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Model To Estimate the Flammability Limits of Fuel–Air–Diluent Mixtures Tested in a Constant Pressure Vessel

Horng-Jang Liaw,^{*,†} Chan-Cheng Chen,[‡] Chih-Heng Chang,[†] Nung-Kai Lin,[§] and Chi-Min Shu[§]

[†]Department of Occupational Safety and Health, China Medical University, 91 Hsueh-Shih Road, Taichung, Taiwan

[‡]Department of Safety, Health, and Environmental Engineering, National Kaohsiung First University of Science and Technology, 1 University Road, Yuanchau, Kaohsiung, Taiwan

[§]Department of Safety, Health, and Environmental Engineering, National Yunlin University of Science and Technology, 123 University Road, Section 3, Douliou, Yunlin, Taiwan

ABSTRACT: Flammability limits are two of the most important variables used to assess the fire and explosion hazards of gases and vapors, and inerting is frequently used in industry to reduce fire and explosion hazards. A model based on the energy balance equation that takes into account thermal radiation loss and constant flame temperature was developed to estimate the flammability envelope of fuel–air–diluent mixtures tested in a constant pressure vessel. The validation of the model was done by comparing the estimated values with the corresponding experimental data for methane, ethylene, propane, propylene, isobutane, and methyl formate with nitrogen or carbon dioxide as the inert gas. The difference in the estimated flammability envelopes between the different heat loss considerations is small. The predictions of the lower flammability limits are in excellent agreement with the experimental data, except for the region approaching the limiting oxygen concentration, where the assumption of complete consumption of the fuel fails. The different behaviors of the lower flammability limit variations for nitrogen and carbon dioxide, when these are both used as inert gases, are attributable to different trends in heat capacity values between air and the two inert gases. Because of the ambiguity of the combustion product distributions, the estimated upper flammability limits are not as precise as the estimated lower flammability limits; however, they are acceptable. Overall, the model describes the experimental data well.

1. INTRODUCTION

A flammable gas burns in air only over a limited range of composition.¹ Below a certain concentration of flammable gas, the lower flammability limit (LFL), or above a certain concentration, the upper flammability limit (UFL), the mixture will not burn, because the mixture is too lean or too rich, respectively.^{1,2} The LFL and UFL are also sometimes called, respectively, the lower and upper explosive limits (LEL and UEL). Flammability limits are two of the most important variables used to evaluate the fire and explosion hazards of gases and vapors. Generally, the wider the range of the flammability limits, the greater the fire potential is.³

Flammability limits are affected by the existence of an inert gas such as nitrogen (N₂), carbon dioxide (CO₂), or steam (H₂O).¹ In commercial processes, the addition of an inert gas to flammable gases or vapors is frequently used to reduce the fire and explosion hazards. Data on the flammability limits for fuel–air–diluent mixtures are rare in the literature, although they are available for a vast group of pure chemicals;^{4,5} even the ones listed in the literature are typically only valid for a specific compound composition. The cost of deriving flammability limit data using test equipment is very high, approximately NT\$30,000/US\$1000 per sample in Taiwan. Thus, a reliable prediction method for the flammability limits of fuel–air–diluent mixtures is necessary and useful.

Kondo et al. modified Le Chatelier's formula with an empirical equation to describe the variation in flammability limits, LFL and UFL, with the quantity of an inert gas added to a variety of gases, and estimated the unknown parameters by fitting with experimental data.^{6–8} Shebeko et al. indicated that a flame cannot propagate unless the temperature is above a specific threshold temperature, the adiabatic flame temperature at flammability limits, at which the reaction rate of propagation prevails over that of termination.⁹

An assumption that such an adiabatic flame temperature is constant is frequently used in the literature to estimate the flammability limits of mixtures with inert gas.^{9–12} Based on this assumption, Vidal et al. discussed an approach to calculate the LFL in the presence of diluents such as N₂ and CO₂.¹⁰ Melhem estimated the flammability limits of mixtures by assuming that the gas composition reached chemical equilibrium after the explosion.¹¹ Hansen and Crowl derived two separate equations for the upper and lower boundaries to estimate the flammability zone of inert gas enriched mixtures.¹² In the application of Melhem's method¹¹ and Hansen and Crowl's equations,¹² the adiabatic flame temperatures at the flammability limits are required. Melhem's results indicated that there are some deviations between the estimation and the corresponding experimental data. In our previous studies, the linear relationship between the reciprocal of LFL/UFL and the reciprocal of the mole fraction of hydrocarbon in the mixture on an air-free basis was derived, and such an equation describes the experimental data over the entire blend composition range, except for the region around the limiting oxygen concentration (LOC).^{13,14} However, the slope of the previously derived linear relationship was determined by curve fitting the experimental data. The flammability limits estimation methods for mixtures with inert gas mentioned above all ignored heat loss during combustion. In this study, we intended to derive a model describing the inert gas dilution effect on the flammability limits by considering thermal radiation loss using only basic thermodynamic data, and to validate this with corresponding experimental data.

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2. THEORY

2.1. Mathematical Model. The model to estimate the flammability envelope of fuel–air–diluent mixtures tested in a constant pressure vessel was derived from an energy balance equation, with thermal radiation loss taken into account. The detailed derivation is included in the Appendix. This model includes the equations to estimate the flame temperature, x_L , x_U , and the lower and upper flammability boundaries.

The flame temperature at the LFL and UFL compositions are estimated by eqs 1 and 2, respectively:

$$L_0(\Delta h_c^\circ) + \int_{298}^T [L_0(Q_L - P_L) + P_L]dT + \int_{T_0}^{298} [L_0(C_{p,f} - P_L) + P_L]dT = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \quad (1)$$

$$\begin{aligned} 0.21 f_U (1 - U_0) (\Delta h_c)_U + \int_{298}^T [U_0 (C_{p,f} - P_{U0}) + P_{U0}]dT + \int_{T_0}^{298} [U_0 (C_{p,f} - P_L) + P_L]dT \\ = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (2)$$

The point of LOC is located at $x = x_L$, and the value of x_L is calculated as

$$x_L = - \frac{0.21 \left[\int_{T_0}^T C_{p,I} dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t \right]}{f_L \left[\int_{T_0}^T P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t \right] + 0.21 \left[\int_{298}^T (Q_L - C_{p,I})dT + \int_{T_0}^{298} (C_{p,f} - C_{p,I}) dT + \Delta h_c^\circ \right]} \quad (3)$$

where x is the mole ratio of the fuel in the blended gas:

$$x = \frac{\text{fuel}}{\text{fuel} + \text{inert}}$$

The lower flammability boundary, L , can be estimated:

$$L = - \frac{\int_{T_0}^T P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{298}^T Q_L dT + \int_{T_0}^{298} C_{p,f} dT - \int_{T_0}^T [C_{p,I} - (C_{p,I} - P_L) \frac{1}{x}] dT + \Delta h_c^\circ} \quad (4)$$

When the concentration of a fuel–air mixture is moved along its upper flammability zone boundary by the addition of an inert gas, the added inert gas replaces the excess fuel, and that makes the value of x decrease. When the value of x decreases below a critical value, x_U , where the ratio of fuel to oxygen is equivalent to the stoichiometric ratio, the ratio of CO_2 to CO increases because the quantity of oxygen is great enough to produce more carbon dioxide. The value of x_U is obtained:

$$x_U = - \frac{0.21 f_U \left[\int_{T_0}^T C_{p,I} dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t \right]}{\int_{298}^T P_U dT + \int_{T_0}^{298} P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t + 0.21 f_U \left[\int_{T_0}^T (C_{p,f} - C_{p,I}) dT + (\Delta h_c)_U \right]} \quad (5)$$

For $x \geq x_U$, the upper flammability boundary, U , can be estimated as

$$U = - \frac{\int_{298}^T P_U dT + \int_{T_0}^{298} P_L dT + 0.21 f_U (\Delta h_c)_U + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{T_0}^T (C_{p,f} - C_{p,I}) dT + \int_{298}^T (C_{p,I} - P_U) \frac{1}{x} dT + \int_{T_0}^{298} (C_{p,I} - P_L) \frac{1}{x} dT - 0.21 f_U \frac{1}{x} (\Delta h_c)_U} \quad (6)$$

For $x < x_U$, the upper flammability boundary is estimated as

$$U = - \frac{\int_{298}^T [P_L - 0.42(C_{p,\text{CO}} - C_{p,\text{CO}_2})] dT + \int_{T_0}^{298} P_L dT + 0.42(\Delta h_{\text{CO/CO}_2}) + \alpha \epsilon A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{298}^T \left[Q_U + \frac{1}{x}(C_{p,\text{I}} - P_L) + (C_{p,\text{CO}} - C_{p,\text{CO}_2}) \left(p + \frac{0.42}{x} \right) \right] dT + \int_{T_0}^{298} [(C_{p,\text{f}} - C_{p,\text{I}}) + \frac{1}{x}(C_{p,\text{I}} - P_L)] dT + (\Delta h_p)} \quad (7)$$

2.2. Procedure for Estimating the Effect of Inerting on the Flammability Limits. The estimation of the flammability envelope is associated with certain critical reaction temperatures, which are the flame temperatures on the lower and upper flammability boundaries. In this work, the CO_2/CO ratios at the lower flammability boundary and upper flammability boundary of $x \geq x_U$ are assumed to be constant; i.e., the flame temperatures on the two boundaries were assumed to be constant. Equations 1 and 2 were used to estimate the flame temperatures at the LFL and UFL, respectively, first. Then, x_L and x_U were estimated by eqs 3 and 5. The lower flammability boundary from $x = 1$ ($1 - x = 0$) to $x = x_L$ ($1 - x = 1 - x_L$) is estimated by eq 4, and the upper flammability boundary from $x = 1$ ($1 - x = 0$) to $x = x_U$ ($1 - x = 1 - x_U$) and from $x = x_U$ ($1 - x = 1 - x_U$) to $x = x_L$ ($1 - x = 1 - x_L$) are estimated by eqs 6 and 7, respectively.

