Short communication

Measurement and numerical analysis of flammability limits of halogenated hydrocarbons

Shigeo Kondo*, Kenji Takizawa, Akifumi Takahashi, Kazuaki Tokuhashi

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

Abstract

Flammability limits measurement was made for a number of halogenated compounds by the ASHRAE method. Most of compounds measured are the ones for which discrepancy was noted between the literature values and predicted values of flammability limits. As a result, it has been found that most of the newly obtained values of flammability limits are not in accordance with the literature values. Numerical analysis was carried out for a set of flammability limits data including the newly obtained ones using a modified analytical method based on F-number scheme. In this method, fitting procedure was done directly to flammability limits themselves instead of fitting to F-number. After the fitting process, the average relative deviation between the observed and calculated values is 9.3% for the lower limits and 14.6% for the upper limits.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Halogenated compounds; Flammability limits; Measurement; Numerical analysis; ASHRAE method

1. Introduction

There are a few methods to predict the flammability limits of combustible gases. Burgess and Wheeler found that a product of lower flammability limit and molar heat of combustion is more or less constant for paraffin compounds [1]. Much later than that, Nuzdha et al. proposed a method to predict the values of upper flammability limits based on the molecular structure [2]. Shebeko et al. proposed a group contribution method to predict both lower flammability limits [3] and upper flammability limits [4]. High and Danner applied the group contribution scheme to develop the method of Nuzdha et al. to predict upper flammability limits [5]. According to High and Danner, the average deviation between the observed and predicted values of upper flammability limits are 39.5% for 117 compounds by Nuzdha's method and 26.4% for 181 compounds by High and Danner's method, both of which are not surprisingly good. Later, Suzuki and Ishida proposed a neural network technique [6] as well as multiple linear regression analysis (MLR) [7,8] to predict flammability limits of organic compounds. They state that

the average absolute errors for 150 compounds analyzed by MLR method are 0.3 and 1.3%, respectively, for lower and upper flammability limits, and ones by neural network method are 0.4 and 3.2%, respectively. The predictability of these methods is definitely much better than the foregoing studies mentioned above. However, their methods require extra information on physical constants such as critical temperature, critical pressure, diffusion coefficient, and heat of combustion. This kind of information is, however, not easy to procure particularly for newly developed compounds.

Recently, we have presented an index called F-number, which is defined by the following equation [9,10]:

$$F = 1 - \left(\frac{L}{U}\right)^{0.5} \tag{1}$$

Here L is the lower flammability limit and U the upper flammability limit. According to this definition, F-number takes values ranging from zero to unity depending on the degree of flammability of substances and therefore can be taken as a normalized flammable range. One advantage of adopting this index is that it can be empirically expressed by a simple linear combination of the terms which represent chemical groups in the molecule [9,10]. Therefore, F-number can provide a simple way of carrying out numerical analysis and prediction of flammability of various sub-

* Corresponding author. Tel.: +81-29-861-4770;
fax: +81-29-861-4770.
E-mail address: s.kondo@aist.go.jp (S. Kondo).

stances. The parameters in the expression can be determined by the least-squares fit to the observed values of flammability limits for a wide variety of organic compounds. In fact, a numerical analysis was carried out in a previous paper [10] fitting F-number values to the values calculated from the flammability limits of 238 compounds taken from Ref. [11]. The data there seem to have been obtained with various vessels under various conditions, but were adopted simply because the number of data was large. As a result, it was found that the majority of the literature data are fairly well explained by the analysis. However, there was a certain portion of data for which discrepancy between the observed and calculated values of F-number was unacceptably large.

As for the flammability limits data, there is a well-known problem that the experimental values are strongly dependent on the apparatus and condition used for the measurement. Recently, we have done extensive studies to investigate the appropriate apparatus and condition to measure the flammability limits of combustible gases. At first we studied the effect of ignition source on the measurement and found optimum conditions both for ac discharge ignition [12] and metal wire fusing ignition [13]. Then, we carried out another extensive study to determine the optimum condition for the explosion vessel [14]. One of the results obtained there is that the method for measuring the flammability limits proposed by American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE) is a practical one to obtain reasonable values of flammability limits [14,15].

In a previous paper, we used an ASHRAE-type spherical vessel to re-measured flammability limits of a number of compounds for which unacceptable disagreement was observed between the literature values and F-number predicted values of flammability limits [16]. The compounds measured there were hydrocarbons, oxygen compounds, and nitrogen compounds. Nowadays we are fortunate that high purity samples are easily available from chemical manufacturers. In the present paper, similar measurement was carried out for halogenated compounds for which agreement between the literature values and calculated values was not good in Ref. [10].

In addition, we have carried out a numerical analysis of a set of flammability limits data including those measured in the present study as well as in a previous paper [16]. In the present study, the scheme of numerical calculation used in our previous study [10] was further developed so that the fitting procedure may be done directly to the upper and lower flammability limits instead of fitting to F-number. This method uses only information on the chemical structure of the molecule and can perform outstanding prediction of flammability limits.

2. Experimental method

The experimental setup follows essentially that of ASHRAE method [15], which is a modification of ASTM E-681 [17]. The explosion vessel is a 12 l spherical glass flask and is equipped with a pair of tungsten electrodes for ac electric discharge together with a fan for gas mixing. The electrodes 2 mm in diameter are sharpened at the top and set opposed to each other at 1/4 in. (1 in. = 2.54 cm) distance. The height of the electrodes is one-third from the bottom to the ceiling of the vessel. The ac electric spark is initiated by a neon transformer where the spark duration time was 0.4 s. The temperature of the explosion vessel was kept at 35 °C, and the total pressure of the sample mixture is 760 Torr (1 Torr = 133.32 Pa) unless otherwise stated. With the ASHRAE method, one can expect to obtain values close to what would be obtained in the free space [14].

