Calculation of minimum ignition energy of premixed gases

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Abstract

The minimum ignition energy of premixed gases has been calculated by using two theoretical expressions and compared with the experimental data. One expression considers the amount of energy that the minimal flame should have, and the other the heat loss from the surface of the minimal flamelet. The former is a cubic function of the quenching distance while the latter is a quadratic function of quenching distance. It has been found that the latter expression gives a better fit to the experimental data than the former, though the discrepancy is considerable even for the latter expression. The calculated widths of the fronts of the minimal flame for various fuels were about one-order of magnitude smaller than the corresponding experimentally determined quenching distances, although no clear correlation relationship between the two quantities was found.
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1. Introduction

There are a variety of indices to express flammability characteristics of fuels. This is because the combustion is a complicated phenomenon and the flammability hazard has to be assessed from various points of view. The minimum ignition energy is one of the most important to consider the potential hazard of various flammable gases and vapors. Two theoretical expressions for calculating the minimum ignition energy are known: one is based on the amount of energy that the minimal incipient flame contains, whereas the other is based on the heat loss from the surface of minimal flame [1]. Since these expressions are

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Nomenclature

C_{av}	molar heat capacity at constant pressure averaged for temperature range from T_u to T_b
C_p	molar heat capacity at constant pressure
d	quenching distance
E_{min}	minimum ignition energy
M	molecular weight
R	gas constant
S_{av}	burning velocity averaged for temperature range from T_u to T_b
S_u	burning velocity
T_b	burnt gas temperature
T_u	unburnt gas temperature

Greek letters

δ	width of flame front
λ_{av}	heat conductivity averaged for the temperature range from T_u to T_b
μ	coefficient of viscosity
ρ_b	molar density of burnt gas at temperature T_b
ρ_u	molar density of unburnt gas at temperature T_u

very simple and approximate, it is of interest to know how precisely they comply with the experimental data.

In the equation based on the energy contained in the minimal flame, the minimum ignition energy is apparently a cubic function of quenching distance, while in the heat loss expression it is a quadratic function of quenching distance. On the other hand, it is known that there is a close relationship between the minimum ignition energy and quenching distance. According to Lewis and von Elbe, the minimum ignition energy is proportional to the cubic power of quenching distance for strong flames and proportional to the square of quenching distance for less strong flames [2]. Comparison of the two expressions is also of interest from this point of view.

The purpose of the present paper is to apply the existing data to the theoretical equations of the minimum ignition energy and examine their validity. Since the data available for the minimum ignition energy and quenching distance are mainly those at the stoichiometric concentration [3], the present calculations will mainly be carried out for the stoichiometric concentrations as well.

2. Theoretical basis

The issue of the minimum ignition energy has extensively been discussed among others by Lewis and von Elbe [1,2]. Therefore, a brief summary of the theory is given here.

In order to ignite a flammable gas mixture it is necessary to give the mixture a certain minimum energy at a spot in a minute. The amount of energy should be enough to heat up a

certain minimal sphere of the mixture to the flame temperature. If the diameter of the sphere can be approximated by the quenching distance d, one may obtain the following equation.

$$E_{min} = \frac{1}{6}\pi d^3 \rho_b C_{av}(T_b - T_u) \tag{1}$$

Here, ρ_b is the molar density of the burnt gas at temperature T_b (the flame temperature), and T_u the unburnt gas temperature (room temperature). The term $C_{av}(T_b - T_u)$ represents an amount of enthalpy required to heat up one mole of burnt gas from T_u to T_b, where C_{av} represents the molar heat capacity at constant pressure averaged for the temperature range.

On the other hand, whether or not the incipient minimal flame begins to grow up outward depends on the balance between the heat of reaction and the heat loss from the surface of the sphere. The minimum ignition energy may be given by the heat loss from the surface of the sphere within a time interval of δ/S_{av}, where δ is the width of flame front and S_{av} the average burning velocity. From this, one obtains the following equation.

$$E_{min} = \pi d^2 \frac{\lambda_{av}(T_b - T_u)}{S_{av}} \tag{2}$$

Here, d is the quenching distance and λ_{av} the heat conductivity averaged for the temperature range. Since there is a large temperature difference between both ends of the flame front (T_u and T_b), the value of heat conductivity must be averaged for the temperature range. On the other hand, S_{av} has been introduced to derive the time for the gas to pass through the width of flame front to complete the combustion reaction. Therefore, the value averaged for the temperature range has to be used as well.

