

Experimental study on flammability limits of perfluorocarbons in a fluorine atmosphere

Hideo OHTANI

Corresponding author: Hideo OHTANI

Academic degree: Dr. of Engineering

Position: Associate Professor

Professional or Academic affiliation: Yokohama National University

Mailing address: 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN

Phone: +81-339-3982

Fax: +81-339-4011

E-mail address: hohtani@ynu.ac.jp

Paper No.031202; JLPPI

ABSTRACT

There sometimes occur explosion incidents in making fluororesin. This explosion is considered to occur because gaseous perfluorocarbons, which are by-products of fluororesin, react with fluorine.

In this study, flammability of perfluorocarbon/fluorine/nitrogen mixtures was examined experimentally. Their flammability areas were revealed quantitatively as triangular flammability diagrams, and the fact that perfluorocarbon reacts with fluorine was ascertained.

1. Introduction

Recently, many kinds of gas have been used in chemical industries. There are several gases, which have not been used widely, so their flammability characteristics are not known well. Lee, Ohtani, Uehara, & Aramaki (1992) and Ohtani, Lee, & Uehara (1994) studied a few gases and reported their flammability characteristics already. However, there are many gases remaining to be examined.

In making fluororesin, there sometimes occurs explosion incident. At an incident, there are gaseous perfluorocarbons and fluorine. Gaseous perfluorocarbons are by-products of fluororesin, and fluorine is an indispensable reactant to make fluororesin. In the series of C_mF_{2m+2} , tetrafluoromethane (CF_4) is the most stable. It suggests other C_mF_{2m+2} can react with fluorine to produce CF_4 . Coexistences of these gases can not be avoided. These gases must exist simultaneously in producing fluororesin. Quantitative evaluation of their flammability diagram should be done for reducing explosion hazard.

Then, in this study, flammability diagrams of C_mF_{2m+2} with fluorine are evaluated quantitatively.

2. Experiments

2.1. Experimental Procedure

(1) Experimental apparatus.

Figure 1 illustrates overall view of an experimental apparatus.

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, and recorded by a digital storage oscilloscope.

(2) Experimental procedure.

The explosion vessel, the mixing vessel, and piping were vacuumed at first, and then each component was introduced into the mixing vessel as each gas had predetermined partial pressure. Composition of the 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 exceeded 0.01 MPa or not.

(3) Sample gases.

In this study, mixtures of C_mF_{2m+2} , fluorine (F_2) and nitrogen were tested. As C_mF_{2m+2} , perfluoroethane (C_2F_6), perfluorobutane (C_4F_{10}), perfluorohexane (C_6F_{14}), and perfluorooctane (C_8F_{18}) were used.

3. Flammability Areas

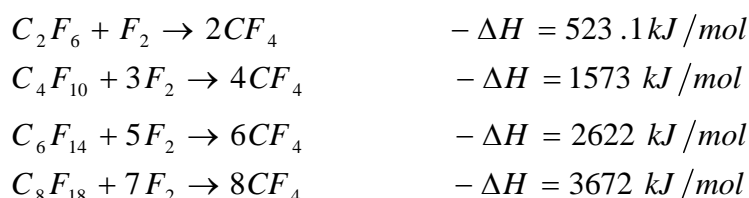
Figures 2-5 show triangular flammability diagrams of $C_2F_6/F_2/N_2$, $C_4F_{10}/F_2/N_2$, $C_6F_{14}/F_2/N_2$, $C_8F_{18}/F_2/N_2$ mixtures. Flammability areas for these mixtures have clear triangular shape. Peak concentration can be determined clearly.

Peak concentration of the C_4F_{10} mixture is much different from that of the C_2F_6 mixture. Flammability area of the C_4F_{10} mixture is wider than that of the C_2F_6 mixture. Compared to the difference between C_2F_6 and C_4F_{10} , flammability diagrams of C_6F_{14} and C_8F_{18} mixtures were close to that of the C_4F_{10} mixture. Peak concentrations and observed lowest concentrations of each component along the flammability area for the $C_mF_{2m+2}/F_2/N_2$ mixtures are summarized in Table 1.