3. RESULTS AND DISCUSSION

3.1. Parameters Used. The proposed model to describe the inert gas dilution effect on flammability limits was used for methane, ethylene, propane, propylene, isobutane, and methyl formate in the presence of either of the following inert gases, nitrogen or carbon dioxide, and validated against the corresponding experimental data from Kondo et al.^{6–8} The standard heat of formation values for the compounds used in this study were adopted from

Poling et al.¹⁵ and are listed in Table 1. The dependence of heat capacity in relation to temperatures obtained from two different databank sources^{15,16} were different, and the two different equations were used in this study for comparison; the formulas and their parameters are listed in Tables 1 and 2. The flammability limits, UFL and LFL, for the pure substances used in this study were previously published^{6–8} and were tested in a spherical glass flask.

In the experiments of Kondo et al.,^{6–8} the standard test method ASTM E681¹⁷ was used to determine whether or not a

Table 1. Standard Heat of Formation, $\Delta H_{f,i,298}^\circ$, and the Parameters Adopted from Poling et al.¹⁵ To Estimate the Heat Capacity of the Studied Compounds

compound name	$C_p/R = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$					$\Delta H_{f,i,298}^\circ$
	a_0	$a_1 \times 10^3$	$a_2 \times 10^5$	$a_3 \times 10^8$	$a_4 \times 10^{11}$	
methane	4.568	−8.975	3.631	−3.407	1.091	−74.52 × 10 ³
ethylene	4.221	−8.782	5.795	−6.729	2.511	52.50 × 10 ³
propane	3.847	5.131	6.011	−7.893	3.079	−104.68 × 10 ³
propylene	3.834	3.893	4.688	−6.013	2.283	20.00 × 10 ³
isobutane	3.351	17.883	5.477	−8.099	3.243	−134.99 × 10 ³
methyl formate	2.277	18.013	1.160	−2.921	1.342	−352.40 × 10 ³
CO	3.912	−3.913	1.182	−1.302	0.515	−110.53 × 10 ³
CO ₂	3.259	1.356	1.502	−2.374	1.056	−393.51 × 10 ³
H ₂	2.883	3.681	−0.772	0.692	−0.213	0.00
H ₂ O(g)	4.395	−4.186	1.405	−1.564	0.632	−241.81 × 10 ³
O ₂	3.630	−1.794	0.658	−0.601	0.179	0.00
N ₂	3.539	−0.261	0.007	0.157	−0.099	0.00

Table 2. Parameters Adopted from DIPPR¹⁶ To Estimate the Heat Capacity of the Studied Compounds

compound name	$C_p = C_1 + C_2[(C_3/T)/\sinh(C_3/T)]^2 + C_4[(C_5/T)/\cosh(C_5/T)]^2$ (J·mol ^{−1} ·K ^{−1})				
	C_1	C_2	C_3	C_4	C_5
methane	3.3298 × 10 ¹	7.9933 × 10 ¹	2086.90	4.1602 × 10 ¹	991.96
ethylene	3.3380 × 10 ¹	9.4790 × 10 ¹	1596.00	5.5100 × 10 ¹	740.80
propane	5.9474 × 10 ¹	1.2661 × 10 ²	844.31	8.6165 × 10 ¹	2482.70
propylene	4.3852 × 10 ¹	1.5060 × 10 ²	1398.80	7.4754 × 10 ¹	616.46
isobutane	7.6394 × 10 ¹	1.6802 × 10 ²	826.54	1.0285 × 10 ²	2483.10
methyl formate	5.0600 × 10 ¹	1.2190 × 10 ²	1637.00	8.9400 × 10 ¹	743.00
CO	2.9108 × 10 ¹	8.7730	3085.10	8.4553	1538.20
CO ₂	2.9370 × 10 ¹	3.4540 × 10 ¹	1428.00	2.6400 × 10 ¹	588.00
H ₂	2.7617 × 10 ¹	9.5600	2466.00	3.7600	567.60
H ₂ O(g)	3.3363 × 10 ¹	2.6790 × 10 ¹	2610.50	8.8960	1169.00
O ₂	2.9103 × 10 ¹	1.0040 × 10 ¹	2526.50	9.3560	1153.80
N ₂	2.9105 × 10 ¹	8.6149	1701.60	1.0347 × 10 ^{−1}	909.79

mixture was flammable, with “flammable” defined as flames that spread upward and outward to the walls of the flask, continuously along an arc greater than that subtended by an angle equal to 90° , as measured from the point of ignition to the walls of the flask. Thus, the distance the flame propagates was almost equal to the radius (R) of the 12-L spherical glass flask used in the tests by Kondo et al. If the fire expanded spherically with flame propagation in a spherical glass flask, then the value of the efficiency factor with respect to the heat exchange surface area, α , is

$$\alpha = \frac{\int_0^R \sigma e (4\pi r^2) (T^4 - T_0^4) \frac{dr}{u}}{\sigma e (4\pi R^2) (T^4 - T_0^4) \Delta t} = \frac{1}{3}$$

where u is the burning velocity and $\Delta t = R/u$. That is, the value of α is approximately $1/3$. The value of σA_s is $3.025 \times 10^{-9} \text{ W}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$ based on a 12-L spherical glass flask, where the experimental data used in this study were obtained by Kondo et al.^{6–8} Since the value of emissivity, e , was less than or equal to unity and the value of the flame propagation duration was estimated to be on the order of 1 s based on the burning velocity of a few centimeters per second near the flammability limits for paraffin hydrocarbons in air,⁵ the values of $\alpha \sigma e A_s \Delta t$ used in this study were selected to be 0, 10^{-9} , and $3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$, representing the adiabatic condition, the most possible value, and an overestimation of heat losses through thermal radiation.

For simplicity, the carbon of the fuel was assumed to be completely converted into carbon monoxide and the quantity of hydrogen was assumed to be negligible on the upper flammability boundary of $x \geq x_U$. Thus, the values of a_1 and b_1 , as presented in Appendix, were selected to be a and 0, respectively; that is, only carbon monoxide and steam were assumed to be produced on the upper flammability boundary of $x \geq x_U$.

3.2. Effect of Nitrogen Dilution on Flammability Limits.

Figure 1 compares the experimental data for the nitrogen

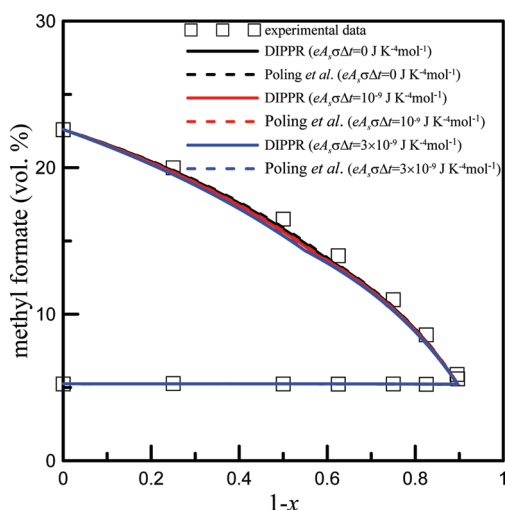


Figure 1. Nitrogen dilution effect on the flammability limits of methyl formate.

dilution effect on the flammability limits of methyl formate adopted from Kondo et al.⁶ with the estimated analogues. For each heat loss, the estimated flammability envelope almost

overlapped, when the two different heat capacity formulas were used. When taking into account each different heat loss, the difference in the estimated upper flammability boundary was not significant and the estimated lower flammability boundary almost overlapped, although the estimated flame temperatures were different (Table 3). The slight difference in the estimated flammability envelope for the different heat losses was also observed for methyl formate diluted with carbon dioxide and ethylene diluted with nitrogen or carbon dioxide (Figures 2–4). For the other systems of methane, propane, propylene, and isobutane diluted with nitrogen or carbon dioxide, the analogous differences were a little greater, but still small (Figures 5–12).