The data of the quenching distance and burning velocity at room temperature used for the calculation as well as the data of minimum ignition energy have been taken from NACA Report 1300 [3]. The data of flame temperature are calculated values of adiabatic flame temperatures. The data of heat capacity and coefficient of heat conductivity at different temperatures have been taken from other sources [4,5] and used to obtain equations to estimate approximate values at higher temperatures.

3. Intermediate calculations of key parameters

3.1. Average values of heat capacity

As stated, the term $C_{av}(T_b - T_u)$ in Eq. (1) is the enthalpy required to heat the burnt gas up to the flame temperature, and therefore C_{av} is the temperature averaged value. Availability of experimental data of heat capacity is limited for relatively low temperatures though. In the present study, the following method has been adopted to estimate the average values.

Fig. 1 shows a plot of experimental values of molar heat capacity against the number of atoms in the molecule for 61 compounds the majority of which are simple organic compounds. Though the dispersion of data points is not so small at room temperature, rapidly it becomes small for higher temperatures and the data points for a given temperature become distributed neatly along a straight line which goes through the origin. This fact suggests that the heat capacity at higher temperatures can be estimated only if the number of atoms in the fuel molecule is known. In the present case, it is advantageous that the contribution
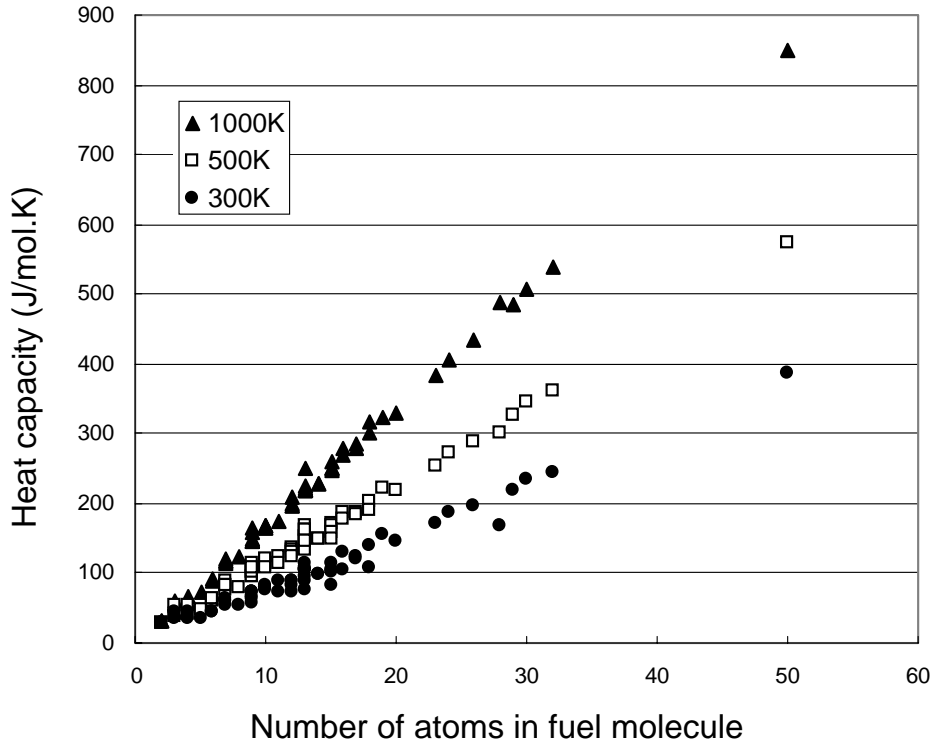
Fig. 1. Plot of heat capacity vs. number of atoms in molecule.

of the values at higher temperatures to the average value is much larger than that of lower temperatures, for the value of heat capacity in general becomes large as the temperature rises. Thus, the value of heat capacity can be approximated by a linear function of the number of atoms in the molecule as follows.

$$C_p = A + Bn \tag{3}$$

Here, the coefficients A and B are functions of temperature T. A quadratic function of absolute temperature has been assumed for each of them. Then, the values of the six coefficient in the following function have been obtained by the least squares fit to the observed values of 61 compounds in total. The temperature range of the data are from 300 to 1500 K for the widest case.

$$C_p = (a + bT + cT^2) + (d + eT + fT^2)n \tag{4}$$

As a result, the values of the coefficients have been determined as $a = 9.40$, $b = -0.0231$, $c = 0.00000912$, $d = 0.909$, $e = 0.0241$, and $f = -0.00000775$, where C_p is expressed in units of J/(mol K). Fig. 2 shows a general feature of the fitting to the 523 data in total for the 61 compounds.

