured by an ion meter as F⁻ ion or Br⁻ ion. This method cannot identify quantity of each fluorine or bromine compound, so all fluorine compounds were measured as equivalent HF concentration, and bromine compounds as HBr concentration.

Relation between Fire Suppressant Concentration and Generated HF

Equivalent HF concentration measured for constant CH₄ concentration (8.0 %), is shown in Fig. A-1. Equivalent HF concentration increased as suppressant concentration increased until it reached a peak value. Then it decreased as suppressant concentration increased. It means that almost all fire suppressant added was decomposed while its concentration was smaller than the peak value. Over the peak value, portion of the suppressant decomposed became smaller.

CF₃Br emitted smaller equivalent HF concentration than others did. It was ca. 2.0 % in maximum. This compound also emitted bromine compounds. But equivalent bromine hydride was about 0.1 %, and almost constant independent of CF₃Br concentration.

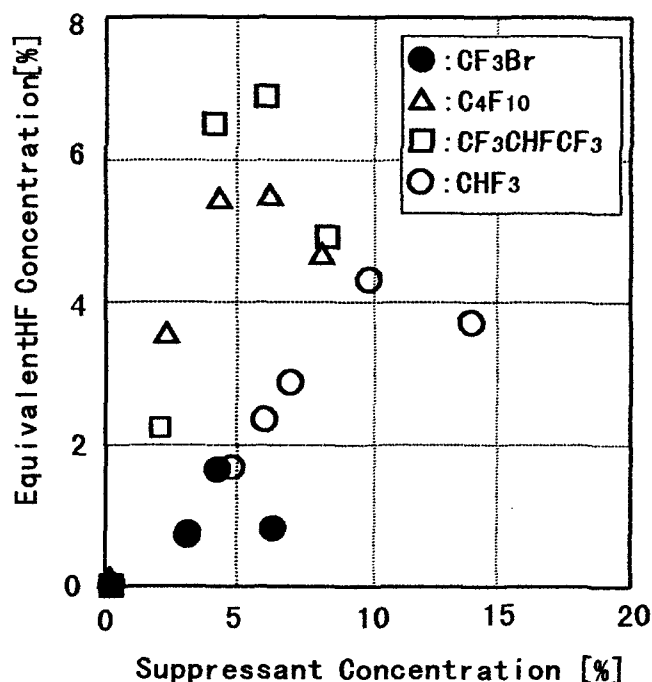


Fig. A-1 Generation of HF after Combustion
CH₄ concentration is fixed at 8.0%.

Predicted Combustion Products by Chemical Equilibrium

Figure A-2 shows predicted fluorine compounds at constant CH₄ concentration (8.0%), for methane/CF₃CHFCF₃/air mixture by chemical equilibrium at adiabatic flame temperature. Adiabatic flame temperature is also shown in this figure.

Total amount of fluorine compounds increases as concentration of suppressant increases. While H atom content is enough for HF formation, all F atoms included in suppressant are converted to HF. As concentration of suppressant increases, number of H atoms becomes insufficient to form HF. Then COF₂ appears. In the case of

suppressants, which have H atom in its molecule, i.e. CHF_3 and $\text{CF}_3\text{CHFCF}_3$, CF_4 is not formed.

Adiabatic flame temperature once increased as concentration of fire suppressant increases, then decreases after the maximum value attained. This is considered to come from partial flammability of suppressant as mentioned before.

Comparing these prediction with equivalent HF concentration obtained experimentally, large discrepancy is observed in quantity. In calculation, gaseous mixture in the explosion vessel is assumed to react entirely. But the maximum pressure recorded in experiment showed larger part of the mixture did not react in reality, especially near the explosion limit. In addition, non-soluble component such as CF_4 was not counted in equivalent HF concentration.

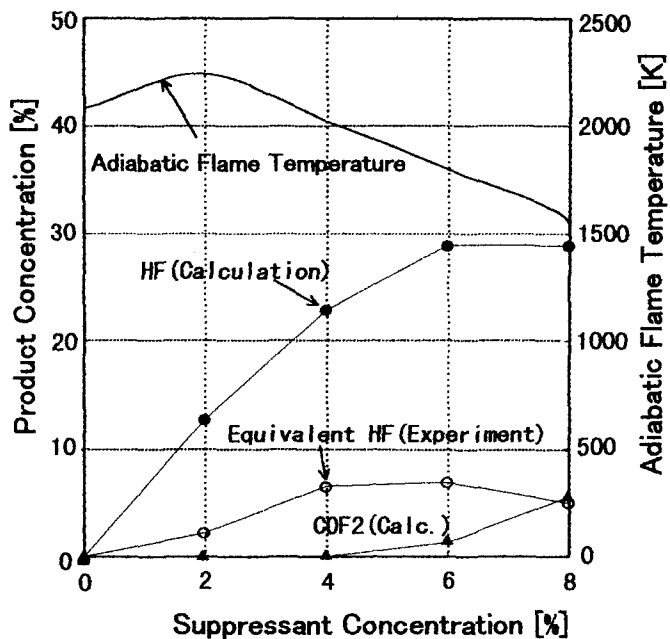


Fig. A-2 Produced Fluorine Compounds

Reference

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