Gas mixtures were prepared in the explosion vessel by the partial pressure method. MKS baratron was used for the pressure measurement. Mixtures were stirred with a fan in the vessel for 10 min and left to settle for one minute before ignition. The criteria for determining the flammability limit followed that of the ASHRAE method: the mixture is considered flammable if the flame moves upward and outward from the point of ignition to reach an arc of the vessel wall which subtends an angle larger than 90° as measured from the ignition point. The decision of flammability limit was made by watching the flame propagation in the dark. Since the movement of the flame in the flammability limit region inside a spherical vessel of this size is relatively slow, there is no difficulty to determine up to where the flame-front has reached. The ambiguity of determining whether the flame head comes out of the 90° fan constitutes a substantial part of the uncertainties given to the observed values.

The samples were purchased from Tokyo Kasei Co. or Wako Chemicals Co. The purities of the samples are about 98% or so unless otherwise stated. They were used without further purification. The exhaust gas from the experiment was treated with soda lime.

3. Experimental flammability limits

The experimentally obtained values of flammability limits are shown in Table 1. Comparison of the observed values with those in Ref. [11] is of particular interest for the F-number analysis in Ref. [10] was done using that data. In this respect, the observed values are classified into three groups. For the first group compounds, the measurement was essentially confirmation of the literature value and the obtained values agree well to the ones in Ref. [11]. For the second group, the observed values are different from the ones in Ref. [11] and are rather close to the calculated ones in Ref. [10]. For the third group, the observed values neither coincide with the values in Ref. [11] or with the calculated ones in Ref. [10]. In the following, the data in other literature are surveyed as well. The number in parenthesis given to each compound complies with the one in Ref. [10].

Table 1
Flammability limits values re-measured for F-number correlation

	Gas	Chemical formula	Molecular weight	bp (°C)	L_{ref}[a] (%)	U_{ref}[a] (%)	L_{calc}[b] (%)	U_{calc}[b] (%)	L_{obs}[c] (%)	U_{obs}[c] (%)	Flame color[d]		Total pressure (Torr)	Purity (%)
											L	U		
2	Methyl fluoride	CH_3F	34.03	−78.4	6.8	20.3	7.1	21.6	7.1 (0.2)	19.9 (0.4)	Pale blue	Orange/blue	–	98
20	1,1-Difluoroethane(HFC-152a)	CH_3CHF_2	66.05	−25.8	4.0	19.6	4.4	18.5	4.35 (0.05)	17.5 (0.5)	Whitish blue	Orange	–	98
24a	1,1,1-Trifluoroethane	CH_3CF_3	84.04	−47.4	–	–	(6.1)	(22.8)	7.40 (0.15)	17.0 (1.0)	Whitish blue	Orange/blue	–	99
66	Allyl chloride	$CH_2:CHCH_2Cl$	76.53	45	2.9	11.1	2.7	12.2	2.71 (0.03)	11.9 (0.3)	Greenish white	Orange red	–	98
65	Propylene	C_3H_6	42.08	−47.7	2.0	11.1	1.7	12.9	2.15 (0.05)	11.2 (0.5)	Whitish blue	Orange red	–	99.8
36	12-cis-Dichloroethylene	$CHClCHCl(cis)$	96.94	60	5.6	12.8	6.7	15.3	6.8 (0.2)	15.5 (0.5)	Whitish gray	Orange red	–	99
36a	12-trans-Dichloroethylene	$CHClCHCl(trans)$	96.94	48	5.6	12.8	(6.7)	(15.3)	6.8 (0.1)	15.3 (0.3)	Whitish gray	Orange red	–	98
48	Methyl chloroacetate	$C_3H_5O_2Cl$	108.53	131	7.5	18.5	4.4	15.3	4.0 (0.2)[e]	–	Pale blue	–	180[e]	98
62	Propylene dichloride	$C_3H_6Cl_2$	112.99	96.2	3.4	14.5	3.5	10.9	3.3 (0.1)	10.7 (0.7)[e]	Greenish white	Orange red	500[e]	98
104a	1-Chloro-2-methyl-propene-1[f]	$(CH_3)_2C:CHCl$	90.55	84	–	–	(2.0)	(9.9)	2.04 (0.03)	8.7 (0.3)	Greenish white	Orange red	–	95
105	Methallyl chloride	$CH_2C(CH_3)CH_2Cl$	90.55	71–72	3.2	8.1	2	9.9	1.99 (0.03)	9.0 (0.3)	Greenish white	Orange red	–	95
29	Vinyl fluoride	CH_2CHF	46.04	−72.2	2.6	21.7	3.2	21	3.41 (0.06)	25.0 (1.0)	Pale blue	Orange red	–	98
31	Vinyl bromide	CH_2CHBr	106.95	15.8	9.0	15.0	8.2	11.1	6.6 (0.2)	13.5 (0.5)	Whitish orange	Orange red	–	99
34	Vinylidene fluoride	CH_2CF_2	64.03	−86	5.5	21.3	4.9	24.3	4.70 (0.15)	21.5 (0.5)	Whitish blue	Orange red	–	99
37	Trichloroethylene	$ClHC:CCl_2$	131.39	87	8.0	10.5	10.3	15.1	12.2 (0.3)[e]	29 (2)[e]	Whitish gray	Orange red	550/220[e]	98
68	Allyl bromide	$CH_2:CHCH_2Br$	120.98	71.3	4.4	7.3	4.7	9.6	3.85 (0.04)	7.7 (0.3)	Whitish orange	Orange red		98
73	2,3-Dichloropropene	CH_2CClCH_2Cl	110.97	94	2.6	7.8	3.89	11.9	3.31 (0.04)	11.0 (0.4)[e]	Orange white	Orange red	500[e]	97
87	Epichlorohydrin	C_3H_5OCl	92.53	116.1	3.8	21.0	3	15.3	2.5 (0.3)[e]	–	Orange gray		620[e]	99
106	1-Crotyl bromide	$CH_3CH:CHCH_2Br$	135.00	97–99	4.6	12.0	3.33	8.4	2.82 (0.07)	7.4 (0.3)[e]	Whitish orange	Orange red	550[e]	[g]
109	1,3-Butadiene	$CH_2CHCHCH_2$	54.09	−4.4	2.0	12.0	1.4	12.1	1.69 (0.05)	16.0 (0.5)	Whitish blue	Orange red		99

[a] The data from Ref. [11].
[b] The values are from Ref. [10].
[c] Numbers in parenthesis are the estimated errors.
[d] Orange/blue means mixture of orange and blue parts.
[e] Measured under reduced pressures.
[f] Substitute for 1-crotyl chloride ($CH_3CH:CHCH_2Cl$).
[g] Contains 14% 3-bromo-1-butene.