It is to be noticed, however, that since the adoption of quadratic functions is an expedient approximation, one must be careful to extrapolate them to the temperature range where
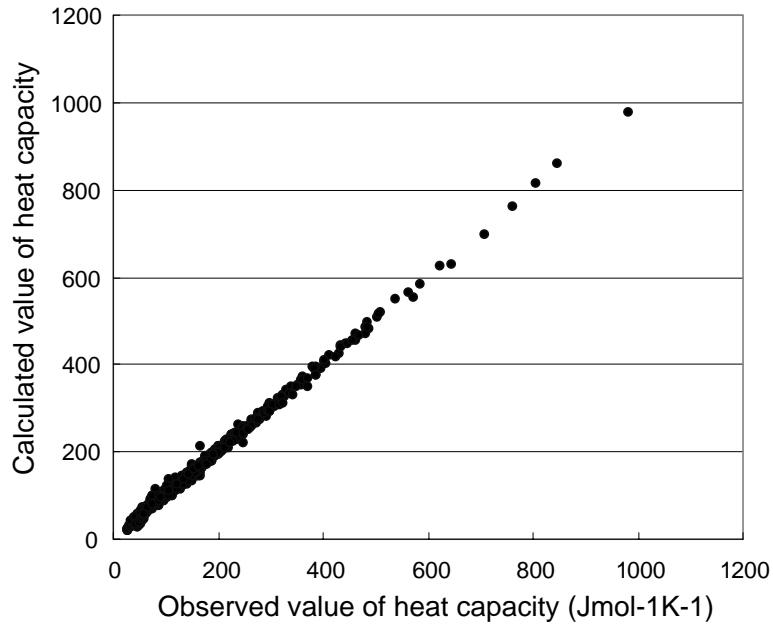
Fig. 2. Fitting to the heat capacity of various molecules at various temperatures.

there are no data available to check the validity of the equations. In the present case, for both the parabolic functions of T (the intercept term and the coefficient of first-order term), in order to calculate the temperature average values we have used the values at the apex of the parabola, i.e. $(4ac - b^2)/4c$ or $(4df - e^2)/4f$, beyond the temperature that corresponds to the apex of the parabola. In this way, the temperature averaged values of heat capacity have been obtained by numerical integration of the right hand side of Eq. (4) for each n value employing the "beyond the apex rule". The result of calculation is shown in 11th column of Table 1. The value of heat capacity at the stoichiometric concentration for each compound has been obtained by taking proportional average of the values of fuel and air and listed in 12th column of Table 1, where the data for air has directly been taken from the literature [4]. The error in the estimated value of temperature averaged heat capacity of each fuel due to the present approximation is reduced by the ratio of dilution to obtain the stoichiometric mixture.

3.2. Average values of heat conductivity

As for heat conductivity λ of polyatomic molecules, Eucken's equation is known [6].

$$\lambda = \left(C_p + \frac{5}{4}R \right) \frac{\mu}{M} \tag{5}$$

Here, R is the gas constant, μ the coefficient of viscosity, and M the molecular weight. This equation shows that λ is a linear function of reciprocal molecular weight. Fig. 3 shows

Table 1
Observed and calculated values of minimum ignition energy and related quantities

