# Flammability limits of olefinic and saturated fluoro-compounds

Shigeo Kondo*, Kenji Takizawa, Akifumi Takahashi, Kazuaki Tokuhashi, Junji Mizukado, Akira Sekiya

*National Institute of Advanced Industrial Science and Technology (AIST) Central 5, Higashi 1-1-1, Tsukuba, Ibaraki, 305-8565, Japan*

## ARTICLE INFO

## ABSTRACT

Flammability limits were measured for a number of olefinic and saturated fluoro-compounds in a 12 l spherical glass vessel. The obtained data together with the ones of previous studies have been analyzed based on the *F*-number scheme of flammability limits. The flammability limits of these compounds have been found to be explained very well by the present scheme of interpretation. The flammability limits are dependent upon distribution of F atoms in a molecule as well as upon F-substitution rate itself. It has been found that –O–CF$_3$ group in a molecule conspicuously decreases the flammability of the compound, while –C–CF$_3$ group does not much. For olefinic compounds, distribution of F atoms around double bonds markedly diminishes the flammability of the molecule.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

The global environmental problem makes it an urgent issue to develop CFC (chlorofluorocarbon) replacements. Up to now, such compounds as hydro-fluoro-carbons (HFCs) and hydro-fluoro-ethers (HFEs) have been developed as candidates for CFC replacements. These compounds contain hydrogen atoms in the molecule, and some of them are flammable. More recently, fluorinated olefins are considered to be new generation CFC alternatives because of their short life times. However, olefinic compounds tend to be more flammable than saturated compounds. If they are flammable, their use will be strictly controlled by public regulations. Therefore, the flammability study is indispensable for the developers and users of these compounds. The flammability limits are most widely used index for assessing flammability of gases and vapors.

In a previous paper, we have investigated the flammability limits of multi-fluorinated compounds [1]. In general, the larger the F-substitution rate of molecule, the less flammable the compound. A compound is expected to be non-flammable if F-substitution rate exceeds a certain limit [1]. F-substitution rate is given by $n_F/(n_H + n_F)$, where $n_H$ and $n_F$ are numbers of hydrogen and fluorine atoms in the molecule, respectively. The flammability is dependent upon distribution of F atoms in a molecule as well. In fact, various compounds which have common chemical formula such as $C_3H_3F_5$ and $C_3H_3F_5O$ were found to have different flammable properties depending upon distribution of F atoms in molecules

[1], and a numerical analysis was carried out for the observed data together with those from the literature, utilizing *F*-number scheme of flammability limits [1,2]. In the analysis, they have included saturated hydro-fluoro-carbons (HFCs), fluorinated ethers (HFEs), and very few fluoro-olefins (HFOs). On the whole the observed data were reasonably well explained. However, agreement between the observed and calculated values of flammability limits was not satisfactory particularly for some of the fluorinated ethers and fluoro-olefins. It is desirable to establish a satisfactory interpretation scheme of flammability limits of such compounds.

In order to accomplish this, it is essential to obtain observed values of flammability limits which are taken accurately and consistently with each other. Since there is a well known problem that the experimental values are dependent upon the apparatus and condition used for the measurement, care should be taken to determine the apparatus and decision criterion to be used in the experiments. Based on our extensive study to clarify how various experimental factors affect the flammability limit measurement of combustible gases [3–5], we have basically adopted the flammability measurement method proposed by American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE), which is considered to give reasonable values of flammability limits [5–7]. This is a modification of ASTM E-681 method [8], and employs a 12 l spherical glass vessel.

In the present study, the flammability limits are measured by the same method as before for additional fluorinated compounds including several fluoro-orefins. These kinds of compounds are considered to be candidates for CFC alternatives. There should be a much bigger chance than before [1] to make clear main factors that determine the flammability limits of fluoro-compounds and improve much the agreement between the observed and calculated

values of flammability limits. It is of particular interest how well the flammability limits of these compounds are explained by adequate parameterization of *F*-number scheme.

## 2. Experimental method

### 2.1. Measurement of flammability limits in dry air

The flammability limits measurements were done with a method similar to that proposed by ASHRAE [7]. The only difference of the present setting from the original ASHRAE method is that the vessel flange is fixed to the top of the vessel, while in the latter the flange is held on the top by spring-loaded clamps. The explosion vessel is a 12 l spherical glass flask equipped with a pair of tungsten electrodes for AC electric discharge as well as with a fan for gas mixing. The electrodes 2 mm in diameter were pointed and set opposed to each other at 1/4 in. (1 in. = 2.54 cm) distance. The height of the electrodes was one-third from the bottom to the shoulder of the vessel. A schematic diagram of experimental setup is shown in Fig. 1. AC electric spark was initiated by a Neon transformer of 15 kV–20 mA. The spark duration was 0.4 s. This corresponds to ignition energy of approximately 10 J. The temperature of the explosion vessel was kept at 35 °C. The gas mixture was determined to be flammable if the flame moved upward and outward from the point of ignition to reach an arc of the vessel wall subtending an angle larger than 90° as measured from the ignition point.