The flammability diagrams shown in Figs. 2-5 are for the mixtures much diluted by nitrogen because fluorine was supplied at low pressure. However, each flammability diagram shows clear triangular shape. So flammability limits at higher perfluorocarbon and/or fluorine concentration regions can be easily estimated by extrapolate the flammability diagrams.

4. Reaction Equations of Perfluorocarbons with Fluorine

Reaction equations of the mixtures were estimated as follows by using the CHETAH program (ASTM(1994)).



As mentioned above, these large heats of reaction are related with differences of heats of formation between reactants and products. Related bond energies are C-F(484kJ/mol), C-

C(344kJ/mol) and F-F(155kJ/mol). Namely, C is more stable when it combines with F than other C, and F is more stable when it combines with C than F. Therefore, the above reaction equations are derived.

Adiabatic flame temperatures at boundaries of the flammability area were calculated by considering chemical and thermal equilibrium. The adiabatic flame temperatures at fluorine-rich side boundaries for C₄F₁₀, C₆F₁₄, and C₈F₁₈ mixtures are all 1700 K. The adiabatic temperature for C₂F₆ mixture is 2100 K. As suggested from difference in the flammability diagrams, there is again difference in the adiabatic flame temperatures. It also comes from difference in C-C bond energy between C₂F₆ and others. The adiabatic flame temperature at fluorine-lean side boundary is about 850 K, but it fluctuates much along the boundary.

5. Conclusion

Flammability areas of perfluorocarbon in fluorine were examined experimentally in this study. Their flammability diagrams and peak concentrations were obtained quantitatively. They will give some measure for avoiding an explosion incident in producing fluororesin.

References

- Lee, S.G., Ohtani, H., Uehara, Y., & Aramaki, M. (1992). Experimental Study on Flammability Limit of Chlorine Trifluoride/Dichlorosilane/Nitrogen Mixture. *Journal of Loss Prevention in the Process Industries*, 5, 192-195.
- Ohtani, H., Lee, S.G., & Uehara, Y. (1994). Combustion Characteristics of Several Flammable Gases with Chlorine Trifluoride. In *Proceedings of the Fourth International Symposium on Fire Safety Science*, Ottawa, Canada, 493-502.
- ASTM (1994). CHETAH ver.7.0 The ASTM Computer Program for Chemical

Thermodynamic and Energy Release Evaluation (NIST Special Database 16), 3rd. Ed. In
ASTM Data Series DS 51B, ASTM, Philadelphia.

List of Tables and Figures

TABLE 1 Peak concentrations of N_2 and lowest flammable concentrations of C_mF_{2m+2} and F_2 for $C_mF_{2m+2}/F_2/N_2$ mixture.

FIGURE 1 Experimental Apparatus for examining flammability of $C_mF_{2m+2}/F_2/N_2$ mixture.

FIGURE 2 Flammability areas of $C_2F_6/F_2/N_2$ mixture.

FIGURE 3 Flammability areas of $C_4F_{10}/F_2/N_2$ mixture.

FIGURE 4 Flammability areas of $C_6F_{14}/F_2/N_2$ mixture.

FIGURE 5 Flammability areas of $C_8F_{18}/F_2/N_2$ mixture.

TABLE 1 Peak concentrations of N₂ and lowest flammable concentrations of C_mF_{2m+2} and F₂ for C_mF_{2m+2}/F₂/N₂ mixture.