| Compound	Molecular weight	No of atoms	HOC (kJ/mol)	C_{st} (vol.%)	T_b (K)	E_{min} ($\phi=1$) (mJ)	d ($\phi=1$) (mm)	S_u (cm/s)	S_{av} (cm/s)	C_{av} (J/(mol K))	C_{av} ($\phi=1$) (J/(mol K))	λ_{av} (10^{-4} W/ (cm K))	λ_{av} ($\phi=1$) (10^{-4} W/ (cm K))	E_{min} by Eq. (1) (mJ)	E_{min} by Eq. (2) (mJ)	δ (mm)
Acetone	58.1	10	1690	4.97	2122	1.150	3.80	50	156	169	40.6	752	632	12.20	3.36	0.076
Acetylene	26.0	4	1251	7.72	2536	0.030	0.70	155	544	66	36.3	854	644	0.07	0.04	0.028
Acrolein	56.1	8	1599	5.64	2363	0.170	1.50	62	207	135	39.5	714	631	0.74	0.44	0.063
Acrylnitrile	53.1	7	1725	5.28	2461	0.360	2.20	47	162	117	38.3	705	630	2.28	1.28	0.086
Benzene	78.1	12	3163	2.71	2305	0.550	2.80	45	148	203	38.4	695	628	4.68	2.09	0.089
1,3-Butadiene	54.1	10	2406	3.66	2375	0.230	1.70	60	201	169	38.8	779	632	1.06	0.59	0.066
n-Butane	58.1	14	2650	3.12	2255	0.760	3.00	41	133	237	40.2	848	633	6.01	2.63	0.094
Carbon disulfide	76.1	3	1104	6.52	2254	0.015	0.50	54	175	49	34.8	531	620	0.02	0.05	0.081
Cyclohexane	84.2	18	3685	2.27	2252	1.380	4.00	42	136	305	40.0	770	629	14.17	4.54	0.092
Cyclopentane	70.1	15	3091	2.71	2263	0.830	3.30	41	133	254	39.8	789	630	7.92	3.18	0.094
Cyclopropane	42.1	9	1959	4.44	2327	0.240	1.80	52	172	152	39.1	856	636	1.27	0.76	0.077
Diethyl ether	74.1	15	2531	3.37	2252	0.490	2.50	44	143	254	41.3	767	631	3.57	1.70	0.085
2,2-Dimethyl-butane	86.2	20	3863	2.16	2252	1.640	4.50	39	126	340	40.5	793	630	20.40	6.19	0.098
Dimethyl ether	46.1	9	1329	6.52	2227	0.450	2.30	50	161	152	41.5	815	638	2.79	1.27	0.075
Ethane	30.1	8	1427	5.64	2244	0.420	2.30	44	142	135	39.5	993	647	2.66	1.47	0.091
Ethene	28.1	6	1323	6.52	2375	0.096	1.20	75	252	100	38.2	930	646	0.37	0.24	0.055
Ethyl acetate	88.1	14	2097	4.02	2223	1.420	4.30	36	116	237	42.0	692	629	18.45	6.07	0.102
Ethylene imine	43.1	8	1518	6.05	2398	0.480	2.50	43	145	135	39.9	811	637	3.49	1.81	0.091
Ethylene oxide	44.1	7	1219	7.72	2411	0.100	1.30	100	339	117	40.3	769	637	0.49	0.21	0.039
n-Heptane	100	23	4485	1.87	2213	1.150	3.80	42	135	391	40.5	777	629	12.27	4.06	0.090
n-Hexane	86.2	20	3881	2.16	2238	0.950	3.50	42	136	340	40.5	793	630	9.59	3.47	0.091
Hydrogen	2.00	2	240	29.5	2376	0.020	0.60	291	977	32	33.3	4453	1755	0.04	0.04	0.044
Methane	16.0	5	799	9.47	2236	0.330	2.50	37	119	83	38.5	1239	684	3.33	2.18	0.117
Methyl alcohol	32.0	6	675	12.2	2219	0.210	1.80	52	167	100	42.0	865	655	1.35	0.77	0.073
2-Methyl-butane	72.1	17	3255	2.55	2252	0.960	3.50	40	130	288	40.3	815	631	9.57	3.66	0.096
n-Pentane	72.1	17	3264	2.55	2250	0.820	3.30	42	136	288	40.3	815	631	8.02	3.10	0.091
cis-2-Pentene	70.1	15	3141	2.71	2241	0.820	3.30	48	155	254	39.8	789	630	7.91	2.70	0.081
Propane	44.1	11	2041	4.02	2250	0.300	1.80	43	139	186	40.0	899	637	1.29	0.91	0.091
Propene	42.1	9	1924	4.44	2338	0.280	2.00	48	160	152	39.1	856	636	1.74	1.02	0.083
Propylene oxide	58.1	10	1810	4.97	2316	0.190	1.80	77	254	169	40.6	752	632	1.31	0.51	0.050
2,2,3-Trimethyl-butane	100	23	4464	1.87	2241	1.000	3.50	39	126	391	40.5	777	629	9.61	3.73	0.097
2,2,4-Trimethyl-pentane	114	26	5080	1.65	2233	0.290	2.00	38	123	442	40.6	764	628	1.79	1.25	0.100
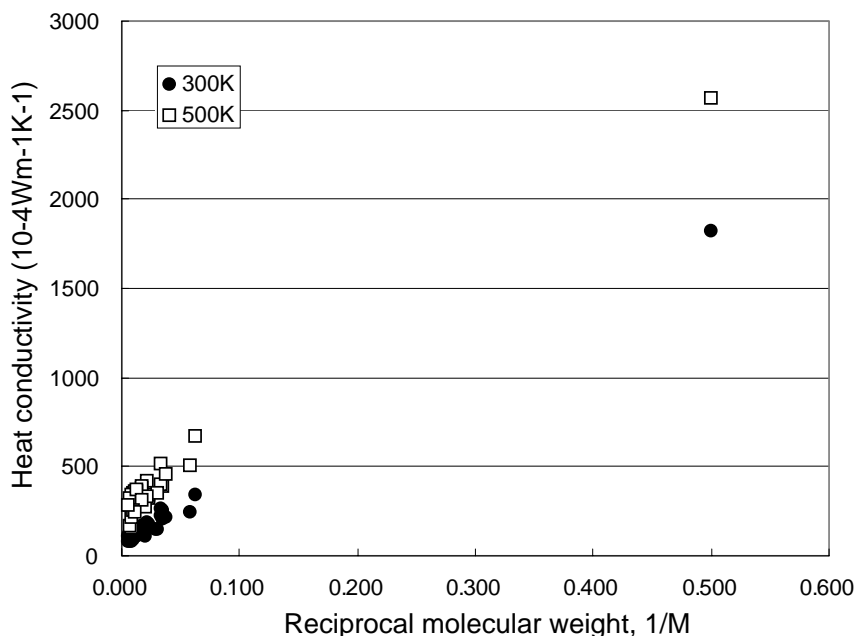
Fig. 3. Plot of heat conductivity vs. reciprocal weight of molecule.