In the experiments, sample gas and air mixtures were prepared in the explosion vessel by the partial pressure method. Two kinds of MKS baratrons were used for the pressure measurement. One is 100 Torr head and the other 1000 Torr head (1 Torr = 133.32 Pa). The gas mixtures were prepared in the vessel at a total pressure a little higher than the ambient pressure, stirred with a fan for 8 min, and left to settle for 1 min. Just before ignition, the pressure inside was balanced with the ambient by opening the valve leading to a soda lime tower 30 cm in diameter and 50 cm in height through a plastic tube 3/8-in. (0.95 cm) in diameter and approximately 100 cm in length. This valve was kept open during and after the ignition. In case this cannot relieve the explosion pressure quickly enough, the vessel was equipped with a 1/2-in. (1.27 cm) relief valve set at 5 psi (34.5 kPa) in relief pressure. The exhaust gases resulting from the experiments were pumped out through another soda lime tower.
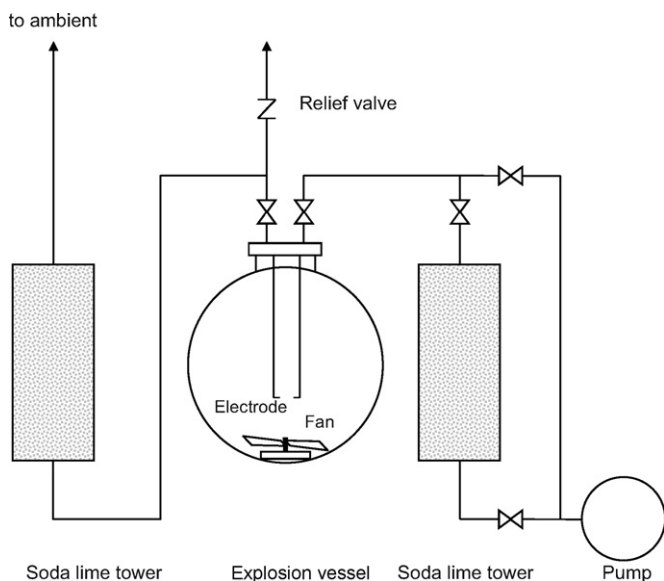


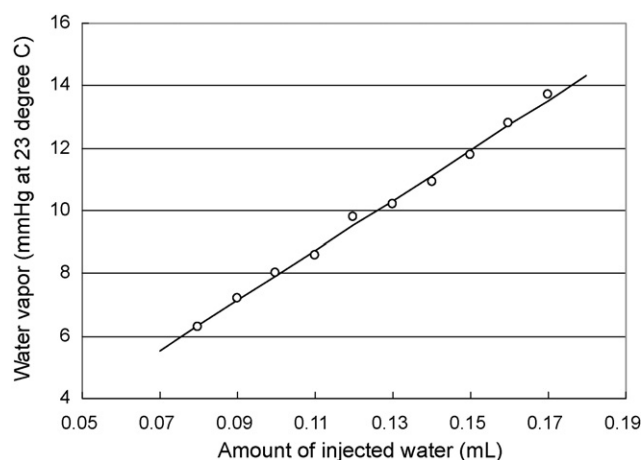**Fig. 1.** Schematic diagram of experimental setup.



**Fig. 2.** Relationship between the amount of injected water (in ml) and the resulting water vapor pressure (in mmHg) at 23 °C in the 12 l explosion vessel.

### 2.2. Measurement in moist air

For compounds which contain more fluorine atoms than hydrogen atoms in the molecules, the measurement was made in moist air of which relative humidity was 50% corrected to 23 °C. The procedure for the measurement in moist air was the same as in dry air except for the preparation of moist condition. After the introduction of sample gas and dry air, an appropriate amount of liquid water was injected by a syringe into the vessel to yield a mixture of sample gas and moist air. The mixture was stirred with the fan for 30 min to attain constant pressure, and left to settle for 1 min. Just before ignition, the pressure inside was balanced with the ambient by opening the valve leading to the soda lime tower.

The relationship between the amount of water injected into the vessel and the resulting water vapor pressure at 23 °C was obtained by monitoring the pressure rise after the water injection into the vessel filled with dry air of approximately one atmospheric pressure. It takes about 30 min to attain constant pressure after the water injection. Fig. 2 shows the relationship between the amount of water injected into the vessel and the resulting water vapor pressure at 23 °C. In the present case, the relationship between the amount of injected water $q$ (ml) and the resulting water vapor pressure $p$ (mmHg) is given by the following equation:

$$p = 80.06q - 0.078 \tag{1}$$

### 2.3. Sample gases

The sample gases of fluorinated compounds used for the measurements are listed in Table 1. They were supplied from chemical companies of Syn-Quest Co., Daikin Industry Co., and Asahi Glass Co. The sample purities were mostly 97% or better, and they were used without further purification. Dry air was G3 grade of Taiyo-Nissan Co. The dew point of the dry air was −80 °C.

## 3. Results and discussion

The flammability limits of sample gases were measured in a 12 l spherical glass vessel basically following the decision criterion of the ASHRAE method [7]. Usually the measurement was done in dry air. For compounds of which F-substitution rate is larger than 0.5, the measurement was done in moist air as well. The moist air here means 50% relative humidity corrected for 23 °C. The experimental values of flammability limits obtained in the present study are summarized in Table 1. For the sake of completeness, the flammability limits data of other than fluorinated compounds were also included