For the first group, we have five compounds in all, i.e., methyl fluoride (#2), 1,1-difluoroethane (#20), an isomer of #24, i.e., 1,1,1-trifluoroethane (#24a), propylene (#65), and allyl chloride (#66). The value of 7.1–19.9% obtained for methyl fluoride is in reasonable agreement with our previous value of 6.8–20.3% measured with a different method [18].

As for 1,1-difluoroethane, our previous measurement is 4.0–19.6% [18], which is a little wider than the present value. Leisenheimer et al. measured the flammable range of this compound with ASTM E681-85 method and obtained the value of 4.5–21.8% [19]. There is another data that the flammability limits are 3.7–18% [20]. Leisenheimer et al. also measured the flammability limits of 1,1,1-trifluoroethane as 7.7–20.9% [19].

For propylene (#65), the values in air, with upward propagation of flame in a 2 in. diameter tube open at the lower end, are 2.40 and 10.3% [21]. For allyl chloride (#66), there is another data of 3.28–11.15%. This was obtained with upward propagation of flame in a 2 in. diameter tube which was open at the firing end [22].

For the second group, we have six compounds, i.e., 1,2-cis-dichloroethylene (#36), 1,2-trans-dichloro-ethylene (#36a), methyl chloroacetate (#48), propylene dichloride (#62), 1-chloro-2-methyl-1-propene (#104a), and methallyl chloride (#105).

For both cis and trans forms of 1,2-dichloroethylene, almost the same values of flammability limits were obtained. Coward and Jones reported that the flammable range of 1,2-dichloroethylene with upward propagation of flame in a 2 in. diameter tube open at its lower end is 9.7–12.8% [23]. In a closed tube 2.25 in. in diameter it was given as 5.6–11.4% [24].

Due to the low vapor pressure, only the lower flammability limit was obtained for methyl chloroacetate (#48) as 4.0% at a total pressure of 180 Torr in this study, whereas the flammable range of 7.5–18.5% was reported in Ref. [11]. Due to a similar reason, the upper limit of propylene dichloride (#62) was measure as 10.7% under a total pressure of 500 Torr while the lower limit is obtained as 3.3% under atmospheric pressure. Jones et al. [25] reported that the lower limit of propylene dichloride 3.4%. The value was obtained with upward propagation of flame in a closed tube 4 in. in diameter and 38 in. in length. The higher limit was 14.5% at 100 °C which was measured with upward propagation in a tube 2.5 in. in diameter and 36 in. in length and was open at the top.

We could not procure sample of 1-crotyl chloride (#104). Instead, we measured flammability limits of 1-chloro-2-methyl-1-propene an isomer of 1-crotyl chloride, whose calculated value is the same as 1-crotyl chloride in the F-number scheme in Ref. [10]. The observed values were in complete accord with the calculated values. On the other hand, Jones and Scott reported that the flammability limits of isocrotyl chloride in air are 4.2 and 19%. This was obtained with upward propagation of flame in a 2 in. diameter tube, open at the lower end [26].

For methallyl chloride (#105), one article reports that the flammable range is 3.2–8.1% [27]. Another report says that the lower flammability limit is 2.3% [28].

For the third group, we have nine compounds, i.e., vinyl fluoride (#29), vinyl bromide (#31), vinylidene fluoride (#34), trichloroethylene (#37), allyl bromide (#68), 2,3-dichloropropene (#73), epichlorohydrin (#87), crotyl bromide (#106), and 1,3-butadiene (#109).

For vinyl fluoride, the flammable range listed in Ref. [11] is somehow slightly shifted to lower concentrations than the present value. In reverse, the flammable range of vinyl bromide in Ref. [11] is shifted to higher concentrations than the present value. As for vinylidene fluoride, the lower flammability limit in Ref. [11] is somewhat larger than the present value.

The flammable range of trichloroethylene is of particular interest. At first, Jones and Scott reported that trichloroethylene vapor does not form flammable mixtures with air at ordinary temperatures and pressures [29]. Later, Perlee et al. reported that the flammable range in a 2 l spherical glass vessel at 100 °C at ambient pressure is 10.5–41% [30]. They also measured the lower limit in a tube 17.8 cm in diameter at 30 °C and obtained the value of 11.8% [30], which is close to the present value of 12.2% measured under pressure of 550 mmHg.

Coward and Jones reported that the flammability limits of allyl bromide (#68) are 4.36 and 7.25%, if they are measured with upward propagation of flame in a 2 in. diameter tube, open at the firing end [22]. This result is not far from the present values of 3.85 and 7.7%, respectively.

Because of the low vapor pressure, the upper flammability limit of 2,3-dichloropropene (#73) was measure as 11.0% at a total pressure of 500 Torr in the present study. Similarly, the lower flammability limit of epichlorohydrin (#87) was measured as 2.5% at a total pressure of 620 Torr. The upper limit of this compound was not obtained in the present study.

The vapor pressure of crotyl bromide (#106) is not enough to measure the upper limit under ambient pressure as well. The value of 7.4% was obtained under a total pressure of 550 Torr. There is no other literature data for crotyl bromide, but the flammability limits of isocrotyl bromide are reported to be 6.4 and 12%, which are obtained with upward propagation of flame in a 2 in. diameter tube open at the lower end [31].