a plot of heat conductivity against reciprocal molecular weight for 35 gases the majority of which are simple organic compounds as well. Though the dispersion of data points is not very small, this figure confirms that the heat conductivity is a linear function of reciprocal molecular weight. However, it also suggests that the plot is better explained if a constant term is added in the equation. As seen in the above, C_p can be considered proportional to the number of atoms in the molecule (n) at the first approximation. Therefore, λ may be given by the following equation.

$$\lambda = C + \frac{D}{M} + \frac{En}{M} \tag{6}$$

The coefficients C, D, and E are functions of temperature T. Fortunately, in this case, it has been found that a linear function of temperature is enough to account for the behaviors of the three coefficients. Then, the value of heat conductivity can be expressed as follows.

$$\lambda = p + qT + \frac{r + sT}{M} + \frac{(t + uT)n}{M} \tag{7}$$

The least-squares calculation to determine the values of coefficients has been carried out fitting to a total of 205 data for 35 compounds, where the widest temperature region available has been from 300 to 1000 K. The numerical coefficients have been obtained as $p = -103.3$, $q = 0.572$, $r = 3700.9$, $s = -0.4555$, $t = -923.1$, and $u = 3.127$ if λ is expressed in units of 10^{-4} W/(m s). Fig. 4 shows a general feature of the fitting.
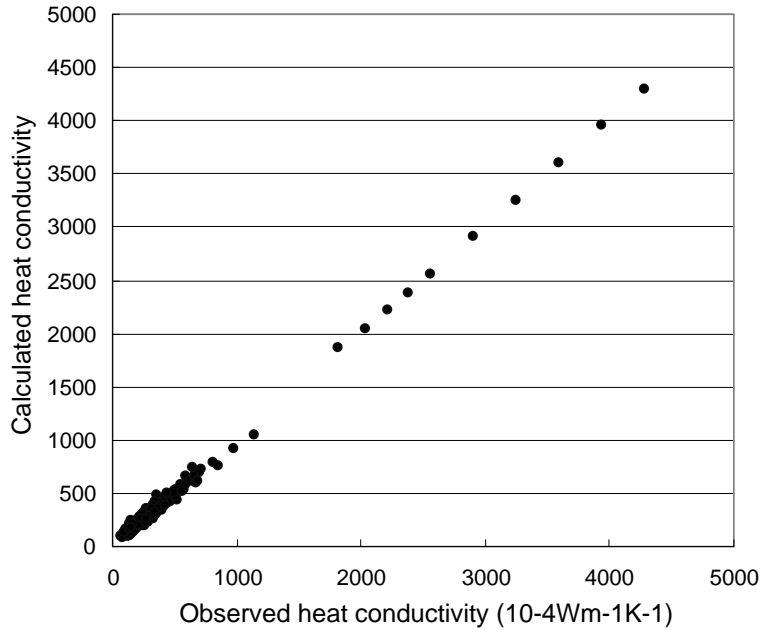
Fig. 4. Fitting to the observed values of heat conductivity.

In order to obtain the value of λ_{av} in Eq. (2), the reciprocal value of λ should be averaged for the temperature range from T_u to T_b. Actually, the reciprocal of the right hand side of Eq. (7) has numerically been integrated from 300 to 2300 K for all compounds for simplicity reason and listed in 13th column of Table 1. Further, the values for the stoichiometric mixtures have simply been obtained by the proportional addition as in the case of heat capacity. The result is shown in 14th column of Table 1.