**Table 1**
Observed values of flammability limits for a number of fluorinated compounds (in vol%).

| Compound | Chemical formula | Purity | F rate | Observed (dry air)[a] | | Observed (moist air)[a,b] | | F-number[b] (moist air) |
|---|---|---|---|---|---|---|---|---|
| | | | | L | U | L | U | |
| Methylene fluoride | $CH_2F_2$ | 99 | 0.50 | 13.5(0.1) | 27.5(0.5) | – | – | 0.299 |
| 1,3-Difluoropropane | $CH_2FCH_2CH_2F$ | 97 | 0.25 | 2.63(0.03) | 12.0(0.3) | – | – | 0.532 |
| 2,2-Difluoropropane | $CH_3CF_2CH_3$ | 97 | 0.25 | 2.88(0.03) | 10.8(0.5) | – | – | 0.484 |
| 1,2,3-Trifluoropropane | $CH_2FCHFCH_2F$ | 97 | 0.38 | 3.05(0.05) | 14.5(0.5)[c] | – | – | 0.541 |
| 1,1,2,2-Tetrafluoropropane | $CHF_2CF_2CH_3$ | 98 | 0.50 | 4.19(0.04) | 15.3(0.7) | – | – | 0.477 |
| HFE-254me | $CF_3CHFOCH_3$ | 99 | 0.50 | 4.90(0.05) | 19.5(0.5) | – | – | 0.499 |
| HFE-263sf | $CH_3CH_2OCF_3$ | 97 | 0.38 | 4.1(0.1) | 15.0(0.7) | – | – | 0.477 |
| HFE-365mf-c | $CF_3CH_2OCF_2CH_3$ | 99 | 0.50 | 3.93(0.10) | 14.8(0.7) | – | – | 0.485 |
| 2-Fluoropropene | $CH_2=CFCH_3$ | 99 | 0.17 | 2.52(0.03) | 11.6(0.5) | – | – | 0.534 |
| 2,3,3-Trifluoropropene | $CH_2=CFCHF_2$ | 97 | 0.50 | 3.51(0.03) | 16.9(0.7) | – | – | 0.544 |
| 3,3,3-Trifluoropropene | $CH_2=CHCF_3$ | 99 | 0.50 | 3.83(0.03) | 15.0(0.7) | – | – | 0.495 |
| 1,3,3,3-Tetrafluoropropene | $CHF=CHCF_3$ | 99 | 0.67 | n.f. | n.f. | 5.86(0.15) | 12.8(0.6) | 0.323 |
| 2,3,3,3-Tetrafluoropropene | $CH_2=CFCF_3$ | 98 | 0.67 | 6.7(0.2) | 11.7(0.5) | 5.5(0.2) | 13.0(0.6) | 0.350 |
| 1,1,3,3,3-Pentafluoropropene | $CF_2=CHCF_3$ | 99 | 0.83 | n.f. | n.f. | 0.000 | | |
| z1,2,3,3,3-Pentafluoropropene | $CHF=CFCF_3$ | 99 | 0.83 | n.f. | n.f. | 0.000 | | |
| Perfluoropropene | $CF_2=CFCF_3$ | 92.5 | 1.00 | n.f. | n.f. | 0.000 | | |

[a] Numbers in parentheses are the estimated errors as measured by ASHRAE criterion.
[b] If F-substitution rate is 0.5 or less, the flammability limits are not affected by humidity of air.
[c] Upper flammability limit was measured under total pressure of 400 Torr.

in the analysis. They were mainly taken from the database of NFPA 325 [9].

### 3.1. Analytical equations

In order to make a simultaneous analysis of the upper flammability limits $U$ and lower flammability limits $L$, utilization of the $F$-number scheme is convenient where the "observed" values of $F$-number and the geometric mean $G$ are obtained from the observed values of $U$ and $L$ through the following equations [1,2]:

$$F = 1 - \sqrt{\frac{L}{U}} \qquad (2)$$

and

$$G = \sqrt{UL} \qquad (3)$$

Alternatively, the calculated values of both the flammability limits can be obtained from the calculated ones of $F$ and $G$ by the following equations:

$$L = G(1 - F) \qquad (4)$$

and

$$U = \frac{G}{1 - F} \qquad (5)$$

where the calculated values of $F$ and $G$ will be given empirically in terms of molecular parameters such as done in the literature [1,2].

In the present study, the analysis was done for a flammability limit data set including hydrocarbons (HCs), saturated hydro-fluoro-carbons (HFCs), saturated fluoro-ethers (HFEs), and fluoro-olefins (HFOs). This data set is unique in that it contains a considerable number of multi-fluorinated compounds which are not included in typical data set such as NFPA 325 [9]. As was found in the preceding study, the dependency of flammability on F-substitution rate is not so simple. The flammability falls down quickly as it approaches to a certain value [1]. In addition, the flammability limits of fluoro-compounds are dependent upon distribution of fluorine atoms in the molecule as well. For example, fluorine atoms attached to a carbon atom neighboring an oxygen atom can decrease markedly the flammability of the concerned compound. Also the distribution of F atoms around unsaturated bonds seems to be important. In order to clarify the characteristics of the flammability of multi-fluorinated compounds, we have

newly introduced parameters concerning distribution of F atoms in molecules. Actually, the following equations of $F$-number and geometric mean $G$ were introduced to make the analysis of flammability limits.

$$F = p_1(1 + p_2C_1 + p_3R_{OE} + p_4R_{US} + p_5E_F + p_6R_{sf3} + p_7R_{df} + p_8R_{dfc}$$
$$+ p_9R_{df2} + p_{10}R_{of} + p_{11}R_{of2} + p_{12}R_{of3}) \qquad (6)$$

$$G = C_{st}[1 + q_1(M - 32) + q_2C_1 + q_3R_{OE} + q_4R_{US} + q_5R_F + q_6R_{df}$$
$$+ q_7R_{dfc} + q_8R_{df2}] \qquad (7)$$

Here, $M$ denotes the molecular weight and, $p_1$ through $p_{12}$ are coefficients for various terms of $F$-number to be determined from the analysis of the observed data of flammability limits.

$q_1$ through $q_8$ are coefficients for various terms of geometric mean to be determined from the analysis of the observed data of flammability limits.

$C_1$ takes the value of one or zero according to whether the molecule has one carbon atom or more than one.

$R_{OE}$ denotes number of ether oxygen in the molecule divided by the number of skeletal carbon atoms minus one. For example, $R_{OE}$ is 1.0 for dimethyl ether.