The predicted LFL behavior was almost constant, irrespective of taking into account heat loss or not, which was in excellent agreement with the corresponding experimental data, except for in the region approaching the intersection of LFL and UFL (LOC), where the experimental LFL value increased slightly (Figure 1). In the estimation of the LFL variation with a quantity of inert gas added, the assumption of complete conversion of the fuel was used. This assumption is supported by our preliminary experimental data tested in a 20-L spherical explosion vessel, which met the requirement of the ASTM E1226-05 standard¹⁸ and was operated according to ASTM E681¹⁷ and ASTM E918-83.¹⁹ The system was analyzed by Fourier transform infrared spectroscopy (FTIR) for acetone and methyl formate diluted with water, with the quantity of fuel being negligible in the combustion products, except for the region approaching the LOC, where a remarkable amount of fuel was observed. Furthermore, the quantity of carbon monoxide was negligible in the tested LFL range. This observation in LFL variation is attributed to insufficient oxygen being present to rapidly burn all the fuel, although the ratio of oxygen to fuel was slightly greater than the stoichiometric ratio around the region approaching the LOC. Since not all the fuel was completely consumed, more fuel was required to keep the flame temperature constant, and this resulted in an increase in the LFL. The measured LFL behavior remained almost constant, except in the region approaching the LOC, where the LFL value increased slightly; this was also observed for other hydrocarbons such as methane, ethylene, propane, propylene, and isobutane (Figures 3, 5–8), based on the data adopted from Kondo et al.^{6,8} The measured LFLs were all in excellent agreement with the predictions, regardless of whether or not heat loss was considered, as confirmed by the low average deviation reported in Table 3.

Figure 1 and Table 3 show that the experimental UFL values for methyl formate are in good agreement with the predictive curves, irrespective of whether or not heat losses were taken into account or which heat capacity equation was used. For extending the curves based on the trends of the predictions, Figures 5–8 indicate that the estimated UFLs are less than the corresponding experimental data adopted from Kondo et al.^{6,8} for the mole ratio of the inert gas in the blended gas, $1 - x > 1 - x_U$, if eq 7 is neglected, for methane, propane, propylene, and isobutane. This deviation decreased remarkably when the effect of more fuel converting to carbon dioxide (eq 7) was taken into account. Chen et al. showed that not only carbon monoxide was observed in the combustion products of pure methane at the UFL, but also carbon dioxide was observed.²⁰ Based on this observation, a simulation using $a_1 < a$ was also done. The differences between simulated UFLs using $a_1 = a$ and those

Table 3. Estimated Flame Temperature at the LFL and UFL, T_L and T_U , and the Deviation between Calculated and Experimental Flammability Limits,^a ΔL , and ΔU , for the Studied Mixtures, Comparing Models

system	T_L (K)		T_U (K)		ΔL (vol %)		ΔU (vol %)	
	Poling et al.	DIPPR	Poling et al.	DIPPR	Poling et al.	DIPPR	Poling et al.	DIPPR
methane + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1468	1470	1744	1893	0.10	0.12	0.27	0.62
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1374	1374	1632	1701	0.11	0.11	0.42	0.68
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1264	1264	1493	1521	0.11	0.11	0.55	0.75
ethylene + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1383	1393	1413	1440	0.08	0.08	0.71	0.66
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1305	1312	1362	1376	0.08	0.08	0.57	0.54
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1209	1214	1286	1292	0.08	0.08	0.39	0.39
propane + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1500	1504	1662	1739	0.06	0.06	0.28	0.37
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1401	1402	1573	1608	0.06	0.06	0.38	0.45
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1287	1287	1454	1466	0.06	0.06	0.51	0.55
propylene + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1516	1518	1742	1842	0.08	0.08	0.28	0.40
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1412	1413	1638	1680	0.08	0.07	0.40	0.47
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1294	1294	1504	1517	0.07	0.07	0.51	0.55
isobutane + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1565	1573	1662	1731	0.05	0.05	0.21	0.27
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1454	1456	1572	1604	0.05	0.05	0.28	0.32
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1329	1329	1453	1464	0.05	0.05	0.38	0.40
methyl formate + N ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1586	1608	1419	1440	0.07	0.06	0.44	0.48
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1480	1488	1366	1377	0.06	0.06	0.52	0.55
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1356	1358	1289	1293	0.06	0.06	0.63	0.64
methane + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1468	1470	1744	1893	0.24	0.31	0.42	0.52
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1374	1374	1632	1701	0.31	0.33	0.44	0.54
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1264	1264	1493	1521	0.35	0.33	0.49	0.55
ethylene + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1383	1393	1413	1440	0.10	0.12	1.08	1.13
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1305	1312	1362	1376	0.13	0.14	1.04	1.07
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1209	1214	1286	1292	0.15	0.16	0.97	0.99
propane + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1500	1504	1662	1739	0.07	0.09	0.40	0.35
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1401	1402	1573	1608	0.09	0.10	0.42	0.39
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1287	1287	1454	1466	0.10	0.11	0.46	0.45
propylene + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1516	1518	1742	1842	0.10	0.14	0.42	0.33
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1412	1413	1638	1680	0.16	0.16	0.40	0.36
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1294	1294	1504	1517	0.16	0.16	0.42	0.40
isobutane + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1565	1573	1662	1731	0.05	0.06	0.42	0.37
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1454	1456	1572	1604	0.06	0.06	0.44	0.41
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1329	1329	1453	1464	0.07	0.07	0.46	0.45
methyl formate + CO ₂								
$ae\sigma A_3\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1586	1608	1419	1440	0.13	0.16	0.67	0.46
$ae\sigma A_3\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1480	1488	1366	1377	0.15	0.19	0.55	0.45
$ae\sigma A_3\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	1356	1358	1289	1293	0.21	0.23	0.50	0.47

^aDeviation of flammability limits: $\Delta L = \sum_N |L_{\text{exp}} - L_{\text{pred}}|/N$; $\Delta U = \sum_N |U_{\text{exp}} - U_{\text{pred}}|/N$.

using $a_1 < a$ were negligible for $1 - x < 1 - x_U$ ($x > x_U$). However, the estimated value of $1 - x_U$ increased when $a_1 < a$ replaced $a_1 = a$, and this resulted in the simulation results deviating from the measurements more significantly for $1 - x > 1 - x_U$ ($x < x_U$). Since no other hydrocarbon except methane was observed at the UFL in the experiments by Chen et al.²⁰ and the predictive capability improved remarkably when the

effect of more fuel converting to carbon dioxide was taken into account, we suspect that the deviation between our predictions and measurements for methane, propane, propylene, and isobutane are associated with the fact that the ratios of CO₂ to CO did not remain constant for $1 - x < 1 - x_U$ ($x > x_U$), but increased with the $1 - x$ value. The value of the heat of reaction for fuel converted to carbon dioxide was greater than that for

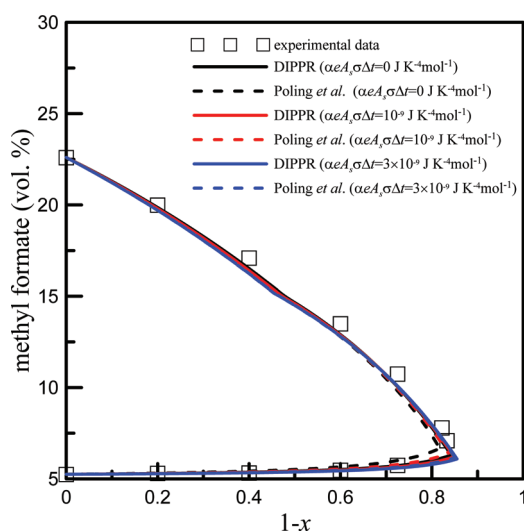


Figure 2. Carbon dioxide dilution effect on the flammability limits of methyl formate.

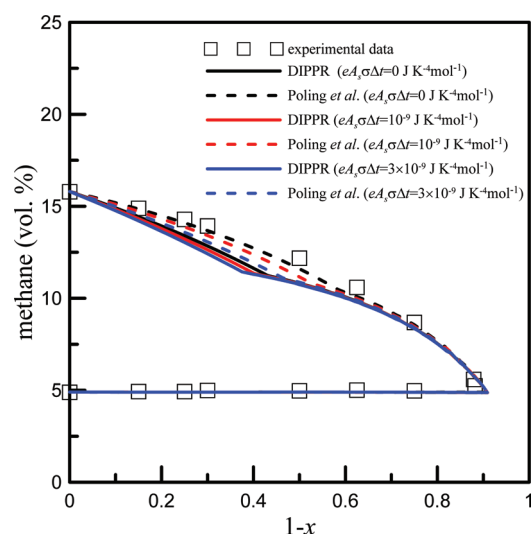


Figure 5. Nitrogen dilution effect on the flammability limits of methane.

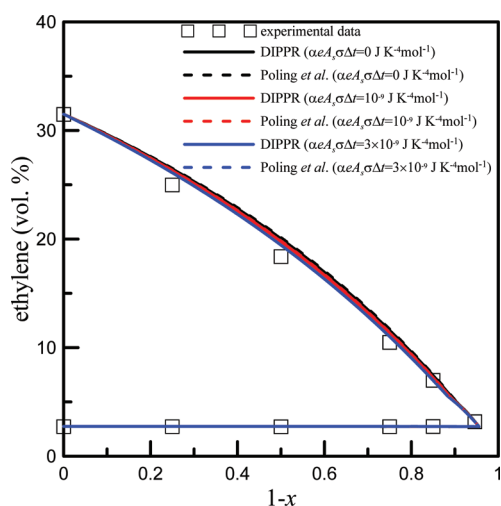


Figure 3. Nitrogen dilution effect on the flammability limits of ethylene.