3.3. Average values of burning velocity

As for the burning velocity, the literature usually lists only the maximum values for the respective fuel–air combinations [1]. Therefore, we have used them instead of the values at the stoichiometric concentrations. The burning velocity is indeed a function of concentration, and the maximum value is usually located in a little richer side of the stoichiometric concentration. However, the difference between the maximum burning velocity and the one at the stoichiometric concentration is not so large; the discrepancy may be 10% or so except for hydrogen.

As stated, the burning velocity appearing in Eq. (2) should be the value averaged for the width of flame front. In this case, the reciprocal value of S_u has to be averaged for the temperature range from T_u to T_b. Since the product of gas density and burning velocity is constant across the flame width, reciprocal burning velocity $1/S_u$ is proportional to gas density ρ, which is equal to P/RT from the ideal gas law equation. Therefore, the average value of burning velocity S_{av} has been obtained through integration of reciprocal temperature

from T_u to T_b, of which reciprocal has to be taken back eventually of course. The result of calculation is shown in 10th column of Table 1.

4. Calculation of minimum ignition energies

4.1. Calculation by Eq. (1)

Calculation of the minimum ignition energy by using Eq. (1) requires the data of quenching distance, gas density, and flame temperature besides the heat capacity. The experimental data of the minimum ignition energy and quenching distance have been used in the present study for various fuels. As stated in the above, the values of heat capacity can be estimated if the number of atoms in the molecule is given, and the average values can be obtained by integrating the expression given in Eq. (4). The flame temperatures are the calculated values of adiabatic flame temperatures. Fig. 5 compares the values of the minimum ignition energy calculated by Eq. (1) with the observed values. Actual numbers are shown in 15th column of Table 1. Although there is a close relationship between the calculated and observed values, the calculated values are almost one-order of magnitude larger than the observed ones. In addition, it is noted that the plotted points are distributed along a line not straight but a little curved upward. It may be that the minimum ignition energy is rather closer to the
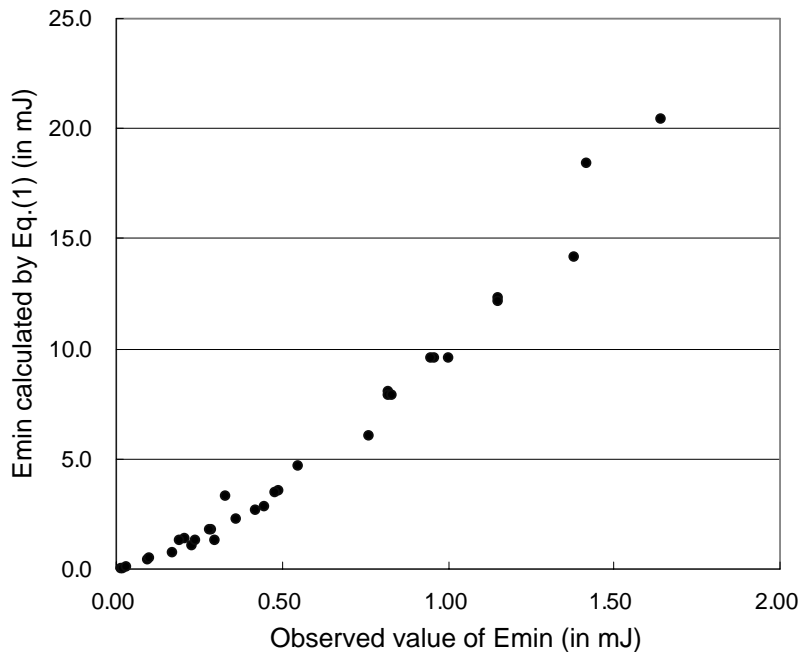

Fig. 5. Minimum ignition energy calculated by Eq. (1) vs. the observed values.
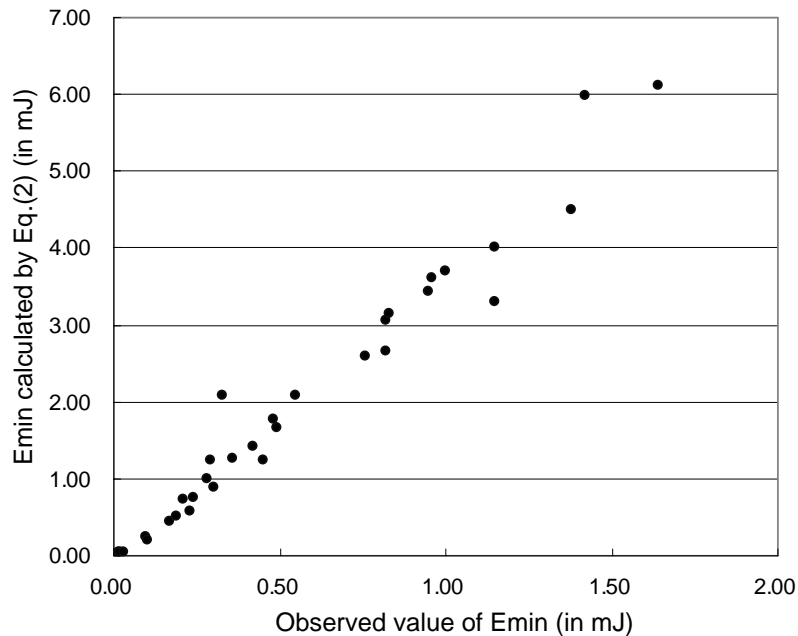
Fig. 6. Minimum ignition energy calculated by Eq. (2) vs. the observed values.