$R_{US}$ denotes the total degree of unsaturation in the carbon skeleton divided by skeletal carbon number minus one. For example, $R_{US}$ is 1.0 for ethylene, 2.0 for acetylene, 2/3 for butadiene, and so forth.

$E_F$ is an ellipse function of $R_F$ which is expressed as follows:

$$E_F = \sqrt{1 - 2.56R_F^2} \quad \text{for} \quad R_F \leq 0.625 \quad \text{and} \qquad (8)$$

$$E_F = 0.0 \quad \text{for} \quad R_F > 0.625. \qquad (9)$$

In the preceding paper, it was found that the compounds with F-substitution rate larger than 0.625 are mostly non-flammable. The function form of $E_F$ is based on this fact.

On the other hand, $R_F$ appearing in Eq. (7) denotes number of F atoms divided by the sum of H and F atoms in the molecule. It is equal to F-substitution rate.

$R_{sf3}$ denotes number of F atoms belonging to $CF_3$–C groups divided by the sum of H and F atoms in the molecule.

$R_{df}$ denotes number of F atoms belonging to CHF=C groups divided by the sum of H and F atoms in the molecule.

$R_{dfc}$ denotes number of F atoms belonging to C–CF=C groups divided by the sum of H and F atoms in the molecule.

**Table 2**
Observed and calculated values of flammability limits and relevant quantities.

| No. | Compound | Chemical formula | Molecular parameters relevant to F atoms | | | | | | | | L (vol%) | L_cal (vol%) | U (vol%) | U_cal (vol%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $R_F$ | $R_{sf3}$ | $R_{df}$ | $R_{dfc}$ | $R_{df2}$ | $R_{of}$ | $R_{of2}$ | $R_{of3}$ | | | | |
| 1 | Methane | $CH_4$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.90 | 4.95 | 15.80 | 15.80 |
| 2 | Ethane | $C_2H_6$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.00 | 2.57 | 12.50 | 12.28 |
| 3 | Propane | $C_3H_8$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.03 | 1.90 | 10.10 | 9.10 |
| 4 | Butane | $C_4H_{10}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.60 | 1.54 | 8.40 | 7.34 |
| 5 | Isobutane | $CH_3CH(CH_3)_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.68 | 1.54 | 7.80 | 7.34 |
| 6 | Pentane | $C_5H_{12}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.50 | 1.30 | 7.80 | 6.23 |
| 7 | Isopentane | $CH_3CH_2CH(CH_3)_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.40 | 1.30 | 7.60 | 6.23 |
| 8 | 2,2-Dimethylpropane | $CH_3C(CH_3)_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.40 | 1.30 | 7.50 | 6.23 |
| 9 | Hexane | $C_6H_{14}$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.10 | 1.14 | 7.50 | 5.46 |
| 10 | Isohexane | $CH_3CH_2CH_2CH(CH_3)_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.00 | 1.14 | 7.00 | 5.46 |
| 11 | 2-Methylpentane | $CH_3CH(CH_3)CH_2CH_2CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.20 | 1.14 | 7.00 | 5.46 |
| 12 | 3-Methylpentane | $CH_3CH_2CH(CH_3)CH_2CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.20 | 1.14 | 7.00 | 5.46 |
| 13 | 2,2-Dimethylbutane | $CH_3C(CH_3)_2CH_2CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.20 | 1.14 | 7.00 | 5.46 |
| 14 | 2,3-Dimethylbutane | $CH_3CH(CH_3)CH(CH_3)CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.20 | 1.14 | 7.00 | 5.46 |
| 15 | Ethylene | $C_2H_4$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.74 | 2.93 | 31.50 | 31.20 |
| 16 | Propylene | $C_3H_6$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.15 | 2.15 | 11.20 | 14.76 |
| 17 | 1-Butene | $C_4H_8$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.60 | 1.69 | 10.00 | 10.18 |
| 18 | cis-2-Butene | $CH_3CH=CHCH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.70 | 1.69 | 9.00 | 10.18 |
| 19 | trans-2-Butene | $CH_3CH=CHCH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.80 | 1.69 | 9.70 | 10.18 |
| 20 | 2-Methylpropene | $CH_2=C(CH_3)CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.80 | 1.69 | 9.60 | 10.18 |
| 21 | 1-Pentene | $CH_2=CHCH_2CH_2CH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.50 | 1.40 | 8.70 | 7.96 |
| 22 | 3-Methyl-1-butene | $CH_2=CHCH(CH_3)_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.50 | 1.40 | 9.10 | 7.96 |
| 23 | 2,4,4-Trimethyl-1-pentene | $CH_2=C(CH_3)CH_2C(CH_3)_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.88 | 0.97 | 6.00 | 5.12 |
| 24 | Acetylene | $C2H_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.50 | 2.32 | 100.00 | 96.35 |
| 25 | 1,3-Butadiene | $CH_2=CHCH=CH_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.69 | 1.81 | 16.00 | 14.21 |
| 26 | Isoprene | $CH_2=C(CH_3)CH=CH_2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.50 | 1.49 | 8.90 | 10.21 |
| 27 | 1,4-Hexadiene | $CH_2=CHCH_2CH=CHCH_3$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1.18 | 1.28 | 7.90 | 8.09 |
| 28 | Methyl fluoride | $CH_3F$ | 1/4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7.10 | 7.10 | 19.90 | 20.70 |
| 29 | Methylene fluoride | $CH_2F_2$ | 2/4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 13.50 | 12.39 | 27.50 | 26.49 |
| 30 | Ethyl fluoride | $C2H5F$ | 1/6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.15 | 3.21 | 17.50 | 14.62 |
| 31 | 1,1-Difluoroethane | $CHF_2CH_3$ | 2/6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.35 | 4.32 | 17.50 | 16.90 |