Jones and Kennedy reported that the flammability limits of 1,3-butadiene (#109) are 2.0 and 11.5%, when measured with upward propagation of flame in a 2 in. diameter tube open at the lower end [32]. This value is to be compared to the present value of 1.69 and 16.0%.

4. Expression of flammability limits in terms of chemical structure

The upper and lower flammability limits, U and L, are connected with F-number, which is given by Eq. (1), and

the geometric mean G of flammability limits, which is given by $(UL)^{0.5}$, through the following equations [10]:

$$L = G(1 - F) \tag{2}$$

and

$$U = \frac{G}{1 - F} \tag{3}$$

The value of G is in general close to but different from the stoichiometric concentration C_{st}. If analytical forms of both F and G are given in terms of parameters related to chemical structure of molecule, it is possible to directly carry out numerical analysis of flammability limits.

In the present study, the analytical forms of these quantities are defined a little different from those in Ref. [10]. In Ref. [10], F-number was a product of two different factors, skeletal factor and substitution factor. However, the separation into two factors does not have much meaning. Here, we have merged them into one to have a simpler form of equation. On the other hand, a very simple form was adopted for the geometric mean of upper and lower flammability limits in Ref. [10]. It was given by the stoichiometric concentration C_{st} multiplied by a correction factor. In the present study, we adopted a similar form as that of F for the correction factor of G. This is done in order to improve the accuracy of predicting the values of flammability limits.

In constructing the analytical forms of F and G, care was particularly taken to make best interpretation of flammability limits of halogenated compounds. Actually, the analytical expressions of F and G were given as follows:

$$
\begin{aligned}
F = p_1(&1 + p_2 C_1 + p_3 R_{OE} + p_4 R_{EP} + p_5 R_{COO} \\
&+ p_6 R_{RNG} + p_7 R_{US} + p_8 R_F + p_9 R_{Cl} + p_{10} R_{Br} \\
&+ p_{11} R_{OH} + p_{12} R_{CF_2} + p_{13} R_{CX_2} + p_{14} R_{CF_3} \\
&+ p_{15} R_{CX_3} + p_{16} R_{US\text{-}F} + p_{17} R_{US\text{-}X})
\end{aligned} \tag{4}
$$

and

$$
\begin{aligned}
G = C_{st}[&1 + q_1(M - 32) + q_2 R_{OE} + q_3 R_{EP} + q_4 R_{COO} \\
&+ q_5 R_{RNG} + q_6 R_{US} + q_7 R_F + q_8 R_{Cl} \\
&+ q_9 R_{Br} + q_{10} R_{US\text{-}F} + q_{11} R_{US\text{-}X}]
\end{aligned} \tag{5}
$$

Here, M denotes the molecular weight and, p_1–p_{17} are coefficients for various terms in F-number to be determined from the fitting procedure to the observed data. q_1–q_{11} are coefficients for various terms in geometric mean to be determined from the fitting procedure to the observed data. C_1 takes the value of one or zero according to whether the molecule is a compound of mono-carbon-skeleton or not. R_{OE}, R_{EP}, and R_{COO} denote numbers of ether, epoxy, and ester groups in the molecule, respectively, divided by skeletal carbon number minus one. R_{US} denotes the total number of un-saturation in the carbon skeleton divided by skeletal carbon number minus one. R_{RNG} denotes number of (aliphatic) rings divided by skeletal carbon number minus 1. R_F, R_{Cl},

R_{Br}, and R_{OH} denote numbers of F, Cl, Br, and OH group, respectively, divided by the total number of hydrogen atoms in the corresponding pure hydrocarbon molecule. R_{CF_2} and R_{CF_3} denote numbers of CF_2 and CF_3 groups divided by skeletal carbon number. R_{CX_2} and R_{CX_3} denote numbers of CX_2 and CX_3 groups divided by skeletal carbon number, where X_2 and X_3 are double halogens other than F_2 and triple halogens other than F_3, respectively. $R_{US\text{-}F}$ and $R_{US\text{-}X}$ denote number of halogen atoms attached to unsaturated carbon atom divided by the total number of hydrogen atoms in the corresponding pure hydrocarbon molecule.

In the present scheme, since the expression of G is given in terms of quite a number of parameters, we do not have to much concern about the definition of the stoichiometric concentration itself, though it does depend on the chemical reaction of combustion as discussed in Ref. [10]. At any rate, it is assumed that if the number of H atoms are larger than or equal to the number of F atoms in a fuel molecule, F atoms are converted to HF in the combustion reaction. Otherwise, they are converted to CF_4. Similarly, if there are enough H atoms available, Cl and Br atoms are converted to HCl and HBr, respectively. Otherwise, they are converted to Cl_2 and Br_2 molecules, respectively. The priority concerning acquisition of H atoms in the reaction was assumed highest for F atoms, next for Cl atoms, and the last for Br atoms.

5. Numerical analysis of flammability limits

The least squares analysis was carried out to fit directly to the values of upper and lower flammability limits of 99 compounds in total, in which the newly obtained values of flammability limits in the present study as well as the ones in Ref. [16] were included. There are 23 such compounds.