enthalpy contained in a thin surface layer rather than that contained in the whole sphere of the minimal flame.

4.2. Calculation by Eq. (2)

Calculation of E_{min} by Eq. (2) requires knowledge of burning velocity and heat conductivity besides the ones used in Eq. (1). The methods of calculating the average values of burning velocity and heat conductivity have already been described in the above.

Fig. 6 shows the result of the calculation, where the values of minimum ignition energy calculated by Eq. (2) are plotted against the observed values. Actual numbers are shown in 16th column of Table 1. Here, a linear relationship is observed between the calculated and observed values, though discrepancy is noted for a few points. This result strongly suggests that the basic concept of Eq. (2) is valid for discussing the issue of minimum ignition energy of various fuel gases. It is to be noted that the calculated values are about three times or more as large as the observed ones. The fact that the calculated values are much larger than the observed ones is quite understandable if one considers that the minimum ignition energy is measured in a free space between a pair of sharpened electrodes while the quenching distance is measured between solid walls by which the propagation flame is severely cooled, although it is difficult to make more quantitative discussion. At any rate, the average ratio between the observed and calculated values of minimum ignition energy can be obtained through regression analysis: actually the average ratio has been found to be 0.282 ± 0.006. This may in turn imply that the
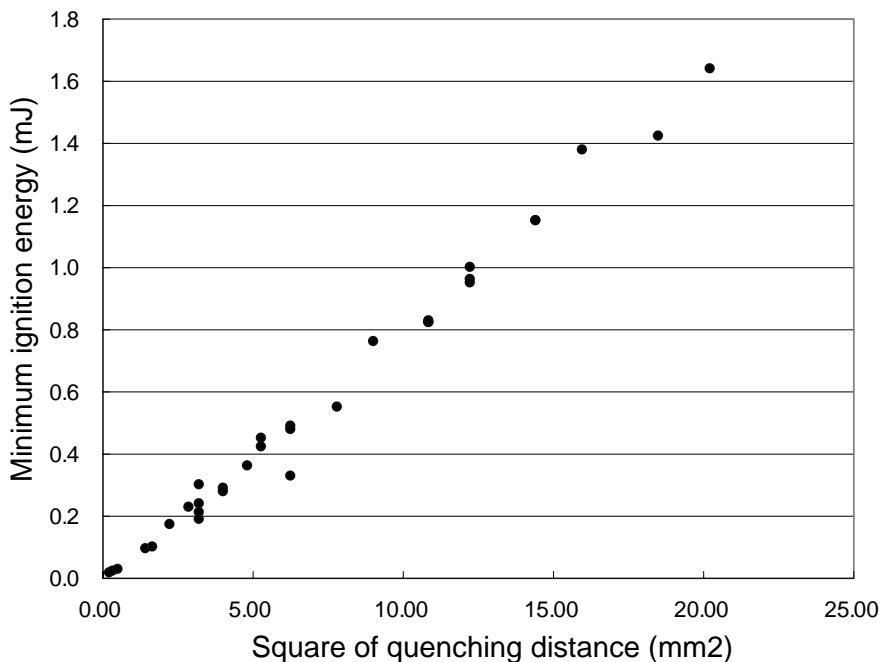
Fig. 7. Plot of minimum ignition energy vs. square of quenching distance.

diameter of minimal flame is on the average a factor of 0.53 smaller than the quenching distance.

On the other hand, Lewis and Elbe's relationship that the minimum ignition energy is proportional to the square of quenching distance for not extremely strong flames seems to be valid even at the stoichiometric concentration for ordinary fuel and air mixtures. Fig. 7 shows a plot of E_{min} against quenching distance d for the present set of compounds. If E_{min} is expressed in units of mJ and quenching distance in mm, the proportionality relationship becomes as follows.

$$E_{min} = (0.0787 \pm 0.0009) \times d^2 \tag{8}$$

5. Discussion

Comparison of the calculated results by the two equations with the observed values clearly shows superiority of Eq. (2) over Eq. (1). Firstly, the calculated values by Eq. (2) is closer to the observed values than that by Eq. (1), and secondly the relation between the calculated and observed values are linear for Eq. (2), while it is non-linear for Eq. (1). This result indicates that the minimum ignition energy is much smaller than the enthalpy contained in the burnt gas of flame temperature that fills the full volume of minimal flame.