	C ₂ F ₆	C ₄ F ₁₀	C ₆ F ₁₄	C ₈ F ₁₈
Peak concentration of N ₂ (vol%)	68	87.0	90.3	91.5
Lowest C _m F _{2m+2} concentration (vol%)	17	3.5	1.8	1.5
Lowest F ₂ concentration (vol%)	11	8.5	6.8	6.5

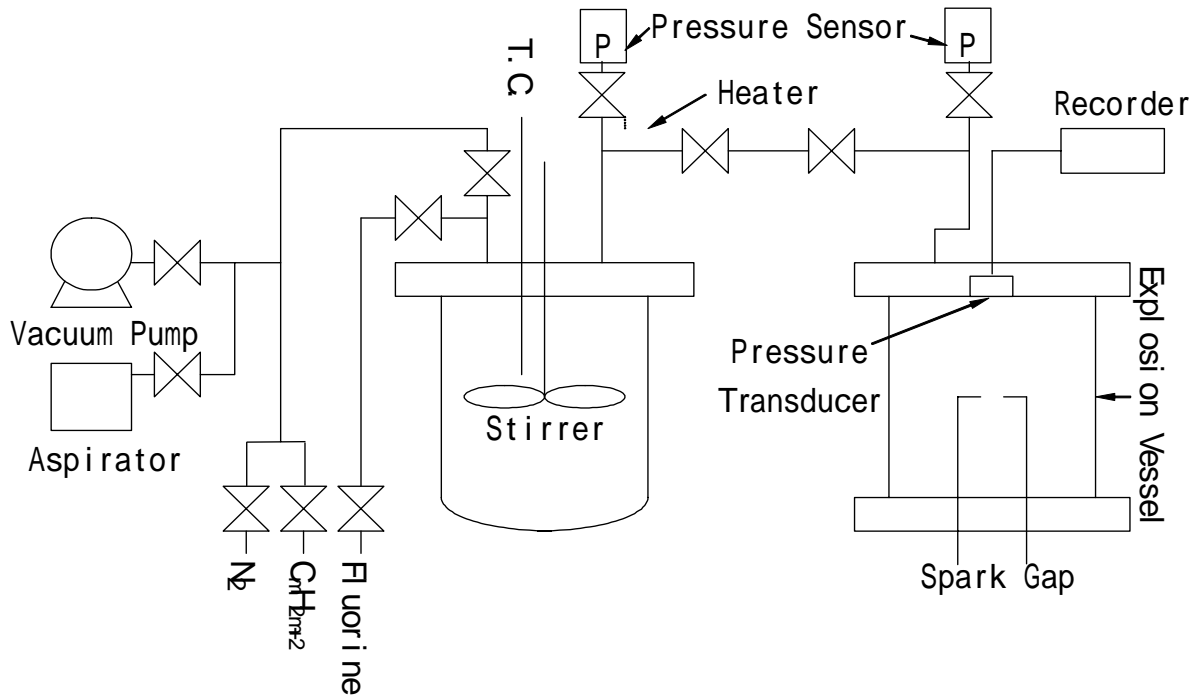


FIGURE 1 Experimental Apparatus for examining flammability of $C_mF_{2m+2}/F_2/N_2$ mixture.