Table 2
Parameter values determined by F-number analysis

Parameter	F-number			Geometric mean		
	p_i	Value	S.D.	q_i	Value	S.D.
Main coefficient	1	0.561	0.012	–	–	–
(M-32)	–	–	–	1	0.00376	0.00042
C1	2	−0.218	0.018	–	–	–
Ether	3	−0.024	0.180	2	−0.071	0.103
Epoxy	4	0.606	0.104	3	0.246	0.184
Ester	5	0.089	0.059	4	0.098	0.089
Aliphatic ring	6	−0.024	0.116	5	0.259	0.147
Un-saturation	7	0.258	0.023	6	0.425	0.056
F	8	−0.384	0.141	7	−0.013	0.079
Cl	9	−0.810	0.127	8	−0.407	0.096
Br	10	−2.764	0.388	9	−1.483	0.354
OH	11	−0.489	0.206	–	–	–
CF2	12	−0.004	0.047	–	–	–
CX2	13	−0.055	0.036	–	–	–
CF3	14	−0.238	0.102	–	–	–
CX3	15	−0.054	0.044	–	–	–
US-F	16	−0.066	0.175	10	−0.684	0.167
US-Cl	17	−0.121	0.203	11	−0.770	0.214

Table 3
Result of F-number analysis: observed and calculated values of L, U, G, and F

No.	Compound	Ref. [3]	L	L_{cal}	U	U_{cal}	G	G_{cal}	F	F_{cal}	No-fit	New
1	CH$_4$	(1)	4.9	5.00	15.8	15.87	8.80	8.91	0.44	0.44		◯
2	C$_2$H$_6$	(14)	3.0	2.46	12.5	12.76	6.12	5.61	0.51	0.56		
3	C$_3$H$_8$	(53)	2.1	1.85	9.5	9.57	4.47	4.20	0.53	0.56		
4	Butane	(88)	1.6	1.51	8.4	7.81	3.67	3.43	0.56	0.56		
5	Isobutane	(89)	1.8	1.51	8.4	7.81	3.89	3.43	0.54	0.56		
6	Pentane	(138)	1.5	1.29	7.8	6.69	3.42	2.94	0.56	0.56		
7	Isopentane	(139)	1.4	1.29	7.6	6.69	3.26	2.94	0.57	0.56		
8	2,2-Dimethylpropane	(140)	1.4	1.29	7.5	6.69	3.24	2.94	0.57	0.56		
9	Hexane	(166)	1.1	1.14	7.5	5.91	2.87	2.60	0.62	0.56		
10	Isohexane	(167)	1.0	1.14	7.0	5.91	2.65	2.60	0.62	0.56		
11	2-Methylpentane	(168)	1.2	1.14	7.0	5.91	2.90	2.60	0.59	0.56		
12	3-Methylpentane	(169)	1.2	1.14	7.0	5.91	2.90	2.60	0.59	0.56		
13	2,2-Dimethylbutane	(170)	1.2	1.14	7.0	5.91	2.90	2.60	0.59	0.56		
14	2,3-Dimethylbutane	(171)	1.2	1.14	7.0	5.91	2.90	2.60	0.59	0.56		
15	n-C$_7$H$_{16}$	(198)	1.1	1.03	6.7	5.35	2.71	2.35	0.59	0.56		
16	Isoheptane	(199)	1.0	1.03	6.0	5.35	2.45	2.35	0.59	0.56		
17	2,3-Dimethylpentane	(200)	1.1	1.03	6.7	5.35	2.71	2.35	0.59	0.56		
18	Octane	(209)	1.0	0.95	6.5	4.91	2.55	2.16	0.61	0.56		
19	Trimethylpentane	(210)	1.1	0.95	6.0	4.91	2.57	2.16	0.57	0.56		
20	Nonane	(221)	0.8	0.88	2.9	4.57	1.52	2.01	0.47	0.56	△	
21	Tetramethylpentane	(222)	0.8	0.88	4.9	4.57	1.98	2.01	0.60	0.56		
22	3,3-Diethylpentane	(223)	0.7	0.88	5.7	4.57	2.00	2.01	0.65	0.56		
23	Decane	(229)	0.8	0.83	5.4	4.30	2.08	1.89	0.62	0.56		
24	C$_2$H$_4$	(28)	2.7	2.71	36.0	31.24	9.86	9.20	0.73	0.71		
25	Propylene	(65)	2.15	2.04	11.2	15.16	4.91	5.56	0.56	0.63		◯
26	1-Butene	(99)	1.6	1.63	10.0	10.63	4.00	4.16	0.60	0.61		
27	*cis*-2-Butene	(100)	1.7	1.63	9.0	10.63	3.91	4.16	0.57	0.61		
28	*trans*-2-Butene	(101)	1.8	1.63	9.7	10.63	4.18	4.16	0.57	0.61		
29	2-Methylpropene	(102)	1.8	1.63	9.6	10.63	4.16	4.16	0.57	0.61		
30	1-Pentene	(150)	1.5	1.37	8.7	8.42	3.61	3.40	0.58	0.60		
31	3-Methyl-1-butene	(151)	1.5	1.37	9.1	8.42	3.69	3.40	0.59	0.60		
32	Trimethylpentene	(211)	0.88	0.98	6.0	5.59	2.30	2.34	0.62	0.58		◯
33	C$_2$H$_2$	(40)	2.5	2.12	100	94.14	15.81	14.13	0.84	0.85		
34	1,3-Butadiene	(109)	1.69	1.72	16.0	14.62	5.20	5.01	0.68	0.66		◯
35	Isoprene	(152)	1.5	1.44	8.9	10.68	3.65	3.92	0.59	0.63		
36	1,4-Hexadiene	(174)	1.18	1.25	7.9	8.57	3.05	3.27	0.61	0.62		◯
37	Cyclopropane	(84)	2.4	2.32	10.4	11.64	5.00	5.19	0.52	0.55		
38	Cyclohexane	(189)	1.3	1.25	8.0	6.42	3.22	2.84	0.60	0.56		
39	Methylcyclopentane	(190)	1.0	1.25	8.4	6.42	2.90	2.84	0.65	0.56		
40	Ethylcyclobutane	(191)	1.2	1.25	7.7	6.42	3.04	2.84	0.61	0.56		
41	Cycloheptane	(205)	1.1	1.12	6.7	5.73	2.71	2.53	0.59	0.56		
42	Methylcyclohexane	(206)	1.2	1.12	6.7	5.73	2.84	2.53	0.58	0.56		
43	Ethylcyclopentane	(207)	1.1	1.12	6.7	5.73	2.71	2.53	0.59	0.56		
44	Ethylcyclohexane	(215)	0.9	1.01	6.6	5.21	2.44	2.30	0.63	0.56		
45	Diethylcyclohexane	(230)	0.8	0.87	6.0	4.49	2.19	1.98	0.63	0.56		
46	Methylcyclopentadiene	(192)	1.3	1.38	7.6	9.32	3.14	3.58	0.59	0.62		
47	CH$_3$F	(2)	7.1	7.57	19.9	20.00	11.89	12.31	0.40	0.38		◯
48	CH$_3$Cl	(3)	8.1	8.01	17.4	17.57	11.87	11.86	0.32	0.32		
49	CH$_3$Br	(4)	10.1	10.07	16.0	11.18	12.71	10.61	0.21	0.05	△	
50	CH$_2$FCl	(9)	14.4	14.13	26.5	22.62	19.53	17.88	0.26	0.21		
51	CH$_2$F$_2$	(10)	13.3	12.46	29.3	27.49	19.74	18.51	0.33	0.33		
52	CH$_2$Cl$_2$	(11)	14.0	14.66	22.0	20.29	17.55	17.25	0.20	0.15		
53	C$_2$H$_5$Cl	(15)	3.8	3.54	15.4	13.37	7.65	6.88	0.50	0.49		
54	C$_2$H$_5$Br	(16)	6.8	4.75	8.0	9.75	7.38	6.80	0.08	0.30		
55	CH$_3$CHF$_2$	(20)	4.35	4.46	17.5	16.93	8.72	8.69	0.50	0.49		◯
56	CH$_2$ClCH$_2$Cl	(21)	6.2	5.10	16.0	14.61	9.96	8.63	0.38	0.41		
57	CH$_2$FCHF$_2$	(24)	6.2	6.19	22.6	20.54	11.84	11.28	0.48	0.45		
58	CH$_3$CF$_3$	(24a)	7.4	8.43	17.0	15.09	11.22	11.28	0.34	0.25		◯
59	CH$_3$CClF$_2$	(25)	6.8	7.10	18.2	17.78	11.12	11.24	0.39	0.37		
60	CH$_3$CFCl$_2$	(26)	9.0	7.53	15.4	16.68	11.77	11.21	0.24	0.33		
61	CH$_3$CCl$_3$	(27)	7.5	7.95	12.5	15.69	9.68	11.17	0.23	0.29		
62	Propyl chloride	(54)	2.6	2.48	11.1	10.08	5.37	5.00	0.52	0.50		
63	Isopropyl chloride	(55)	2.8	2.48	10.7	10.08	5.47	5.00	0.49	0.50		