Eq. (2) has been derived through consideration of the heat loss from the surface of minimal flame during the time the gas passes through the width of flame front. On the other hand,

another equation of the minimum ignition energy is obtained from the amount of sensible energy of the unburnt gas which enters the flame surface during the same time period. In this case, the minimum ignition energy may be given by the following equation.

$$E_{\min} = \pi d^2 S_u \rho_u C_{av}(T_b - T_u)\frac{\delta}{S_{av}} \tag{9}$$

Here, S_u is the burning velocity at room temperature, ρ_u molar density of unburnt gas, and δ width of flame front. The quantity given by this equation should indeed be equal to that of Eq. (2). By equating the two expressions, the following equation is obtained.

$$\delta = \frac{\lambda_{av}}{\rho_u S_u C_{av}} \tag{10}$$

The values of δ have been calculated by this equation from the data already prepared for calculating Eqs. (1) and (2), and are shown in 17th column of Table 1.

Fig. 8 shows a plot of the calculated values of δ against quenching distance. The calculated values of flame front width are on the whole about one-order of magnitude smaller than the quenching distances. As expected, there is a general tendency that the larger the quenching distance the larger the width of flame front. However, the dispersion of the plotted points is so large that we cannot see any clear relationship between the two quantities. This result combined with the fact that the values of minimum ignition energy calculated by Eq. (2) are in linear relationship with the observed values confirms that the minimum ignition energy is proportional to the square rather than the cubic power of quenching distance even at the stoichiometric concentration with air for the fuels treated in the present paper.
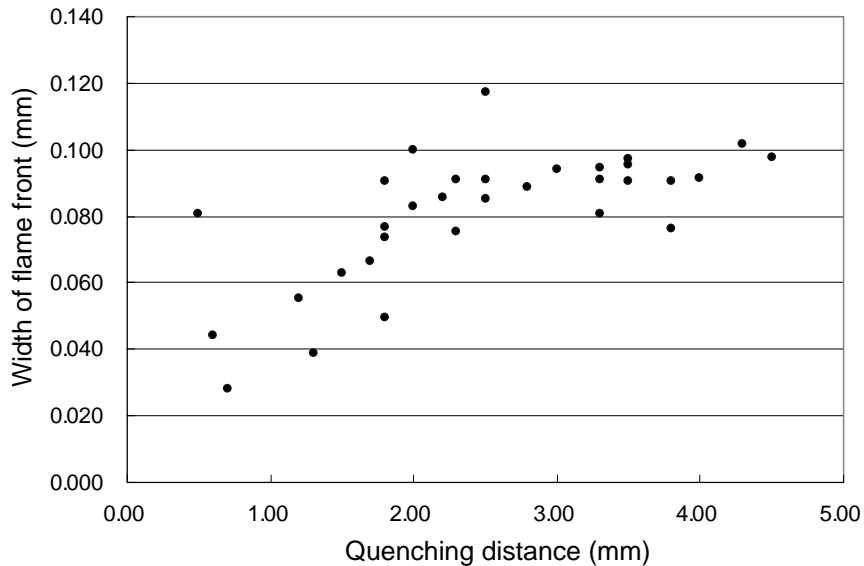

Fig. 8. Plot of width of flame front vs. quenching distance.

6. Conclusion

The minimum ignition energy has been calculated by using two different equations for various combustible gases. One equation is based on the enthalpy that fills the whole volume of minimal flame, and the other due to the heat loss from the surface of the minimal flame. Of the two equations, the latter can better explain the experimental data than the former. In addition, from the balance between the heat loss from the surface of the minimal flame and the sensible energy contained in the unburnt gas that enters the flame front in the same time period, a relationship between the width of flame front for minimal flame and quenching distance has been derived. As a result, it has been found that the width of flame front is in general one-order of magnitude smaller than the quenching distance, though there is no systematic relationship between the two quantities. In conclusion, the whole of the present calculations supports the superiority of Eq. (2) over Eq. (1) as the expression of minimum ignition energy. From the analysis by using Eq. (2), we can obtain information on the width of flame front and the difference of the heat loss rates for minimum ignition energy and quenching distance measurements as well.

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