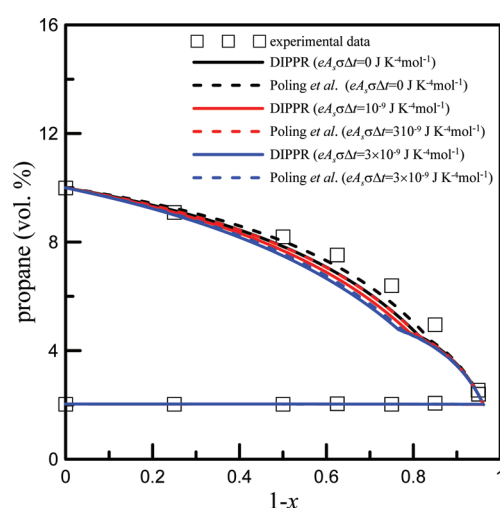


Figure 6. Nitrogen dilution effect on the flammability limits of propane.

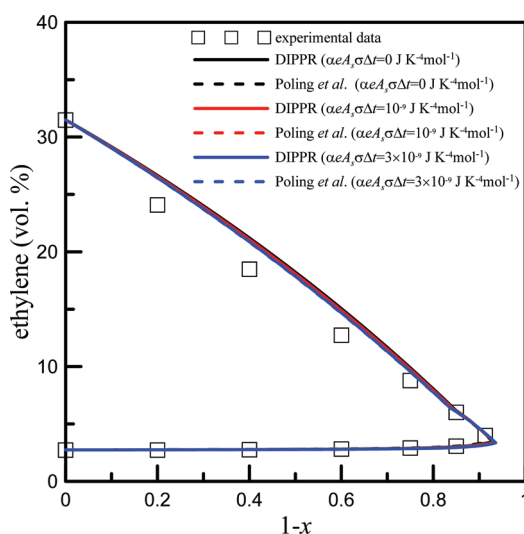


Figure 4. Carbon dioxide dilution effect on the flammability limits of ethylene.

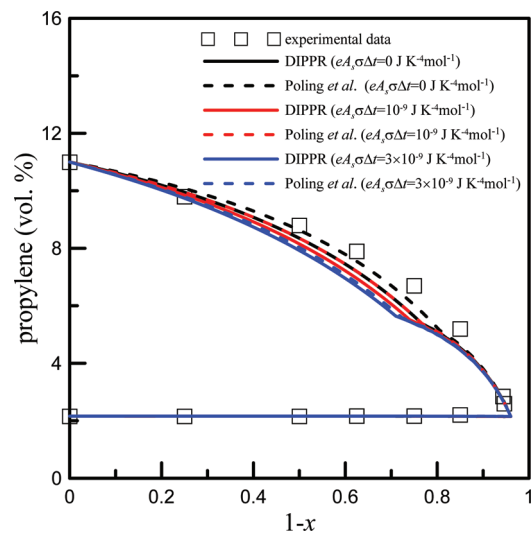


Figure 7. Nitrogen dilution effect on the flammability limits of propylene.

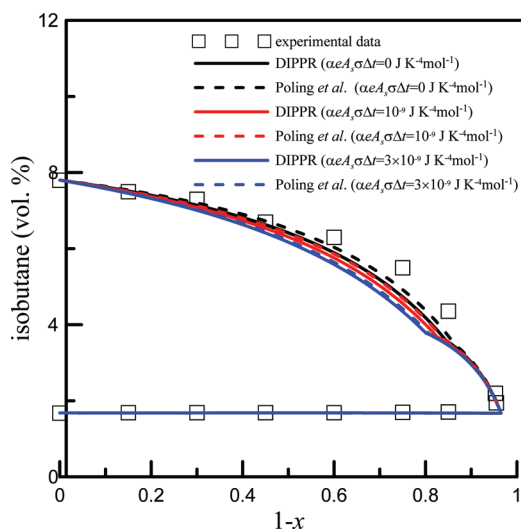


Figure 8. Nitrogen dilution effect on the flammability limits of isobutane.

fuel converted to carbon monoxide; increasing the ratio of CO_2 to CO made the requirement for the limiting reactant, O_2 , less than expected, which increased the UFL, in order to keep the flame temperature constant. We suspected that the ratio of CO_2 to CO increased with the quantity of the inert, which was consistent with the chemical equilibrium result. Nonetheless, further verification with more experimental data is required.

Compared to the situation with methane, as estimated using the DIPPR's heat capacity equation, the predicted UFLs for methyl formate, propane, propylene, and isobutane were more in agreement with the measurements (Figures 1, 5–8 and Table 3), although there were still deviations between the predictions and measurements for the latter three in the neighborhood of $x = x_U$. Maybe the combustion product distributions of the four studied compounds at their upper flammability boundary of $1 - x < 1 - x_U$ are more consistent with our assumption and there is little variation of CO/CO_2 ratio. In fact, our preliminary experimental data indicated that only CO and not CO_2 was observed in the combustion products of methyl formate diluted with water at the UFL, except at the region approaching the LOC. The observation that there was no significant deviation around the region of $x = x_U$ for methyl formate is consistent with this deduction.

Table 3 shows that the deviations of UFL were greater for ethylene, especially in the adiabatic condition, compared to the other substances. Figure 3 shows that the measured UFLs were less than the predicted UFLs and there was no significant deviation around the region of $x = x_U$ for ethylene, which differed from the situation with methane, propane, propylene, and isobutane. This deviation is suspected to be due to the presence of oxygenated hydrocarbons, such as ether, and soot, which are the relatively novel combustion products of ethylene. In order to remain at a constant flame temperature, the lower heat released when a fuel is oxidized into oxygenated hydrocarbons and soot created the requirement for the limiting reactant, O_2 , to be greater than expected, which decreased the UFL values. Nonetheless, this still needs to be verified experimentally.

In summary, the trends of combustion product distributions at the UFL seemed to depend on the burned fuel, approaching the chemical equilibrium for methane, propane, propylene, and

isobutane and deviating from equilibrium for methyl formate and ethylene.

Vidal et al. pointed out that the predicted results gave the best agreement with the existing experimental data for methane and ethylene at their LFLs, when the adiabatic flame temperature was about 1400 K.¹⁰ The calculated adiabatic flame temperatures at the LFLs for methane (1468, 1470 K) and ethylene (1383, 1393 K) when the heat capacity equations of Tables 1 and 2 were used, were close to the empirical one determined by Vidal et al.¹⁰

Table 4 shows that the different heat capacity equations and heat loss considerations did not have a significant effect on the estimated values of $1 - x_L$ when there was a nitrogen dilution effect. Using the example of methyl formate, the estimated values were very close, 0.897–0.896, ($x_L = 0.103$ –0.104), which are almost identical to the experimentally derived value, 0.896 ($x_L = 0.104$). For other studied hydrocarbons upon dilution with nitrogen, the estimated values of $1 - x_L$, irrespective of whether or not heat loss was taken into account or which heat capacity equation was used, were all close to the corresponding experimental data, although they were not as precise as was the case with methyl formate (Table 4).

3.3. Effect of Carbon Dioxide Dilution on Flammability Limits. The LFL experimental values for methyl formate adopted from Kondo et al.⁷ increased with the $1 - x$ value, the mole ratio of carbon dioxide as the blended gas (Figure 2), which was quite different from the effect of nitrogen, where the LFL values remained almost constant. This behavior was also predicted by our proposed model, although there were slight differences between the predicted and experimental data for the region approaching the LOC. As was the case with the nitrogen dilution effects mentioned above, this deviation around the point of the LOC was attributable to the existence of unburned methyl formate in this region, which was inconsistent with the assumption of complete fuel consumption. For other hydrocarbons such as methane, ethylene, propane, propylene, and isobutane, as was the case of methyl formate, the measured values of LFL increased with the mole ratio of carbon dioxide as the blended gas, and this variation was more significant in the region approaching the LOC (Figures 4, 9–12).

The constant LFL behavior when using nitrogen as the inert gas is attributed to the mean value of the heat capacity for nitrogen being close to that of air. Using methane as an example, under the condition of $\alpha\sigma\epsilon\Delta T = 10^{-9} \text{ J K}^{-4} \text{ mol}^{-1}$, which is the most possible heat loss, the mean values of heat capacity from the initial temperature, 308 K, to the flame temperature at the LFL, 1374 K, for nitrogen, were 31.4 and 31.7 $\text{J mol}^{-1} \text{ K}^{-1}$, when the heat capacity equations in Tables 1 and 2 were used. These values are close to the analogous heat capacity data of air, namely 31.8 and 32.0 $\text{J mol}^{-1} \text{ K}^{-1}$, respectively. Addition of inert gas into the mixture of fuel and air to change the reaction along the lower flammability boundary caused the air to be replaced by the inert gas. The almost equivalent value of heat capacity for nitrogen and air made the LFL values remain almost invariant in order to keep the flame temperature constant. However, in the case of carbon dioxide as the inert gas, the analogous mean values for heat capacity for carbon dioxide were 52.8 and 50.7 $\text{J mol}^{-1} \text{ K}^{-1}$, which are quite different from that of air, namely 31.8 and 32.0 $\text{J mol}^{-1} \text{ K}^{-1}$. To maintain a constant flame temperature, the greater heat capacity of carbon dioxide caused an increase in the LFL.