| 32 | 1,2-Difluoroethane | $CH_2FCH_2F$ | 2/6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.15 | 4.32 | 19.00 | 16.90 |
| 33 | 1,1,1-Trifluoroethane | $CF_3CH_3$ | 3/6 | 3/6 | 0 | 0 | 0 | 0 | 0 | 0 | 7.40 | 6.23 | 17.00 | 19.41 |
| 34 | 1,1,2-Trifluoroethane | $CHF_2CH_2F$ | 3/6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 6.20 | 6.39 | 22.60 | 18.90 |
| 35 | 1-Fluoropropane | $CH_2FCH_2CH_3$ | 1/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.38 | 2.25 | 10.20 | 10.45 |
| 36 | 2-Fluoropropane | $CH_3CHFCH_3$ | 1/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.38 | 2.25 | 10.00 | 10.45 |
| 37 | 1,3-Difluoropropane | $CH_2FCH_2CH_2F$ | 2/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.69 | 2.75 | 12.00 | 11.77 |
| 38 | 2,2-Difluoropropane | $CH_3CF_2CH_3$ | 2/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 2.88 | 2.75 | 10.80 | 11.77 |
| 39 | 1,1,1-Trifluoropropane | $CF_3CH_2CH_3$ | 3/8 | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 3.60 | 3.44 | 12.40 | 13.31 |
| 40 | 1,2,3-Trifluoropropane | $CH_2FCHFCH_2F$ | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3.05 | 3.52 | 14.50 | 13.02 |
| 41 | 1,1,1,3-Tetrafluoropropane | $CF_3CH_2CH_2F$ | 4/8 | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 4.30 | 4.66 | 14.50 | 14.34 |
| 42 | 1,1,2,2-tetafluoropropane | $CHF_2CF_2CH_3$ | 4/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 4.19 | 4.75 | 15.30 | 14.05 |
| 43 | 1,1,1,2,3-Pentafluoropropane | $CF_3CHFCH_2F$ | 5/8 | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 7.80 | 7.09 | 11.00 | 12.40 |
| 44 | 1,1,2,2,3-Pentafluoropropane | $CHF_2CF_2CH_2F$ | 5/8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 7.70 | 7.20 | 11.50 | 12.21 |
| 45 | 1,1,1,3,3-Pentafluorobutane | $CF_3CH_2CF_2CH_3$ | 5/10 | 3/10 | 0 | 0 | 0 | 0 | 0 | 0 | 3.65 | 3.83 | 12.20 | 11.69 |
| 46 | 1,1,1,4,4,4-Hexafluorobutane | $CF_3CH_2CH_2CF_3$ | 6/10 | 6/10 | 0 | 0 | 0 | 0 | 0 | 0 | 7.30 | 4.96 | 9.60 | 11.28 |
| 47 | HFE-143m | $CF_3OCH_3$ | 3/6 | 0 | 0 | 0 | 0 | 0 | 0 | 3/6 | 10.50 | 10.11 | 21.50 | 21.07 |
| 48 | HFE-245mc | $CF_3CF_2OCH_3$ | 5/8 | 3/8 | 0 | 0 | 0 | 0 | 2/8 | 0 | 9.50 | 7.86 | 16.50 | 17.28 |
| 49 | HFE-254me | $CF_3CHFOCH_3$ | 4/8 | 3/8 | 0 | 0 | 0 | 1/8 | 0 | 0 | 4.90 | 4.95 | 19.50 | 20.14 |
| 50 | HFE-254pc | $CHF_2CF_2OCH_3$ | 4/8 | 0 | 0 | 0 | 0 | 0 | 2/8 | 0 | 5.10 | 4.99 | 19.70 | 19.98 |
| 51 | HFE-263mf | $CF_3CH_2OCH_3$ | 3/8 | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 4.10 | 3.52 | 18.00 | 18.50 |
| 52 | HFE-263sf | $CH_3CH_2OCF_3$ | 3/8 | 0 | 0 | 0 | 0 | 0 | 0 | 3/8 | 4.10 | 5.16 | 15.00 | 12.64 |
| 53 | HFE-356mec | $CF_3CHFCF_2OCH_3$ | 6/10 | 3/10 | 0 | 0 | 0 | 0 | 2/10 | 0 | 4.95 | 5.43 | 14.50 | 14.33 |
| 54 | HFE-356mmz | $CF_3CH(CF_3)OCH_3$ | 6/10 | 6/10 | 0 | 0 | 0 | 0 | 0 | 0 | 5.15 | 5.42 | 15.20 | 14.35 |
| 55 | HFE-356pcf | $CHF_2CF_2CH_2OCHF_2$ | 6/10 | 0 | 0 | 0 | 0 | 0 | 2/10 | 0 | 4.40 | 5.51 | 14.20 | 14.12 |
| 56 | HFE-365mcf | $CF_3CH_2CF_2OCH_3$ | 5/10 | 3/10 | 0 | 0 | 0 | 0 | 0 | 0 | 3.60 | 4.11 | 16.20 | 14.92 |
| 57 | HFE-365mf-c | $CF_3CH_2OCF_2CH_3$ | 5/10 | 3/10 | 0 | 0 | 0 | 0 | 2/10 | 0 | 3.93 | 4.04 | 14.80 | 15.16 |
| 58 | HFE-374pc-f | $CHF_2CF_2OCH_2CH_3$ | 4/10 | 0 | 0 | 0 | 0 | 0 | 2/10 | 0 | 2.90 | 3.14 | 13.70 | 14.01 |
| 59 | Vinyl fluoride | $CH_2=CHF$ | 1/4 | 0 | 1/4 | 0 | 0 | 0 | 0 | 0 | 3.41 | 3.29 | 25.00 | 23.80 |
| 60 | 1,1-Difluoro ethene | $CH_2=CF_2$ | 2/4 | 0 | 0 | 0 | 2/4 | 0 | 0 | 0 | 4.70 | 4.77 | 21.50 | 21.40 |
| 61 | 2-Fluoropropene | $CH_2=CFCH_3$ | 1/6 | 0 | 0 | 1/6 | 0 | 0 | 0 | 0 | 2.52 | 2.04 | 11.60 | 11.83 |
| 62 | 3,3,3-Trifluoropropene | $CH_2=CHCF_3$ | 3/6 | 3/6 | 0 | 0 | 0 | 0 | 0 | 0 | 3.83 | 4.59 | 15.00 | 19.05 |
| 63 | 1,3,3,3-Tetrafluoropropene | $CHF=CHCF_3$ | 4/6 | 3/6 | 1/6 | 0 | 0 | 0 | 0 | 0 | 5.86 | 6.24 | 12.80 | 12.61 |
| 64 | 2,3,3,3-Tetrafluoropropene | $CH_2=CFCF_3$ | 4/6 | 3/6 | 0 | 1/6 | 0 | 0 | 0 | 0 | 5.50 | 5.79 | 13.00 | 11.83 |
| 65 | HFE-227me | $CF_3CHFOCF_3$ | 7/8 | 3/8 | 0 | 0 | 0 | 1/8 | 0 | 3/8 | 16.57 | 14.47 | 16.57 | 18.98 |
| 66 | HFE-245mf | $CF_3CH_2OCHF_2$ | 5/8 | 3/8 | 0 | 0 | 0 | 0 | 2/8 | 0 | 11.65 | 7.86 | 11.65 | 17.28 |
| 67 | HFE-245pf | $CHF_2CH_2OCF_3$ | 5/8 | 0 | 0 | 0 | 0 | 0 | 0 | 3/8 | 11.65 | 10.33 | 11.65 | 13.14 |
| 68 | HFE-347mcc | $CF_3CF_2CF_2OCH_3$ | 7/10 | 3/10 | 0 | 0 | 0 | 0 | 2/10 | 0 | 10.00 | 7.03 | 10.00 | 14.24 |
| 69 | HFE-347mmy | $CF_3CF(CF_3)OCH_3$ | 7/10 | 6/10 | 0 | 0 | 0 | 1/10 | 0 | 0 | 10.00 | 7.00 | 10.00 | 14.30 |
| 70 | HFE-347pc-f | $CHF_2CF_2OCH_2CF_3$ | 7/10 | 3/10 | 0 | 0 | 0 | 0 | 2/10 | 0 | 10.00 | 7.03 | 10.00 | 14.24 |
| 71 | HFE-458mecf | $CF_3CHFCF_2CH_2OCHF_2$ | 8/12 | 3/12 | 0 | 0 | 0 | 0 | 2/12 | 0 | 8.05 | 5.78 | 8.05 | 11.23 |
| 72 | 1,1,3,3,3-Pentafluoropropene | $CF_2=CHCF_3$ | 5/6 | 3/6 | 0 | 0 | 2/6 | 0 | 0 | 0 | 9.57 | 6.75 | 9.57 | 13.58 |
| 73 | 1,2,3,3,3-Pentafluoropropene | $CHF=CFCF_3$ | 5/6 | 3/6 | 1/6 | 1/6 | 0 | 0 | 0 | 0 | 7.63 | 5.54 | 7.63 | 10.51 |
| 74 | Perfluoropropene | $CF_2=CFCF_3$ | 6/6 | 3/6 | 0 | 1/6 | 2/6 | 0 | 0 | 0 | 8.26 | 6.01 | 8.26 | 11.36 |