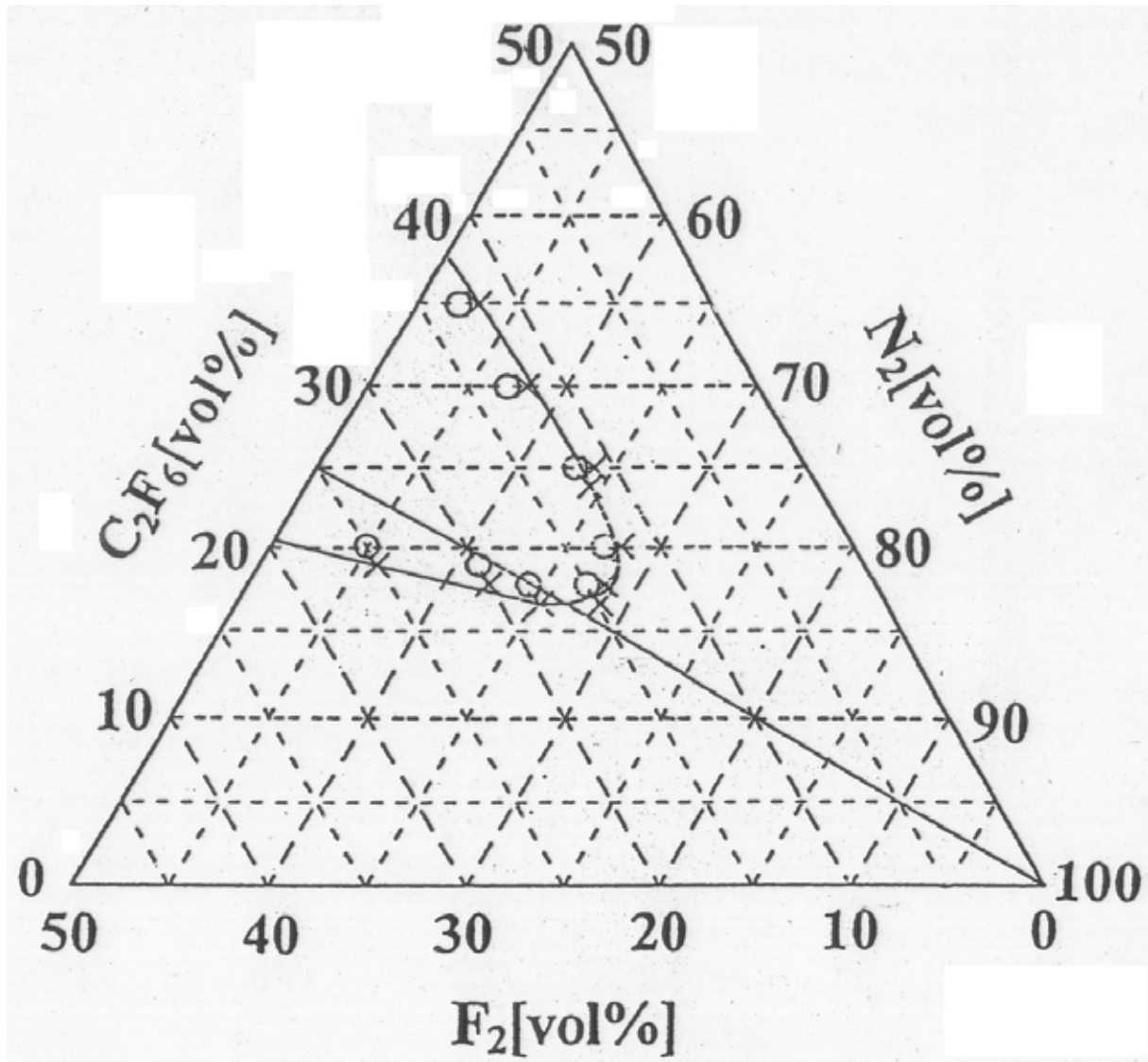


FIGURE 2 Flammability areas of $C_2F_6/F_2/N_2$ mixture.