As was the case when nitrogen was used as the inert gas, the predictions of the UFL were in good agreement with the

Table 4. Comparison of $1 - x$ and Flammability Limit Value at the LOC between the Estimations and Corresponding Experimental Data

system	simulation				experimental data	
	Poling et al.		DIPPR			
	$1 - x_L$	fuel (vol %)	$1 - x_L$	fuel (vol %)	$1 - x_L$	fuel (vol %)
methane + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.908	4.90	0.909	4.87	0.882	5.25
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.909	4.87	0.909	4.87		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.909	4.88	0.909	4.88		
ethylene + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.955	2.72	0.955	2.72	0.946	3.18
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.955	2.73	0.955	2.72		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.955	2.73	0.955	2.72		
propane + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.961	2.01	0.961	2.02	0.950	2.40
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.961	2.02	0.961	2.02		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.961	2.02	0.961	2.02		
propylene + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.960	2.14	0.960	2.15	0.946	2.60
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.960	2.15	0.960	2.15		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.960	2.15	0.960	2.15		
isobutane + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.966	1.67	0.965	1.67	0.955	1.95
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.965	1.67	0.965	1.67		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.965	1.67	0.965	1.67		
methyl formate + N ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.897	5.20	0.896	5.22	0.896	5.60
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.896	5.22	0.896	5.23		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.896	5.22	0.896	5.23		
methane + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.850	6.17	0.862	5.97	0.794	6.47
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.861	5.98	0.866	5.88		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.870	5.81	0.872	5.78		
ethylene + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.927	3.58	0.931	3.49	0.913	4.00
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.931	3.43	0.933	3.43		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.935	3.37	0.936	3.36		
propane + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.932	2.59	0.939	2.49	0.915	2.90
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.938	2.50	0.941	2.45		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.943	2.42	0.944	2.40		
propylene + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.930	2.80	0.938	2.67	0.913	3.25
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.936	2.69	0.940	2.63		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.942	2.59	0.943	2.57		
isobutane + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.936	2.14	0.945	2.03	0.922	2.30
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.944	2.05	0.948	2.00		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.949	1.98	0.950	1.96		
methyl formate + CO ₂						
$\alpha\sigma_{A_2}\Delta t = 0 \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.817	6.67	0.842	6.30	0.833	7.10
$\alpha\sigma_{A_2}\Delta t = 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.836	6.40	0.848	6.20		
$\alpha\sigma_{A_2}\Delta t = 3 \times 10^{-9} \text{ J}\cdot\text{K}^{-4}\cdot\text{mol}^{-1}$	0.851	6.16	0.855	6.09		

measurements for the studied compounds diluted with carbon dioxide, although there were deviations in the neighborhood of the point $1 - x = 1 - x_{UJ}$, for methane, propane, propylene, and isobutane (Figures 2, 4, 9–12). Compared to other compounds, the deviation of the UFL was relatively greater for ethylene (Table 3); however, it was acceptable. Overall, the predictions of LFL and UFL were all close to the measured values.

Table 4 indicates that the estimated values of $1 - x_L$ varied with the quantity of heat loss when there was a carbon dioxide dilution effect, the behavior of which was different from that of the nitrogen dilution effect, with only slight variation in such values. Compared to the nitrogen dilution effect, the deviations of the estimated values of $1 - x_L$ between the estimations and the measurements for the carbon dioxide dilution effect were relatively greater, with the deviations increasing

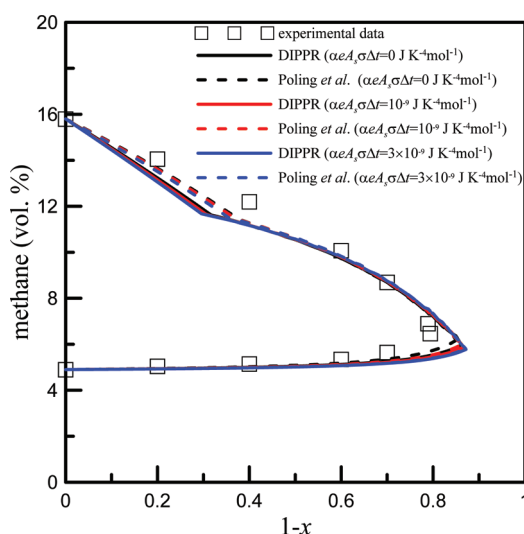


Figure 9. Carbon dioxide dilution effect on the flammability limits of methane.

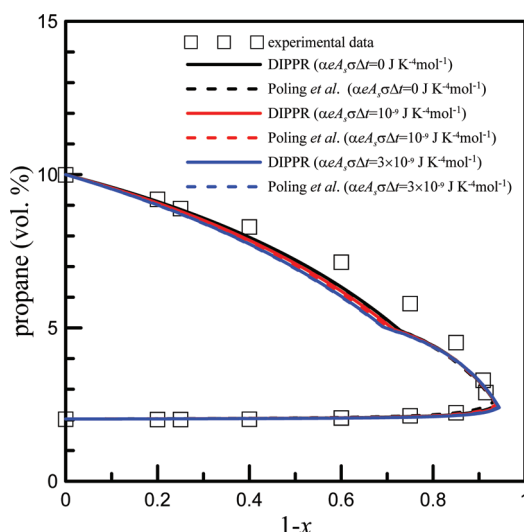


Figure 10. Carbon dioxide dilution effect on the flammability limits of propane.

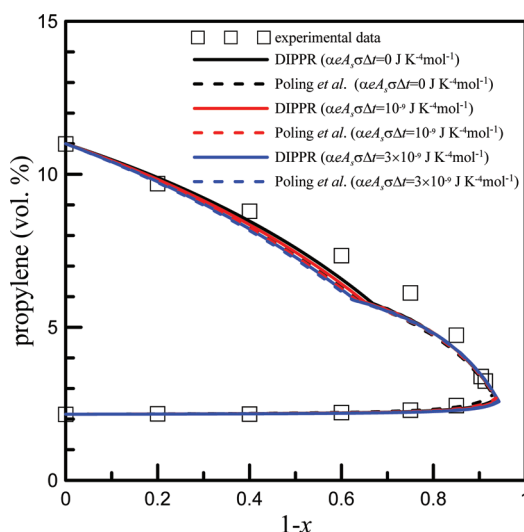


Figure 11. Carbon dioxide dilution effect on the flammability limits of propylene.

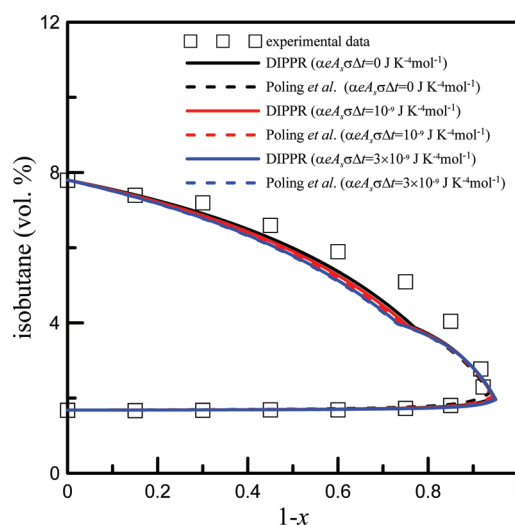


Figure 12. Carbon dioxide dilution effect on the flammability limits of isobutane.

with the quantity of heat loss. Nonetheless, these deviations were acceptable, except for those of methane, which had the greatest deviation (Table 4).

Except for the case of ethylene, the estimated upper flammability boundary for the studied compounds under adiabatic assumption was closer to the experimental data than when heat loss was considered (Table 3). Since the assumption of a constant CO/CO₂ ratio in the combustion product along the upper flammability boundary is used in this study, deviation in this ratio can occur during the real process and we could not conclude that combustion was adiabatic at the UFL. Nonetheless, it seems that the adiabatic assumption can be used to estimate the inert dilution effect on flammability limits approximately, if there is a lack of heat loss data.

4. CONCLUSION

We modeled the effect of inert gas dilution on the flammability limits for a constant pressure system using an energy balance equation. The differences in the estimated flammability envelope between different heat loss considerations are small. The predicted LFL values are in excellent agreement with the experimental data, except for the region approaching the LOC, where the assumption of complete fuel consumption fails. The behavior of the LFL as inert gas is added to a fuel is dependent on the type of inert gas, and remains almost constant for nitrogen, while it increases for carbon dioxide. This difference in behavior is attributable to the mean heat capacity value of nitrogen being close to that of air, and there being greater differences in heat capacity values between carbon dioxide and air. Due to the complexity of the reaction kinetics and ambiguity of combustion product distributions on the upper flammability boundary, a simple equation to describe the combustion product distributions for all fuels at the UFL seems impossible at this stage. The proposed model supplies a tool to estimate the flammability envelope of fuel–air–diluent mixtures for any combustion product distribution. Although the deviations between the predictions and measurements of the UFL are greater than those of the LFL are, they are acceptable. Overall, the proposed model describes the flammability limit variations well when a quantity of inert gas is added to the combustion mixture.