Table 3 (*Continued*)

No.	Compound	Ref. [3]	L	L_{cal}	U	U_{cal}	G	G_{cal}	F	F_{cal}	No-fit	New
64	Propylene dichloride	(62)	3.3	3.31	10.7	10.83	5.94	5.99	0.44	0.45		○
65	Butyl chloride	(90)	1.8	1.94	10.1	8.26	4.26	4.01	0.58	0.52		
66	Isobutyl chloride	(91)	2.0	1.94	8.8	8.26	4.20	4.01	0.52	0.52		
67	Butyl bromide	(92)	2.6	2.50	6.6	7.08	4.14	4.21	0.37	0.41		
68	Amyl chloride	(141)	1.6	1.62	8.6	7.10	3.71	3.39	0.57	0.52		
69	Isoamyl chloride	(142)	1.5	1.62	7.4	7.10	3.33	3.39	0.55	0.52		
70	*tert*-Amyl chloride	(143)	1.5	1.62	7.4	7.10	3.33	3.39	0.55	0.52		
71	CH_2CHF	(29)	3.41	3.61	25.0	28.18	9.23	10.08	0.63	0.64		○
72	CH_2CHCl	(30)	3.6	4.10	33.0	22.65	10.90	9.63	0.67	0.57	△	
73	CH_2CHBr	(31)	6.6	6.18	13.5	12.65	9.44	8.84	0.30	0.30		○
74	CH_2CF_2	(34)	4.7	4.80	21.5	26.84	10.05	11.35	0.53	0.58		○
75	CH_2CCl_2	(35)	6.5	6.01	15.5	17.47	10.04	10.25	0.35	0.41		
76	*cis*-CHClCHCl	(36)	6.8	5.70	15.5	18.44	10.27	10.25	0.34	0.44		○
77	*trans*-CHClCHCl	(36a)	6.8	5.70	15.3	18.44	10.20	10.25	0.33	0.44		○
78	$CHClCCl_2$	(37)	12.2	6.23	29.0	12.11	18.81	8.69	0.35	0.28	△	○
79	CF_2CF_2	(38)	10.0	9.39	50.0	30.93	22.36	17.04	0.55	0.45	△	
80	CF_2CFCl	(39)	8.4	8.60	16.0	20.53	11.59	13.29	0.28	0.35		
81	Allyl chloride	(66)	2.71	2.89	11.9	14.75	5.68	6.53	0.52	0.56		○
82	1-Chloropropylene	(67)	4.5	2.67	16.0	12.98	8.49	5.89	0.47	0.55	△	
83	Allyl bromide	(68)	3.85	4.05	7.7	10.35	5.44	6.47	0.29	0.37		○
84	1,3-Dichloropropene	(72)	5.3	3.73	14.5	13.28	8.77	7.03	0.40	0.47	△	
85	2,3-Dichloropropene	(73)	3.31	3.73	11.0	13.28	6.03	7.03	0.45	0.47		○
86	2-Chlorobutene-2	(103)	2.3	2.03	9.3	9.77	4.62	4.46	0.50	0.54		
87	1-Crotyl chloride	(104)	4.2	2.15	19.0	10.74	8.93	4.81	0.53	0.55	△	
88	$CHCl=C(CH_3)2$	(104a)	2.04	2.15	8.7	10.74	4.21	4.81	0.52	0.55		○
89	Methallyl chloride	(105)	1.99	2.15	9.0	10.74	4.23	4.81	0.53	0.55		○
90	1-Crotyl bromide	(106)	2.82	2.88	7.4	8.43	4.57	4.93	0.38	0.42		○
91	Chloro-13-butadiene	(110)	4.0	2.25	20.0	12.16	8.94	5.23	0.55	0.57	△	
92	2,3-Dichlorobutadiene	(111)	1.0	2.84	12.0	10.61	3.46	5.49	0.71	0.48	△	
93	$CH_2ClCH_2OH(l)$	(22)	4.9	4.83	15.9	15.37	8.83	8.62	0.44	0.44		
94	Methyl chloroacetate	(48)	4.0	4.00	18.5	18.50	8.60	8.60	0.54	0.54		○
95	Epichlorohydrin	(87)	2.5	2.50	21.0	21.00	7.25	7.25	0.65	0.65		○
96	CH_3OCF_3(HFE-143m)[a]	–	10.5	10.99	21.5	18.97	15.02	14.44	0.30	0.24		
97	$CH_3OCF_2CF_3$(HFE-245mc)[a]	–	10.5	9.50	13.5	18.55	11.91	13.28	0.12	0.28	△	
98	CF_3CHFCH_2F(HFC-245eb)[b]	–	9.6	7.53	10.7	15.03	10.14	10.64	0.05	0.29	△	
99	$CF_3CH_2CH_2CF_3$(HFC-356mffm)[b]	–	7.3	6.50	9.6	10.99	8.37	8.45	0.13	0.23		

