# Estimation of the lower flammability limit of organic compounds as a function of temperature

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ABSTRACT

A new method of estimating the lower flammability limit (LFL) of general organic compounds is presented. The LFL is predicted at 298 K for gases and the lower temperature limit for solids and liquids from structural contributions and the ideal gas heat of formation of the fuel. The average absolute deviation from more than 500 experimental data points is 10.7%. In a previous study, the widely used modified Burgess–Wheeler law was shown to underestimate the effect of temperature on the lower flammability limit when determined in a large-diameter vessel. An improved version of the modified Burgess–Wheeler law is presented that represents the temperature dependence of LFL data determined in large-diameter vessels more accurately. When the LFL is estimated at increased temperatures using a combination of this model and the proposed structural-contribution method, an average absolute deviation of 3.3% is returned when compared with 65 data points for 17 organic compounds determined in an ASHRAE-style apparatus.

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## 1. Introduction

The lower flammability limit (LFL) is the lowest concentration of fuel in air that will support flame propagation, typically given in vol% [1,2]. Accurate knowledge of the LFL for a variety of chemicals is needed to design safe chemical and petrochemical processes. Experimental data obtained at 298 K are available for many commonly used gases [3–14]. However, little or no data exist for a wide range of chemicals, and values are rare for most chemicals at non-ambient conditions.

Many methods have been developed to estimate the LFL of pure chemicals at a single temperature point, usually 298 K [11,15–48]. A review of a few of these methods is provided by Vidal et al. [49]. However, to our knowledge only three distinct methods of estimating the temperature-dependence of the LFL of general organic compounds have been published. The most well-known of these methods is the modified Burgess–Wheeler law [50],

$$\frac{\mathrm{LFL}(T)}{\mathrm{LFL}(T_0)} = 1 - \frac{\bar{C}_{p,\mathrm{fuel-air}}}{\mathrm{LFL}(T_0)(-\Delta H_c)}(T - T_0), \tag{1}$$

where $\bar{C}_{p,\mathrm{fuel-air}}$ is the total ideal gas heat capacity of the fuel-air mixture at constant pressure, $\Delta H_c$ is the molar heat of combustion, LFL $(T_0)$ is the LFL at temperature $T_0$, and LFL $(T)$ is the estimated LFL at temperature $T$. The values of the heat of combustion and total heat capacity in the modified Burgess–Wheeler law are typically taken at $T_0$.

The modified Burgess–Wheeler law is based on the assumption that the adiabatic flame temperature ($T_\mathrm{ad}$) of a lower limit fuel–air mixture is independent of initial temperature. This was previously shown to be true only for LFLs determined in narrow tubes (diameters less than about 6 cm) using a full flame propagation criterion [51]. Calculated adiabatic flame temperatures corresponding to LFL data determined in larger diameter tubes, however, were shown to decrease with increasing initial fuel–air temperature. Consequently, Eq. (1) underestimates the temperature-dependence of LFLs determined in large-diameter vessels.

The method of Britton and Frurip [18,19] also assumes $T_\mathrm{ad}$ is independent of initial temperature:

$$\mathrm{LFL}(T) = \mathrm{LFL}(T_0) \cdot \frac{T_\mathrm{ad} - T}{T_\mathrm{ad} - T_0}, \tag{2}$$

where $T_\mathrm{ad}$ and LFL $(T_0)$ are calculated from correlations provided by the authors. Unsurprisingly, this method yields similar results as the modified Burgess–Wheeler law.

On the other hand, Catoire and Naudet [52] developed an empirically based prediction method for fuels containing C, H, or O atoms:

$$\mathrm{LFL}(T) = 519.957 \cdot X^{0.70936} \cdot n_\mathrm{C}^{-0.197} \cdot T^{-0.51536}, \tag{3}$$

where

$$X = \frac{1}{1 + 5n_\mathrm{C} + 5/4 n_\mathrm{H} - 5/2 n_\mathrm{O}} \tag{4}$$

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**Table 1**
Ideal gas heat of formation and heat capacity values at 298 K for Eq. (10).

| Species | $H^o$ (kJ/mol) | $c_p$ (J/mol K) |
|---|---|---|
| Air | 0 | 28.9937 |
| $O_2$ | 0 | 29.3468 |
| $N_2$ | 0 | 29.1260 |
| $CO_2$ | −393.51 | 37.2433 |
| $H_2O$ | −241.81 | 33.5780 |
| $SO_2$ | −296.84 | 39.8980 |
| $SiO_2$ | −305.43 | 44.0254 |
| HF | −273.30 | 29.1361 |
| HCl | −92.31 | 29.1436 |
| HBr | −36.29 | 29.1327 |
| HI | −26.50 | 29.1583 |

and $n_C$, $n_H$, and $n_O$ are the number of carbon, hydrogen, and oxygen atoms in the fuel, respectively. The structures of the modified Burgess–Wheeler law and the method of Britton and Frurip are advantageous over the model proposed by Catoire and Naudet, as any predicted or experimental LFL may be used as a reference point. In other words, satisfactory methods of estimating the temperature dependence of the LFL that are similar in structure to Eqs. (1) and (2) may still be used as new experimental data or more accurate single-point LFL prediction methods become available.