**Table 3**
Average deviations and average relative deviations between observed and calculated values for each group of compounds.

| Group | Members | Ave. dev. (vol%) | Ave. rel. dev. (%) |
|---|---|---|---|
| Lower flammability limits | | | |
| Hydrocarbons | 27 | 0.11 | 6.4 |
| Flammable HFCs | 19 | 0.45 | 7.7 |
| Flammable HFEs | 12 | 0.55 | 10.8 |
| Flammable fluoro-olefins | 6 | 0.35 | 9.3 |
| Non-flammable[a] | 10 | 2.56 | 25.8 |
| Overall | 74 | 0.62 | 10.3 |
| Upper flammability limits | | | |
| Hydrocarbons | 27 | 1.21 | 12.9 |
| Flammable HFCs | 19 | 1.24 | 8.1 |
| Flammable HFEs | 12 | 0.67 | 4.2 |
| Flammable fluoro-olefins | 6 | 1.16 | 7.5 |
| Non-flammable[a] | 10 | 3.55 | 36.0 |
| Overall | 74 | 1.44 | 12.9 |

[a] For non-flammable compounds, the values of geometric mean $G$ of both limits were always assumed to be equal to the calculated values. See the text.

$R_{df2}$ denotes number of F atoms belonging to $CF_2=C$ groups divided by the sum of H and F atoms in the molecule.

$R_{of}$ denotes number of single F atoms attached to carbon atom adjacent to ether oxygen divided by the sum of H and F atoms in the molecule.

$R_{of2}$ denotes number of double F atoms attached to carbon atom adjacent to ether oxygen divided by the sum of H and F atoms in the molecule.

$R_{of3}$ denotes number of F atoms in $CF_3$–O– groups in the molecule divided by the sum of H and F atoms in the molecule.