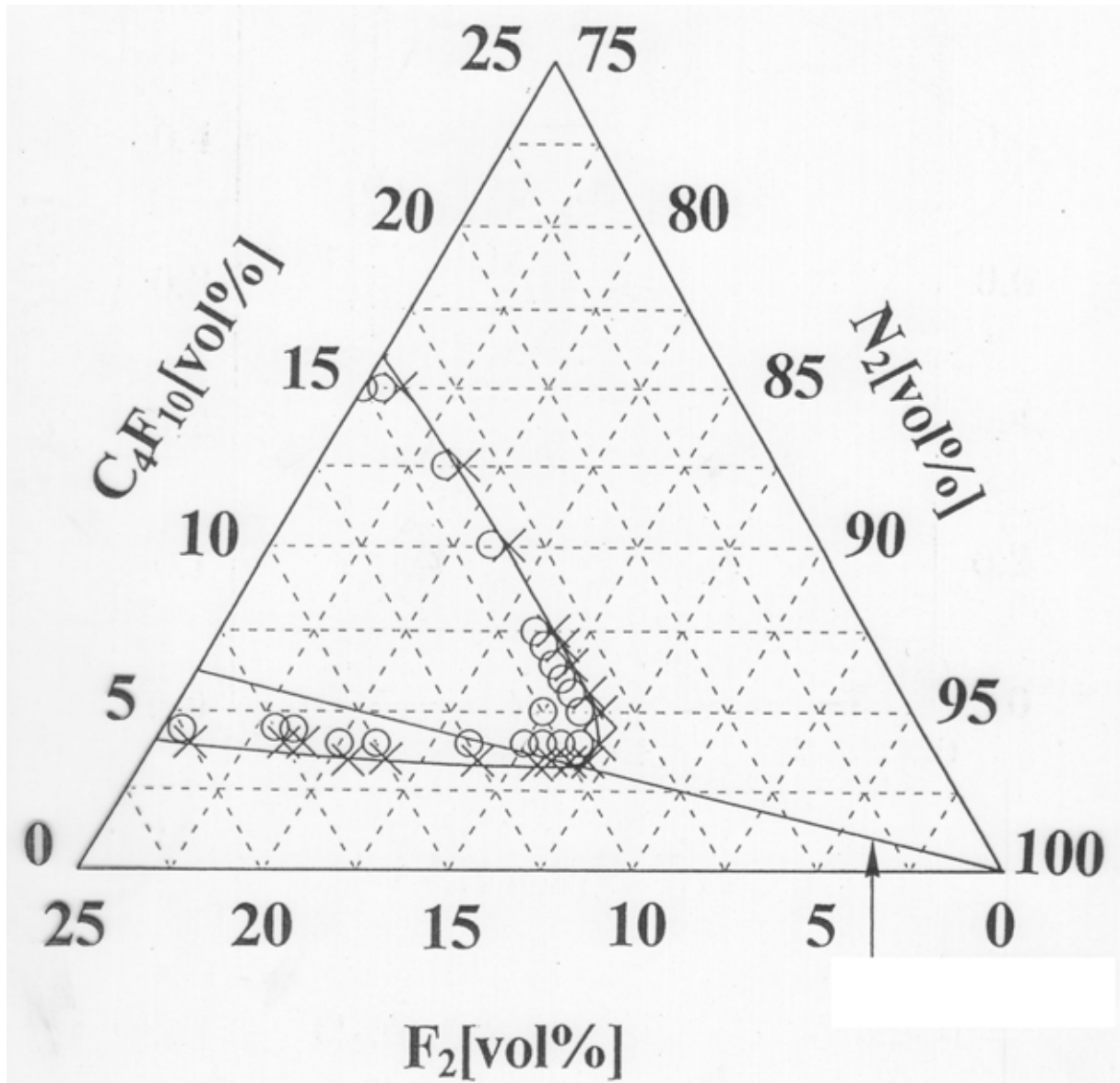


FIGURE 3 Flammability areas of $C_4F_{10}/F_2/N_2$ mixture.