■ APPENDIX

Energy Balance Equation

When the flammability limits are tested in a spherical glass flask or a cylindrical vessel, the system is a closed system of constant pressure, with the pressure remaining at almost atmospheric pressure. Total heat exchange is associated with heat losses ranging from burnt gas to unburnt gas via heat convection and heat radiation, with heat radiation being significantly more dominant than heat convection at high temperature. The heat loss through thermal radiation, Q_r , is accounted for in this study. Thus, the energy balance equation is described as

$$\Delta H = Q_r \quad (A1)$$

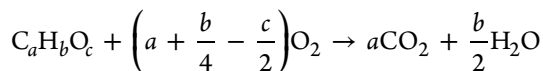
where the quantity of heat is regarded as positive when it is transferred to the system from the surroundings. If the combustion mixture is at ambient temperature, T_0 , initially, and the final temperature after the combustion is T , the above equation can be reformulated as

$$\Delta H_{298}^\circ + \sum_{\text{reactants}} \int_{T_0}^{298} n_i C_{p,i} dT + \sum_{\text{products}} \int_{298}^T n_i C_{p,i} dT = Q_r \quad (A2)$$

where ΔH_{298}° is the standard heat of reaction at the temperature of 298 K. The second term of eq A2, denoted as reactants, is for the mixture before burning, and the third term, denoted as products, is for the mixture after burning.

Lower Flammability Boundary

The fuels considered in this paper are organic compounds made up of carbon, hydrogen, and oxygen. At the LFL, the quantity of oxygen is sufficient to convert the fuel into carbon dioxide and steam completely; thus, the stoichiometry of a combustion reaction for a lean limit mixture of a typical fuel $C_aH_bO_c$ is assumed to be



For brevity in notation, the following notations are defined:

$$\begin{aligned} f_L &= a + \frac{b}{4} - \frac{c}{2} \\ g_L &= a \\ h_L &= \frac{b}{2} \end{aligned} \quad (A3)$$

$$\begin{aligned} \sum_{\text{products}} n_i C_{p,i} &= 0.79 \left(1 - \frac{L}{x}\right) C_{p,N_2} + \left[0.21 \left(1 - \frac{L}{x}\right) - f_L L\right] C_{p,O_2} + L \left(\frac{1}{x} - 1\right) C_{p,I} + g_L L C_{p,CO_2} + h_L L C_{p,H_2O} \\ &= L \left[-\frac{0.79}{x} C_{p,N_2} - \left(\frac{0.21}{x} + f_L\right) C_{p,O_2} + \left(\frac{1}{x} - 1\right) C_{p,I} + g_L C_{p,CO_2} + h_L C_{p,H_2O} \right] \\ &\quad + [0.79 C_{p,N_2} + 0.21 C_{p,O_2}] \end{aligned} \quad (A8)$$

Let

$$P_L \equiv 0.79 C_{p,N_2} + 0.21 C_{p,O_2} \quad (A9)$$

$$Q_L \equiv -f_L C_{p,O_2} + g_L C_{p,CO_2} + h_L C_{p,H_2O} \quad (A10)$$

The enthalpy change of burning 1 mol of fuel at the LFL, $(\Delta h_c)_L$, can be estimated as

$$\begin{aligned} (\Delta h_c)_L &= a \Delta H_{f,CO_2,298}^\circ + \frac{b}{2} \Delta H_{f,H_2O,298}^\circ \\ &\quad - \Delta H_{f,C_aH_bO_c,298}^\circ \\ &= \Delta h_c^\circ \end{aligned} \quad (A4)$$

where $\Delta H_{f,i,298}^\circ$ is the standard heat of formation for component i at 298 K, and Δh_c° is the standard heat of combustion for a fuel.

Let x be the mole ratio of the fuel in the blended gas, that is

$$x = \frac{\text{fuel}}{\text{fuel} + \text{inert}} \quad (A5)$$

Now, consider the case of burning 1 mol of combustible mixture at its lower flammability boundary, where the number of moles of hydrocarbon is L . Under the assumption of the fuel being completely consumed, the quantities of each component in the mixture before and after burning are as listed in Table 5.

Table 5. Quantity of Each Component in the Mixture at the LFL before and after Burning

compound	no. of mol before burning	no. of mol after burning
fuel	L	0
nitrogen	$0.79(1 - L/x)$	$0.79(1 - L/x)$
oxygen	$0.21(1 - L/x)$	$0.21(1 - L/x) - f_L L$
inert	$L(1/x - 1)$	$L(1/x - 1)$
carbon dioxide	0	$g_L L$
steam	0	$h_L L$

The standard heat of reaction at 298 K for burning 1 mol of fuel mixture at the lower flammability boundary is

$$\Delta H_{298}^\circ = L(\Delta h_c)_L = L(\Delta h_c^\circ) \quad (A6)$$

The heat capacity before burning is

$$\begin{aligned} \sum_{\text{reactants}} n_i C_{p,i} &= L C_{p,f} + 0.79 \left(1 - \frac{L}{x}\right) C_{p,N_2} \\ &\quad + 0.21 \left(1 - \frac{L}{x}\right) C_{p,O_2} + L \left(\frac{1}{x} - 1\right) C_{p,I} \end{aligned} \quad (A7)$$

The heat capacity after burning is

Thus

$$\sum_{\text{reactants}} n_i C_{p,i} = L(C_{p,f} - C_{p,I}) + (C_{p,I} - P_L) \frac{L}{x} + P_L \quad (A11)$$

$$\sum_{\text{products}} n_i C_{p,i} = L(Q_L - C_{p,I}) + (C_{p,I} - P_L) \frac{L}{x} + P_L \quad (A12)$$

Heat losses per mole of fuel–air–diluent mixture through thermal radiation can be estimated using eq A13:

$$Q_r = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \quad (\text{A13})$$

where σ is the Stefan–Boltzmann constant, e is the emissivity, A_s is the heat exchange surface area per mole mixture, and Δt is the flame propagation duration; α is an efficiency factor with respect to the heat exchange surface area, which expands gradually with flame propagation. Substituting eqs A6, A11,

A12, and A13 into eq A2, eq A14 therefore, is

$$\begin{aligned} & \int_{T_0}^{298} [L(C_{p,f} - C_{p,i}) + (C_{p,i} - P_L) \frac{L}{x} + P_L] dT \\ & + \int_{298}^T [L(Q_L - C_{p,i}) + (C_{p,i} - P_L) \frac{L}{x} + P_L] dT \\ & + L(\Delta h_c^\circ) = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (\text{A14})$$

The following equation can then be obtained:

$$L = - \frac{\int_{T_0}^T P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{298}^T Q_L dT + \int_{T_0}^{298} C_{p,f} dT - \int_{T_0}^T [C_{p,i} - (C_{p,i} - P_L) \frac{1}{x}] dT + \Delta h_c^\circ} \quad (\text{A15})$$

A.2.1. Estimation of x_L . The fuel is the limiting reactant on its lower flammability boundary. As the concentration of a fuel–air–diluent mixture varies along the lower flammability zone boundary as the quantity of inert gas increases, the air is replaced by the inert gas, and the value of x decreases. When the value of x , defined in eq A5, decreases to less than the critical value, x_L , where the ratio of fuel to oxygen equals the stoichiometric ratio, the limiting reactant is no longer the fuel, but is the oxygen. Since the oxygen is not sufficient enough to convert all the fuel to carbon dioxide, the lower flammability

boundary is assumed to be terminated at this point. That is, the point of LOC is defined to be located at $x = x_L$ in this study.

At the point where x equals x_L , the ratio of fuel to oxygen is equivalent to the stoichiometric ratio:

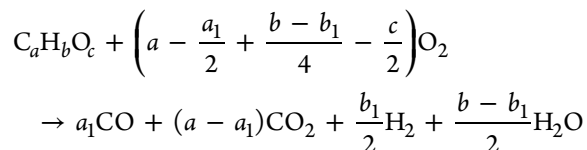
$$\frac{\text{fuel}}{\text{oxygen}} = \frac{L}{0.21(1 - L/x_L)} = \frac{1}{a + \frac{b}{4} - \frac{c}{2}} = \frac{1}{f_L}$$

Substituting eq A15 into the above equation, the result is

$$x_L = - \frac{0.21[\int_{T_0}^T C_{p,i} dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t]}{f_L [\int_{T_0}^T P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t] + 0.21[\int_{298}^T (Q_L - C_{p,i}) dT + \int_{T_0}^{298} (C_{p,f} - C_{p,i}) dT + \Delta h_c^\circ]} \quad (\text{A16})$$

Upper Flammability Boundary

As complete combustion will not occur due to oxygen insufficiency at the upper flammability boundary, the fuel may be converted to carbon dioxide, carbon monoxide (CO), steam, hydrogen (H_2), unsaturated hydrocarbons (such as ethylene, propylene), ether, and soot. However, for simplicity, the fuel is assumed to be converted to carbon dioxide, carbon monoxide, steam, and hydrogen. The corresponding stoichiometry of such a combustion reaction is expressed as