Actual values of $R_{sf3}$, $R_{df}$, $R_{dfc}$, $R_{df2}$, $R_{of}$, $R_{of2}$, and $R_{of3}$ for each compound are given in Table 2. It should be noted that all the terms in Eqs. (6) and (7) are additive except for $p_1$ for $F$-number. The terms from $p_6$ to $p_{12}$ for $F$-number represent corrections to the main fluorine substitution effect of $p_5E_F$. Similarly, the terms of $q_6$, $q_7$, and $q_8$ for $G$ are corrections to the main fluorine substitution effect of $q_5R_F$.

## 3.2. Result of analysis

For the actual analysis, the data taken in moist air were used for the compounds of which F-substitution rate is larger than 0.5. For completeness, the data of non-flammable compounds were also included in the analysis.

Now, if a flammable gas is mixed with inert gas step by step, the mixture may become less and less flammable and both the upper and lower flammability limits approach to each other until they finally coincide with each other. At this stage, if we assume that the value of $G$ is equal to the calculated one, we can define the "observed" values of $U$ and $L$ for any non-flammable compound and/or mixture using Eqs. (4) and (5).

Table 2 summarizes the observed and calculated values of flammability limits. On the whole, agreement between the observed and calculated values is good. As summarized in Table 3, the average deviation of the observed values of lower flammability limits from the calculated ones is 0.62 vol% and the average relative deviation is 10.3 relative percent. Similarly, the average deviation of the observed values of upper flammability limits from the calculated ones is 1.44 vol% and the average relative deviation is 12.9 relative percent.

Now, the compounds included in the present analysis are classified into five groups, i.e., four flammable groups and one non-flammable group. They are HCs, flammable HFCs, flammable HFEs, flammable HFOs, and non-flammable fluoro-compounds. The aver-

age values of absolute and relative deviations of calculated values from the observed ones for both limits are also given for each group of compounds in Table 3. As to the lower flammability limits, the values of average relative deviations for the individual groups are 6.4, 7.7, 10.8, 9.3, and 25.8 relative percent, respectively, for HC, HFC, HFE, HFO, and non-flammable group. The value is the smallest for HC group, and there is not much difference among HFC, HFE, and HFO groups. Naturally, the value for non-flammable group is relatively large.

For the upper flammability limits, the values of average relative deviations between the observed and calculated values are 12.9, 8.1, 4.2, 7.5, and 36.0 relative percent, respectively, for HC, HFC, HFE, HFO, and non-flammable group. Indeed, the value is the largest for the non-flammable group. Among the flammable compounds, the value is the largest for HC group and there is not much difference among HFC, HFE, and HFO groups. Thus, HFC, HFE, and HFO groups are by no means inferior to HC group concerning the agreement between the observed and calculated values of flammability limits. This means that the fundamental nature of flammability limits of these compounds is very well explained by the present model of interpretation.

As stated, we have included non-flammable compounds in the analysis. This is important to adequately interpret the flammability limits of weakly flammable fluoro-compounds. For non-flammable compounds, the observed value of F-number is zero. The "observed" values of both limits were obtained by assuming that the geometric mean $G$ is equal to the calculated value. For non-flammable compounds, the average deviation of calculated values from the "observed" ones is 2.56 vol% for lower flammability limits and 3.55 vol% for upper limits. These values are of course much larger than the ones for the flammable compounds (Table 3).

Table 4 shows the resulting values of parameters. As for the parameters of F-number, the negative value of $p_2$ indicates that $C_1$ compounds are in general more weakly flammable than the other components in the same series of compounds. The large positive value of $p_3$ reflects the flammability enhancing effect of ether group. Also the flammability enhancing effect of double bond is apparent on the value of $p_4$. The large magnitude of $p_5$ indicates the impor-

**Table 4**
Parameter values resulting from flammability limits analysis.

| (1) $F$-number | | | |
|---|---|---|---|
| $p_i$ | Description[a] | Value | S.D. |
| 1 | Main coefficient | 0.232 | 0.035 |
| 2 | $C_1$ | −0.441 | 0.081 |
| 3 | Ether | 0.619 | 0.310 |
| 4 | Unsaturation | 0.651 | 0.102 |
| 5 | F | 1.337 | 0.357 |
| 6 | sf3 | 0.131 | 0.302 |
| 7 | df | −0.682 | 0.264 |
| 8 | dfc | −0.580 | 0.713 |
| 9 | df2 | −0.360 | 0.119 |
| 10 | of | 0.091 | 1.016 |
| 11 | of2 | 0.175 | 0.699 |
| 12 | of3 | −2.194 | 0.628 |

| (2) $G$-value | | | |
|---|---|---|---|
| $q_i$ | Description[a] | Value | S.D. |
| 1 | (M-32) | 0.00290 | 0.00054 |
| 2 | $C_1$ | −0.021 | 0.012 |
| 3 | Ether | −0.015 | 0.054 |
| 4 | Unsaturation | 0.476 | 0.035 |
| 5 | F | 0.018 | 0.099 |
| 6 | df | −1.505 | 0.269 |
| 7 | dfc | −2.004 | 0.336 |
| 8 | df2 | −1.022 | 0.120 |

[a] More detailed explanation is given in the text.

tance of $E_f$ function (Eqs. (8) and (9)) to explain the flammability characteristics of fluorine compounds. Generally, the flammability falls down rapidly if F-substitution rate approaches the value of 0.625. All these observations are in good accord with what was obtained in the preceding study [1].