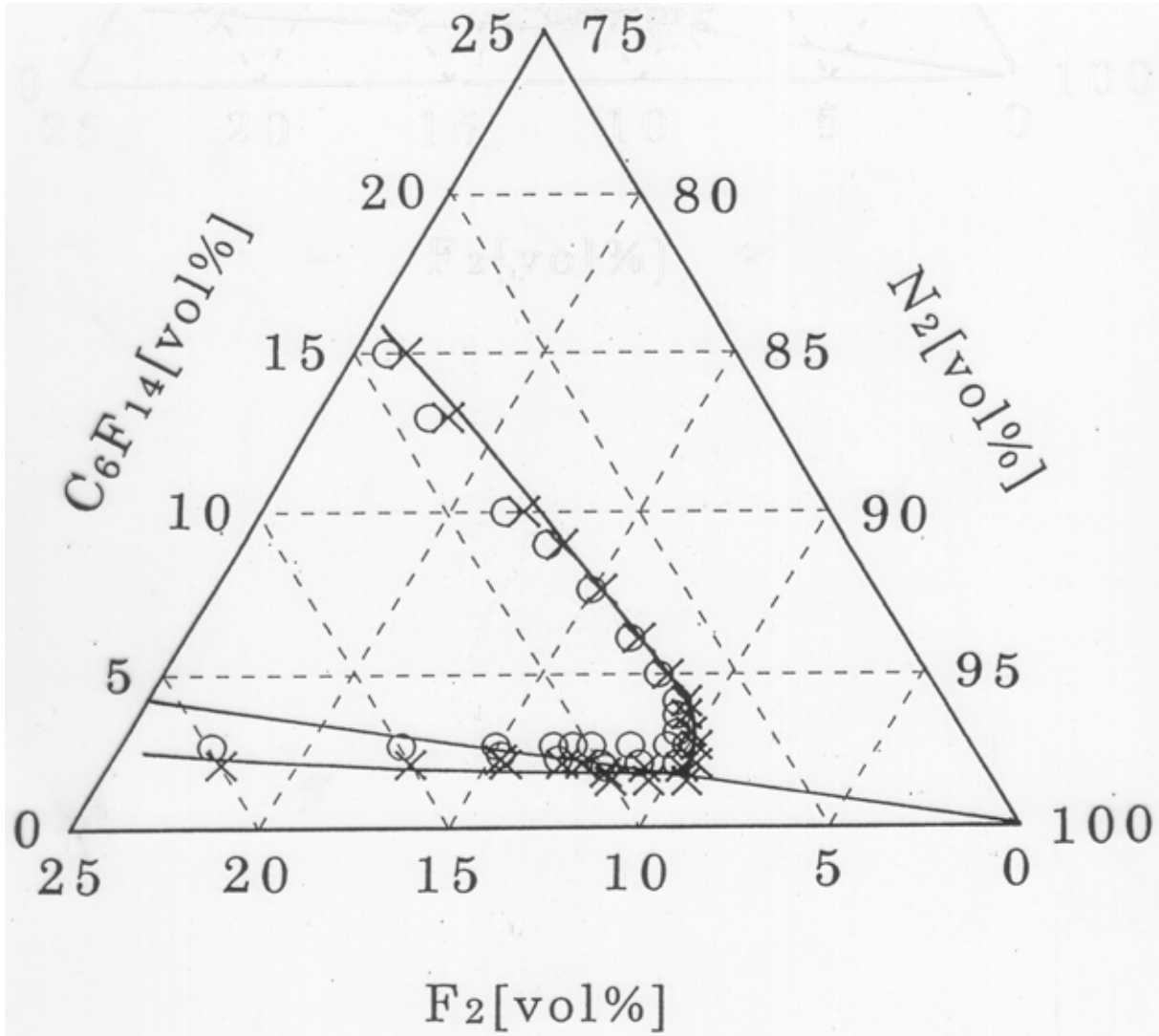


FIGURE 4 Flammability areas of C₆F₁₄/ F₂/N₂ mixture.