Thus, the method proposed in this study is limited to the compounds whose combustion products on the upper flammability boundary follow this assumption. For brevity in notation, the following notations are defined:

$$\begin{aligned} f_U &= \frac{1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \\ q_U &= \frac{a_1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \\ g_U &= \frac{a - a_1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \\ t_U &= \frac{\frac{b_1}{2}}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \\ h_U &= \frac{\frac{b - b_1}{2}}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \end{aligned} \quad (\text{A17})$$

The enthalpy change of burning 1 mol of fuel at the UFL is estimated as

$$\begin{aligned} (\Delta h_c)_U &= a_1 \Delta H_{f,CO,298}^\circ + (a - a_1) \Delta H_{f,CO_2,298}^\circ + \frac{b - b_1}{2} \Delta H_{f,H_2O,298}^\circ - \Delta H_{f,C_a H_b O_c,298}^\circ \\ &= \left(a \Delta H_{f,CO_2,298}^\circ + \frac{b}{2} \Delta H_{f,H_2O,298}^\circ - \Delta H_{f,C_a H_b O_c,298}^\circ \right) - a_1 (\Delta H_{f,CO,298}^\circ - \Delta H_{f,CO_2,298}^\circ) - \frac{b_1}{2} (\Delta H_{f,H_2O,298}^\circ) \quad (\text{A18}) \\ &= \Delta h_c^\circ - a_1 (\Delta h_{CO/CO_2}^\circ) - \frac{b_1}{2} (\Delta h_{H_2O}^\circ) \end{aligned}$$

where $\Delta h_{\text{CO}/\text{CO}_2}^\circ$ is the standard heat of reaction for the oxidation of 1 mol of CO to CO_2 , that is

$$\Delta h_{\text{CO}/\text{CO}_2}^\circ = \Delta H_{f,\text{CO}_2,298}^\circ - \Delta H_{f,\text{CO},298}^\circ$$

$\Delta h_{\text{H}_2\text{O}}^\circ$ is the standard heat of reaction for 1 mol of H_2 oxidized to H_2O , which is equivalent to the standard heat of formation of H_2O , and

$$\Delta h_{\text{H}_2\text{O}}^\circ = \Delta H_{f,\text{H}_2\text{O},298}^\circ$$

A.3.1. Estimation of UFL for $x \geq x_U$. For a fuel–air mixture, the fuel is in excess at its UFL. On adding inert gas into such a mixture to change the reaction along the upper flammability zone boundary, if the quantity of added inert gas is not great enough to replace a large quantity of fuel, then oxygen is still the limiting reactant. Under this condition, oxygen is assumed to be completely consumed. Consider the case of burning 1 mol of the total mixture on the upper flammability boundary; the quantities of each component in the mixture before and after burning are listed in Table 6.

Table 6. Quantity of Each Component in the Mixture at the UFL before and after Burning

compound	no. of mol before burning	no. of mol after burning ($x \geq x_U$)	no. of mol after burning ($x < x_U$)
fuel	U	$U - 0.21f_U(1 - U/x)$	0
nitrogen	$0.79(1 - U/x)$	$0.79(1 - U/x)$	$0.79(1 - U/x)$
oxygen	$0.21(1 - U/x)$	0	$0.21(1 - U/x) - U/f_U$
inert	$U(1/x - 1)$	$U(1/x - 1)$	$U(1/x - 1)$
carbon monoxide	0	$0.21q_U(1 - U/x)$	$(q_U/f_U)U$
carbon dioxide	0	$0.21g_U(1 - U/x)$	$(g_U/f_U)U$
hydrogen	0	$0.21t_U(1 - U/x)$	$(t_U/f_U)U$
steam	0	$0.21h_U(1 - U/x)$	$(h_U/f_U)U$

Since oxygen is assumed to be consumed completely, the standard heat of reaction for burning 1 mol of the total mixture

is calculated as

$$\Delta H_{298}^\circ = 0.21f_U \left(1 - \frac{U}{x}\right) (\Delta h_c)_U \quad (\text{A19})$$

The heat capacity before burning is

$$\sum_{\text{reactants}} n_i C_{p,i} = UC_{p,f} + 0.79 \left(1 - \frac{U}{x}\right) C_{p,\text{N}_2} + 0.21 \left(1 - \frac{U}{x}\right) C_{p,\text{O}_2} + U \left(\frac{1}{x} - 1\right) C_{p,\text{I}} \quad (\text{A20})$$

The heat capacity after burning is

$$\begin{aligned} \sum_{\text{products}} n_i C_{p,i} = & \left(U - 0.21f_U \left(1 - \frac{U}{x}\right) \right) C_{p,f} \\ & + 0.21q_U \left(1 - \frac{U}{x}\right) C_{p,\text{CO}} + 0.21g_U \left(1 - \frac{U}{x}\right) C_{p,\text{CO}_2} \\ & + 0.21t_U \left(1 - \frac{U}{x}\right) C_{p,\text{H}_2} + 0.21h_U \left(1 - \frac{U}{x}\right) C_{p,\text{H}_2\text{O}} \\ & + 0.79 \left(1 - \frac{U}{x}\right) C_{p,\text{N}_2} + U \left(\frac{1}{x} - 1\right) C_{p,\text{I}} \end{aligned} \quad (\text{A21})$$

Let

$$\begin{aligned} P_U \equiv & 0.21q_U C_{p,\text{CO}} + 0.21g_U C_{p,\text{CO}_2} + 0.21t_U C_{p,\text{H}_2} \\ & + 0.21h_U C_{p,\text{H}_2\text{O}} + 0.79 C_{p,\text{N}_2} - 0.21f_U C_{p,f} \end{aligned} \quad (\text{A22})$$

Thus

$$\sum_{\text{reactants}} n_i C_{p,i} = U(C_{p,f} - C_{p,\text{I}}) + \frac{U}{x}(C_{p,\text{I}} - P_U) + P_U \quad (\text{A23})$$

$$\sum_{\text{products}} n_i C_{p,i} = U(C_{p,f} - C_{p,\text{I}}) + \frac{U}{x}(C_{p,\text{I}} - P_U) + P_U \quad (\text{A24})$$

Inserting eqs A13, A19, A23, and A24 into eq A2, eq A25 is derived as

$$\begin{aligned} & 0.21f_U \left(1 - \frac{U}{x}\right) (\Delta h_c)_U + \int_{298}^T [U(C_{p,f} - C_{p,\text{I}}) + \frac{U}{x}(C_{p,\text{I}} - P_U) + P_U] dT + \int_{T_0}^{298} [U(C_{p,f} - C_{p,\text{I}}) + \frac{U}{x}(C_{p,\text{I}} - P_U) + P_U] dT \\ & = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (\text{A25})$$

The following equation is, thus, obtained:

$$U = - \frac{\int_{298}^T P_U dT + \int_{T_0}^{298} P_U dT + 0.21f_U (\Delta h_c)_U + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{T_0}^T (C_{p,f} - C_{p,\text{I}}) dT + \int_{298}^T (C_{p,\text{I}} - P_U) \frac{1}{x} dT + \int_{T_0}^{298} (C_{p,\text{I}} - P_U) \frac{1}{x} dT - 0.21f_U \frac{1}{x} (\Delta h_c)_U} \quad (\text{A26})$$

A.3.2. Estimation of x_U . When the concentration of a fuel–air mixture is moved along its upper flammability zone boundary by the addition of an inert gas, the added inert gas replaces the excess fuel, and that makes the value of x decrease. When the value of x decreases below a critical value, x_U , where the ratio of fuel to oxygen is equivalent to the stoichiometric ratio, the ratio of CO_2 to CO will increase because the quantity of oxygen is great enough to produce

more carbon dioxide. At the point that $x = x_U$:

$$\begin{aligned} \frac{\text{fuel}}{\text{oxygen}} &= \frac{U}{0.21(1 - U/x_U)} \\ &= \frac{1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} = f_U \end{aligned}$$

Substituting eq A26 into the above equation, the resulting equation is

$$x_U = - \frac{0.21f_U [\int_{T_0}^T C_{p,I} dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t]}{\int_{298}^T P_U dT + \int_{T_0}^{298} P_L dT + \alpha e A_s \sigma (T^4 - T_0^4) \Delta t + 0.21f_U [\int_{T_0}^T (C_{p,f} - C_{p,I}) dT + (\Delta h_c)_U]} \quad (A27)$$

A.3.3. Estimation of the UFL for $x < x_U$. When the value of x is less than that of x_U , the quantity of oxygen is great enough to convert more fuel to carbon dioxide on the upper flammability zone boundary, and that makes the ratio of CO_2 to CO increase. In the case of burning 1 mol of the total fuel mixture on the upper flammability zone boundary where $x < x_U$, the quantities of each component in the mixture after burning are estimated as listed in Table 6, under the assumption of the fuel and oxygen being completely consumed.