[a] The observed values of flammability limits are from Ref. [25].
[b] The observed values of flammability limits are from Ref. [26].

Also, the flammability limits data of a few multi-fluorinated compounds were employed in the analysis [33,34]. For completeness, we added the data of pure hydrocarbons other than aromatics in the calculation.

Table 2 shows the values of parameters p_1–p_{17} and q_1–q_{11} resulting from the analysis. The value of parameter p_2 has been found to be negative, which means that the compounds of mono-carbon skeleton are less flammable than other compounds. The value of p_7 is positive means that unsaturated compounds are more flammable than the saturated ones. The flammability enhancing effect of unsaturated bonds is well known. The parameters p_8–p_{10} are of particular interest. These are concerned with halogen substitution to H atoms. The values of these parameters are negative and the substitution of halogen atoms decreases the flammability; the effect is larger for chlorine than that for fluorine and the largest for bromine. Compared with these, the magnitude of p_{14} is rather small, which means that the flame quenching effect of CF_3 group is not worthy of special mention.

As for q_i parameters, several things are noted as well. One is a large positive value of q_6. This may be relevant to the tendency toward explosive decomposition of such molecules as acetylene and ethylene. This tendency is reduced if the hydrogen atoms attached to a carbon atom adjacent to an unsaturated bond are substituted for halogen atoms, which appears as large negative values of q_{10} and q_{11}. On the other hand, the large and negative values of q_8 and in particular q_9 may be due to the fact that Cl and Br atoms tend to yield Cl_2 and Br_2 molecules instead of HCl and HBr in the combustion reaction, which has been discussed in Ref. [10].

On the other hand, Table 3 shows the observed and calculated values for the individual compounds. The observed and calculated values of lower flammability limits are listed in the fourth and fifth columns, and those of upper flammability limits in sixth and seventh columns. The eighth and ninth columns are for the observed and calculated values for geometric mean and 10th and 11th columns are for F-number. Agreement between the observed and calculated values is good though there are some for which agreement is poor.

The average relative deviation of the calculated values from the observed ones is 9.3% for the lower flammability limits, 14.6% for the upper limits, and 10.2% in total. Similarly, the average relative deviation is 12.1% for F and 8.2% for G. For comparison, we did the same procedure employing the old flammability limits data for the 23 compounds. The residual value for the least squares calculation was 14 300 as compared to 6480 as obtained in the above study. The average relative deviation of the calculated values from the observed was 15.2% for the lower flammability limits, 16.9% for the upper limits, and 15.5% in total. Similarly, the average relative deviation was 16.2% for F and 10.1% for G. Superiority of the present data over the previous one is apparent.

As regards the compounds for which extreme discrepancy is noted between the observed and calculated flammability limits, a triangle mark is put in 12th column of Table 3. Number of such compounds is 12. Most of them are halogenated ones. The reason for the discrepancy is not clear but may be different for different compounds. There is no question that one possibility is differences in equipment and condition used for measurements. Also, there must be some for which the sample purity was not good. In this respect, we are happy indeed because the techniques for chemical analysis and purification have recently made a big progress and nowadays high purity samples are available from gas makers.

On the other hand, a circle in 13th column indicates that the data are from the new measurement, either measured in the present work or in Ref. [16]. As stated, there are 23 such compounds. It is remarkable that there is nothing but only one among these compounds that has a triangle mark in 12th column. The exception is trichloroethylene. The flame supported by trichloroethylene is known for its characteristic double structure [35]. Probably the wide flammable range of this compound is related to this phenomenon.

6. Conclusion

The flammability limits measurement was carried out for the halogenated compounds for which the F-number analysis made in a previous study could not explain the literature values well [10]. As a result, it has been found that the newly measured values are classified into three groups. For one group of compounds, the present values of flammability limits agree well to the literature values. For the second group, the observed values of flammable range are different from the literature values but are rather close to the calculated ones. For the third group, the observed values neither coincide to the literature values nor to the calculated ones. For the second and third group compounds, revision of flammability limits data in Ref. [11] is recommended.