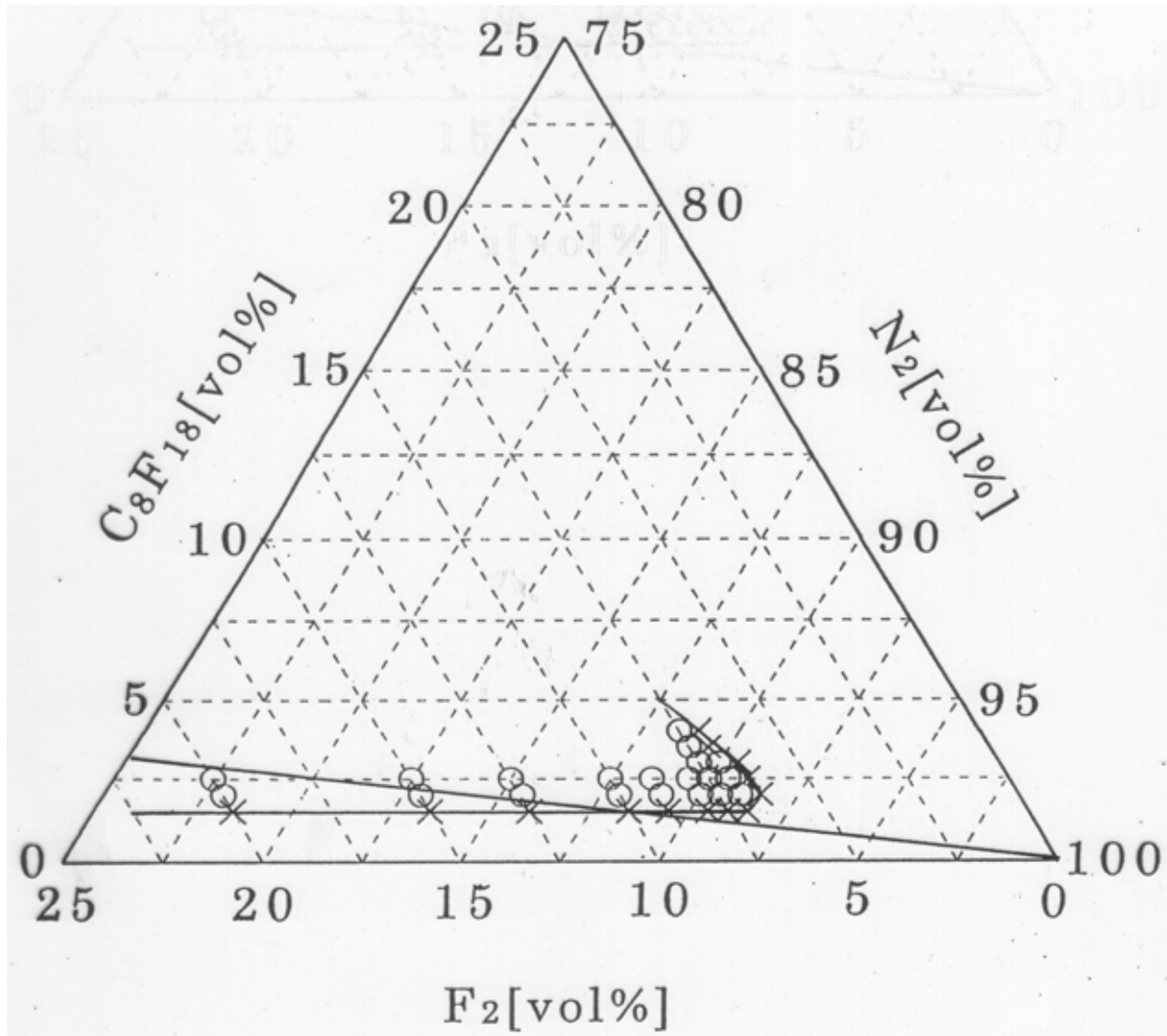


FIGURE 5 Flammability areas of $C_8F_{18}/F_2/N_2$ mixture.

Replies to the reviewer's comments

- a) I think some explanation on “the first type mixture” and “the third type mixture” should be added.

I'm pretty sorry. It is completely my mistake. There is no comparative mixture in this work. So I deleted the words “the first type mixture” and “the third type mixture”.

- b) In figure 1, methane should be corrected as fluorine.

It is also my mistake. I corrected just as the reviewer's comment.

- c) The measured flammability limits are for relatively diluted mixtures with nitrogen, and I think the author should provide some discussion concerning the mixture of higher concentration.

I added short comments on this matter at the end of “3. Flammability areas” section.