As to the parameters concerning the distribution of fluorine atoms in molecules, the small magnitude of $p_6$ means that the effect of C–$CF_3$ group is not much more than just the existence of three F atoms in a molecule. This is also in good accord with the previous study where the corresponding parameter ($p_{14}$ there) was small [1]. On the other hand, the flammability diminishing effect of F atoms adjacent to double bond is apparent on the parameter values of $p_7$, $p_8$ and $p_9$, i.e., F atoms attached to the carbon atom adjacent to double bond can cancel the flammability enhancing effect of a double bond. This is one of the points newly observed in the present study. In the preceding paper, since the data of olefinic fluorine compounds were very few, this point was not apparent on the corresponding parameter ($p_{17}$). Another interesting observation here is that the values of $p_{10}$ and $p_{11}$ are small, while the value of $p_{12}$ is very large. This shows that the existence of O–$CF_3$ group conspicuously diminishes the flammability of the compound, while O–$CF_2$– and O–CF= groups do not. In the preceding paper [1], this point appeared on the parameter value of $p_{16}$ there just as an average of the present parameters of $p_{10}$, $p_{11}$, and $p_{12}$.

On the other hand, the positive value of $q_4$ for the geometric mean $G$ is a little noted. This may be due to increasing effect on upper flammability limit due to thermal decomposition tendency of unsaturated compounds. This effect is cancelled by the existence of F atoms attached to a carbon atom adjacent to double bond. The latter effect is also apparent on the large negative values of $q_6$, $q_7$, and $q_8$.

Talking about the flammability characteristics, the burning velocity is another important index. There have been several burning velocity studies on relatively simple fluoro-compounds [10–15]. Among others, Takizawa et al. pointed out that the velocity diminishing effect of chemical group is strongest for $CF_3$, next for $CF_2$, and smallest for CF group [15]. This is interesting because in the present study the flammability diminishing effect of –O–$CF_3$ group ($p_{12}$) is much larger than that of $CF_3$ group ($p_6$).

## 4. Conclusion

Flammability limits of a number of fluoro-compounds were measured in a 12 l spherical glass vessel following the ASHRAE criteria.

A numerical analysis was carried out for the experimental values of flammability limits. As a result, the factors which determine the flammability of fluoro-compounds have become clear, i.e., much

clearer than in the preceding study [1]. For example, if fluorine atoms are attached to carbon atoms adjacent to double bonds, the flammability is decreased. As for F atoms in the vicinity of ether oxygen, –O–$CF_3$ group markedly decreases the flammability of the compound while –O–CF= and –O–$CF_2$– groups have no particular effect. On the other hand, –C–$CF_3$ group does not have any particular flammability diminishing effect. On the whole, agreement between the observed and calculated values of flammability limits has become satisfactory. In particular, it is satisfying that the flammability limits of HFCs, HFEs, and HFOs can be explained with accuracy at least similar to hydrocarbon compounds. On the contrary, discrepancy is noted between the observed and calculated values for non-flammable compounds of high F-substitution rate. In fact, many of them are non-flammable even though the calculation tends to predict them to be flammable.

## References

[1] S. Kondo, Y. Urano, K. Takizawa, A. Takahashi, K. Tokuhashi, A. Sekiya, Flammability limits of multi-fluorinated compounds, Fire Safety J. 41 (2006) 46–56.
[2] S. Kondo, Y. Urano, K. Tokuhashi, A. Takahashi, K. Tanaka, Prediction of flammability of gases by using *F*-number analysis, J. Hazard. Mater. A82 (2001) 113–128.
[3] S. Kondo, Y. Urano, A. Takahashi, K. Tokuhashi, Reinvestigation of flammability limits measurement of methane by the conventional vessel method with AC discharge ignition, Combust. Sci. Technol. 145 (1999) 1–15.
[4] A. Takahashi, Y. Urano, K. Tokuhashi, H. Nagai, M. Kaise, S. Kondo, Fusing ignition of various metal wires for explosion limits measurement of methane/air mixture, J. Loss Prevent. Process Ind. 11 (1998) 353–360.
[5] A. Takahashi, Y. Urano, K. Tokuhashi, S. Kondo, Effect of vessel size and shape on experimental flammability limits of gases, J. Hazard. Mater. A105 (2003) 27–37.
[6] R.G. Richard. (Allied Signal, Inc), Refrigerant Flammability Testing in Large Volume Vessels, March 1998. Contact ARTI Database c/o James M. Calm, Engineering Consultant. 10887 Woodleaf Lane, Great Falls, VA, 22066-3003.
[7] American Society of Heating, Refrigerating and Air-conditioning Engineers, Designation and safety classification of refrigerants. ANSI/ASHRAE Standard 34-2007, Atlanta, GA, 2007.
[8] American Society of Testing and Materials, Designation: E681-04, Philadelphia, 2004.
[9] NFPA 325, Guide to fire hazard properties of flammable liquids, gases, and volatile solids, Fire Protection Guide to Hazardous Materials, 13th ed., 2001.
[10] G.T. Linteris, L. Truett, Inhibition of premixed methane–air flames by fluoromethanes, Combust. Flame 105 (1996) 15–27.
[11] G.T. Linteris, D.R. Burgess Jr., V. Babushock, M. Zachariah, W. Tsang, P. Westmoreland, Inhibition of premixed methane–air flames by fluoroethanes and fluoropropanes, Combust. Flame 113 (1998) 164–180.
[12] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurement of fluorinated compounds by the spherical-vessel method, Combust. Flame 141 (2005) 298–307.
[13] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurement of HFC-41, HFC-152, and HFC-161 by the spherical-vessel method, J. Fluorine Chem. 127 (2006) 1547–1553.
[14] G.T. Linteris, Burning velocity of 1,1-difluoroethane (R-152a), ASHRAE Trans. 111 (2006) 448–458.
[15] K. Takizawa, A. Takahashi, K. Tokuhashi, S. Kondo, A. Sekiya, Burning velocity measurements of fluoropropenes by the spherical-vessel method, J. Fluorine Chem. 129 (2008) 713–719.