Since the fuel is assumed to be consumed completely, the heat of reaction for burning 1 mol of the total mixture is calculated as

$$\Delta H_{298}^\circ = U(\Delta h_c)_U \quad (A28)$$

The heat capacity before burning is given as eq A23. The heat capacity after burning is

$$\begin{aligned} \sum_{\text{products}} n_i C_{p,i} &= 0.79 \left(1 - \frac{U}{x}\right) C_{p,N_2} + \left(0.21 \left(1 - \frac{U}{x}\right) - \frac{U}{f_U}\right) C_{p,O_2} + U \left(\frac{1}{x} - 1\right) C_{p,I} + a_1 U C_{p,CO} \\ &\quad + (a - a_1) U C_{p,CO_2} + 0.5 b_1 U C_{p,H_2} + 0.5 (b - b_1) U C_{p,H_2O} \\ &= 0.79 \left(1 - \frac{U}{x}\right) C_{p,N_2} + \left(0.21 \left(1 - \frac{U}{x}\right) - \frac{U}{f_U}\right) C_{p,O_2} + U \left(\frac{1}{x} - 1\right) C_{p,I} + a_1 U (C_{p,CO} - C_{p,CO_2}) \\ &\quad + a U C_{p,CO_2} + \frac{t_U}{f_U} U C_{p,H_2} + \frac{h_U}{f_U} U C_{p,H_2O} \end{aligned} \quad (A29)$$

Let

$$\begin{aligned} Q_U &\equiv a C_{p,CO_2} + \frac{t_U}{f_U} C_{p,H_2} \\ &\quad + \frac{h_U}{f_U} C_{p,H_2O} - C_{p,I} - \frac{1}{f_U} C_{p,O_2} \end{aligned} \quad (A30)$$

Thus

$$\begin{aligned} \sum_{\text{products}} n_i C_{p,i} &= U \left[a_1 (C_{p,CO} - C_{p,CO_2}) \right. \\ &\quad + a C_{p,CO_2} + \frac{t_U}{f_U} C_{p,H_2} \\ &\quad + \left. \frac{h_U}{f_U} C_{p,H_2O} - C_{p,I} - \frac{1}{f_U} C_{p,O_2} \right] \\ &\quad + \frac{U}{x} (C_{p,I} - P_L) + P_L \\ &= U Q_U + a_1 U (C_{p,CO} - C_{p,CO_2}) \\ &\quad + \frac{U}{x} (C_{p,I} - P_L) + P_L \end{aligned} \quad (A31)$$

Substituting eqs A13, A23, A28, and A31 into eq A2, and replacing $(\Delta h_c)_U$ by use of eq A18, the resulting equation is

$$\begin{aligned} &U \left(\Delta h_c^\circ - a_1 (\Delta h_{CO/CO_2}^\circ) - \frac{b_1}{2} (\Delta h_{H_2O}^\circ) \right) \\ &\quad + \int_{298}^T [U Q_U + a_1 U (C_{p,CO} - C_{p,CO_2}) \\ &\quad + \frac{U}{x} (C_{p,I} - P_L) + P_L] dT \\ &\quad + \int_{T_0}^{298} \left[U (C_{p,f} - C_{p,I}) + \frac{U}{x} (C_{p,I} - P_L) + P_L \right] \\ &\quad dT = -\alpha e A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (A32)$$

Since the CO_2/CO ratio is not a constant in this region, the value of a_1 will vary with the quantity of inert gas. Oxygen is completely consumed on the upper flammability zone boundary of $x < x_U$; thus, the quantity of oxygen is

$$0.21 \left(1 - \frac{U}{x}\right) - \frac{U}{f_U} = 0 \quad (A33)$$

Substituting f_U , eq A17, into the above equation, the result is

$$\begin{aligned} a_1 &= 2a + \frac{b - b_1}{2} - c - 0.42 \left(\frac{1}{U} - \frac{1}{x} \right) \\ &= p - 0.42 \left(\frac{1}{U} - \frac{1}{x} \right) \end{aligned} \quad (A34)$$

where

$$p = 2a + \frac{b - b_1}{2} - c \quad (\text{A35})$$

$$U = - \frac{\int_{298}^T [P_L - 0.42(C_{p,\text{CO}} - C_{p,\text{CO}_2})] dT + \int_{T_0}^{298} P_L dT + 0.42(\Delta h_{\text{CO/CO}_2}) + \alpha \epsilon A_s \sigma (T^4 - T_0^4) \Delta t}{\int_{298}^T \left[Q_U + \frac{1}{x}(C_{p,\text{I}} - P_L) + (C_{p,\text{CO}} - C_{p,\text{CO}_2}) \left(p + \frac{0.42}{x} \right) \right] dT + \int_{T_0}^{298} [(C_{p,\text{f}} - C_{p,\text{I}}) + \frac{1}{x}(C_{p,\text{I}} - P_L)] dT + (\Delta h_p)} \quad (\text{A36})$$

where

$$(\Delta h_p) = \Delta h_c^\circ - \frac{b_1}{2}(\Delta h_{\text{H}_2\text{O}}^\circ) - \left(p + \frac{0.42}{x} \right) (\Delta h_{\text{CO/CO}_2}^\circ) \quad (\text{A37})$$

At the point that $x = x_U$, the temperature is equivalent to the flame temperature of the UFL, T_U , and at the LOC, the temperature is equivalent to the flame temperature of the LFL, T_L . We assume the temperature in this region is linear with the quantity of carbon monoxide, a_1 . Thus, the temperature in eq A36 is described as

$$T = \frac{a_1}{a_{1U}} T_U + \left(1 - \frac{a_1}{a_{1U}} \right) T_L \quad (\text{A38})$$

where a_{1U} is the value of a_1 at the point that $x = x_U$.

Flame Temperature

In the case of a combustible mixture without the addition of any inert gas

$$x = 1$$

$$L = L_0$$

$$U = U_0$$

and

$$P_U = P_{U0}$$

where L_0 is the LFL, U_0 is the UFL, and P_{U0} is the P_U value of such a fuel–air mixture. Under this condition, eqs A14 and A25 are reducible, respectively, to

$$\begin{aligned} L_0(\Delta h_c^\circ) + \int_{298}^T [L_0(Q_L - P_L) + P_L] dT \\ + \int_{T_0}^{298} [L_0(C_{p,\text{f}} - P_L) + P_L] dT \\ = -\alpha \epsilon A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (\text{A39})$$

and

$$\begin{aligned} 0.21 f_U (1 - U_0) (\Delta h_c) + \int_{298}^T [U_0(C_{p,\text{f}} - P_{U0}) \\ + P_{U0}] dT + \int_{T_0}^{298} [U_0(C_{p,\text{f}} - P_L) + P_L] dT \\ = -\alpha \epsilon A_s \sigma (T^4 - T_0^4) \Delta t \end{aligned} \quad (\text{A40})$$

Substituting eq A34 into eq A32, the following equation is obtained:

AUTHOR INFORMATION

Corresponding Author

*Tel.: 886-4-22053366, ext 6209. Fax: 886-4-22030418. E-mail: hjliaw@mail.cmu.edu.tw.

NOMENCLATURE

A_s = heat exchange surface area per mole of mixture, $\text{m}^2 \cdot \text{mol}^{-1}$

a = number of carbon atoms in a fuel molecule

a_i = parameters adopted from Poling et al.¹⁵ to estimate the heat capacity

a_1 = mole of carbon atom convert to CO when burning one mole of fuel at UFL

b = number of hydrogen atoms in a fuel molecule

b_1 = mole of hydrogen atom convert to H_2 when burning one mole of fuel at UFL

c = number of oxygen atoms in a fuel molecule

C_i = parameters adopted from DIPPR¹⁶ to estimate the heat capacity

C_p = heat capacity, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

e = emissivity

f_L = defined in eq A3

f_U = defined in eq A17

g_L = defined in eq A3

g_U = defined in eq A17

h = specific enthalpy, $\text{J} \cdot \text{mol}^{-1}$

h_L = defined in eq A3

h_U = defined in eq A17

L = lower flammability limit

n = mole, mol

P_L = defined in eq A9

P_U = defined in eq A22

p = defined in eq A35

Q_L = defined in eq A10

Q_r = heat loss through thermal radiation, $\text{J} \cdot \text{mol}^{-1}$

Q_U = defined in eq A30

q_U = defined in eq A17

R = gas constant, $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

T = temperature, K

T_0 = ambient temperature, K

T_L = adiabatic flame temperature of LFL, K

T_U = adiabatic flame temperature of UFL, K

t_U = defined in eq A17

U = upper flammability limit

u = burning velocity

x = mole ratio of the fuel in the blended gas

ΔH = enthalpy change, J

ΔH_{298}° = standard heat of reaction at 298 K, J

$\Delta H_{f,i,298}^\circ$ = standard heat of formation for component i at 298 K, J·mol⁻¹

$\Delta h_{H_2O}^\circ$ = standard heat of reaction for 1 mol of H₂ oxidized to H₂O, J·mol⁻¹

$\Delta h_{CO/CO_2}^\circ$ = standard heat of reaction for the oxidation of 1 mol of CO to CO₂, J·mol⁻¹

Δh_c = enthalpy change of burning 1 mol of fuel, J·mol⁻¹

Δh_c° = standard heat of combustion for a fuel, J·mol⁻¹

Δh_p = defined in eq A37, J·mol⁻¹

Δt = flame propagation duration, s

Greek Symbols

α = efficiency factor with respect to the heat exchange surface area

σ = Stefan–Boltzmann constant, W·m⁻²·K⁻⁴

Subscripts

c = combustion

exp = experimental data

f = fuel

i = species i

I = inert

L = lower flammability limit

pred = predictive value

U = upper flammability limit

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