In order to make a numerical analysis of flammability limits, the scheme of interpreting the flammability limits developed previously [9,10] was revised and the fitting procedure was directly done to upper and lower flammability lim-

its instead of fitting to F-number. Numerical analysis was carried out for a set of flammability limits data of 99 compounds in total. They include all halogenated compounds available together with pure hydrocarbons, among which 23 compounds newly measured either in the present study or in Ref. [16] are involved. It has been obtained that the average relative deviation between the observed and calculated values is 9.3% for the lower flammability limit, 14.6% for the upper limit, and 10.2% in total. The compounds for which discrepancy between the observed and calculated values is noted are mostly due to old measurements.

The present scheme of numerical analysis is very simple and uses only information on the chemical structure of molecules to predict the flammability limits of organic compounds. Still the performance level of the method has been found excellent. For compounds for which deviation between the observed and calculated values of flammability limits is noted, it is desirable that the values be reexamined. We are planning to apply further the present numerical analysis to a wider variety of compounds.

References

[1] M.J. Burgess, R.V. Wheeler, J. Chem. Soc. 99 (1911) 2013.
[2] L. Nuzdha, M.A. Glinkin, E.E. Rafales-Lamarka, N.F. Tyupalo, Sov. Chem. Ind. 11 (1979) 230.
[3] Y.N. Shebeko, A.V. Ivanov, T.M. Dmitrieva, Sov. Chem. Ind. 15 (1983) 311.
[4] Y.N. Shebeko, A.V. Ivanov, E.N. Alekhina, A.A. Barmakova, Sov. Chem. Ind. 15 (1983) 1203.
[5] M.S. High, R.P. Danner, Ind. Eng. Chem. Res. 26 (1987) 1395.
[6] T. Suzuki, M. Ishida, Fire Mater. 19 (1995) 179.
[7] T. Suzuki, Fire Mater. 18 (1994) 333.
[8] T. Suzuki, K. Koide, Fire Mater. 18 (1994) 393.
[9] S. Kondo, M. Iwasaka, K. Tokuhashi, H. Nagai, M. Kaise, J. High Pressure Gas Safety Inst. Jpn. 31 (1994) 272–276 (in Japanese).
[10] S. Kondo, Y. Urano, K. Tokuhashi, A. Takahashi, K. Tanaka, J. Hazard. Mater. A 82 (2001) 113–128.
[11] NFPA, Fire hazard properties of flammable liquids, gases, volatile solids, in: Fire Protection Guide on Hazardous Materials, 9th ed., 325M, 1984.
[12] S. Kondo, Y. Urano, A. Takahashi, K. Tokuhashi, Combust. Sci. Technol. 145 (1999) 1–15.
[13] A. Takahashi, Y. Urano, K. Tokuhashi, H. Nagai, M. Kaise, S. Kondo, J. Loss Prevent. Process Ind. 11 (1998) 353–360.
[14] A. Takahashi, Y. Urano, K. Tokuhashi, S. Kondo, J. Hazard. Mater. A 105 (2003) 27–37.
[15] American Society of Heating, Refrigerating and Air-conditioning Engineers, Number designation and safety classification of refrigerants—third public review, BSR/ASHRAE Addendum "p" to ANSI/ASHRAE 34-1992, Atlanta, GA, 2000.
[16] S. Kondo, A. Takahashi, K. Tokuhashi, J. Hazard. Mater. A 100 (2003) 27–36.
[17] American Society of Testing and Materials, Designation: E681-94, Philadelphia, 1994.
[18] Y. Urano, S. Horiguchi, K. Tokuhashi, M. Iwasaka, S. Kondo, J. High Pressure Gas Safety Inst. Jpn. 27 (1990) 416–422 (in Japanese).
[19] B. Leisenheimer, W. Leuckel, L. Oellrich, Explosibility characteristics of some alternative refrigerants, in: Proceedings of the International Symposium on Hazards, Prevention and Mitigation of Industrial Explosions, Bergen, Norway, June 1996.

[20] I. Mellan, Source Book of Industrial Solvents, vol. 2: Halogenated Hydrocarbons, Reinhold, 1957.

[21] G.W. Jones, R.E. Kennedy, Bureau Mines Rep. Investig. 3395 (1938) 1.

[22] H.F. Coward, G.W. Jones, US Bureau Mines Bull. 503 (1952) 1.

[23] H.F. Coward, G.W. Jones, Ind. Eng. Chem. 18 (1926) 970–974; H.F. Coward, G.W. Jones, Ind. Eng. Chem. 19 (1927) 430–431.

[24] A.H. Nuckollis, Comparative life, fire, and explosion hazards of common refrigerants, Rep. Underwriter's Lab. Misc. Hazards 2375 (1933) 118.

[25] G.W. Jones, W.E. Miller, H. Seaman, Ind. Eng. Chem. 25 (1933) 771–773.

[26] D.F. Marsh, Univ. Calif. Pubs. Pharmacol. 1 (1940) 31–39.

[27] K. Nabert, G. Schon, Sicherheitstechnishe Kennzahlen brennbarer Gase und Dampfe, Physikalish-Technichen Bundesanstalt, 2 Aufl., 1963.

[28] Natl. Fire Protect. Assoc., National Fire Codes 325-12, vol. 1, 1964–1965.

[29] G.W. Jones, G.S. Scott, US Bureau Mines Rep. Investig. 3666 (1942) 1.

[30] H.E. Perlee, G.S. Scott, G.H. Martindill, US Bureau Mines Rep. Investig. 6766 (1966) 1.

[31] D.F. Marsh, Univ. Calif. Pubs. Pharmacol. 1 (1940) 31–39.

[32] H.F. Coward, R.E. Kennedy, US Bureau Mines Rep. Investig. 3565 (1941) 1.

[33] Y. Urano, A. Takahashi, S. Kondo, in: Proceedings of the 31st Annual Meeting of Japan Safety Engineering Society, 1998, p. 75 (in Japanese).

[34] I.R. Shankland, G.M. Knopeck, D.J. Williams, in: Proceedings of the UTECH Asia'95, Singapore, Paper 20, 1995.

[35] B. Kaesche-Krischer, Combust Flame 6 (1962) 183–191.