A new method of estimating the LFL of general organic compounds is presented in this work that includes a theoretically based correlation for the effect of initial temperature of the fuel–air mixture prior to combustion. The accuracy of this method is then compared with the accuracy of previously published methods.

## 2. Method

Prediction of the LFL is split into two parts: estimation of the magnitude of the LFL at a single reference temperature, and estimation of the effect of initial temperature.

### 2.1. Estimation of magnitude

Data for the single point estimation were taken from the DIPPR® 801 database [53]. Predicted points in the database were excluded from this work, leaving a total of 509 LFL values for general organic compounds. These experimental data were divided into a training set (309 points), from which model parameters were determined, and a test set, to test the predictive power of the proposed model. Parameters were obtained by minimizing the sum of the absolute average deviation (AAD),
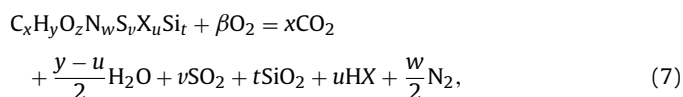
$$\text{AAD}(\%) = \frac{1}{p} \sum_p \left| \frac{\text{predicted} - \text{experimental}}{\text{experimental}} \right| \times 100\%, \tag{5}$$

where $p$ is the number of points in the training set.

The proposed model takes advantage of the relationship between the LFL and $T_{ad}$:

$$\text{LFL}(T^o)H_{fuel}(T^o) + (100 - \text{LFL}(T^o))H_{air}(T^o)$$
$$= \text{LFL}(T^o) \sum_{products} n_i H_i(T_{ad}) + (100 - \text{LFL}(T^o))H_{air}(T_{ad})$$
$$- \text{LFL}(T^o)\beta H_{O_2}(T_{ad}), \tag{6}$$

where $H_{fuel}(T^o)$ and $H_{air}(T^o)$ are the enthalpies of the fuel and air at the test temperature, $T^o$, $n_i$ is the moles of combustion product $i$ following complete combustion of the fuel at the LFL, and $H_i(T_{ad})$ and $H_{O2}(T_{ad})$ are the enthalpies for combustion product $i$ and oxygen at the adiabatic flame temperature. Combustion is assumed to follow the typical oxidation reaction:

$$C_xH_yO_zN_wS_vX_uSi_t + \beta O_2 = xCO_2$$
$$+ \frac{y-u}{2}H_2O + vSO_2 + tSiO_2 + uHX + \frac{w}{2}N_2, \tag{7}$$

where X represents halogen atoms and $\beta$ is given by

$$\beta = x + \frac{y-u}{4} + v + t - \frac{z}{2}. \tag{8}$$

**Table 2**
Structural contributions for Eq. (12).

| $j$ | Group | $\Delta T$ | Example | $j$ | Group | $\Delta T$ | Example |
|---|---|---|---|---|---|---|---|
| 1 | ≡C– | 991.44 | Vinylacetate | 29 | $N_a$ | 2622.13 | Pyridine |
| 2 | ≡CH | 1237.85 | Acetylene | 30 | $N_R$ | 2124.88 | Piperazine |
| 3 | =C< | 1834.42 | Isobutene | 31 | NH | 1566.76 | n-Pentylamine |
| 4 | =CH | 1751.82 | trans-2-Butene | 32 | $N-(C_a)$ | 2695.31 | n-Ethylaniline |
| 5 | $=CH_2$ | 1558.49 | 1-Hexene | 33 | N≡C | 939.73 | Benzonitrile |
| 6 | $=CH-(C_a)$ | −76.72 | Styrene | 34 | N=C=O | 1147.48 | Methyl isocyanate |
| 7 | $=C-(C_a)$ | 2091.1 | α-Methylstyrene | 35 | $NO_2$ | 1777.58 | Nitroethane |
| 8 | >C< | 1957.78 | Neopentane | 36 | S | 1056.05 | Thiophene |
| 9 | –CH | 1558.73 | Isopropanol | 37 | SH | 1727.5 | Ethyl mercaptan |
| 10 | $-CH_2$ | 1705.21 | Propane | 38 | S= | 272.36 | Carbon disulfide |
| 11 | $-CH_3$ | 1856.3 | Butane | 39 | Si | −55.66 | Trimethyl silane |
| 12 | $CH_3-(C_a)$ | 1862.04 | Toluene | 40 | $Si(O_3)$ | 2095.22 | Tetraethoxysilane |
| 13 | $C_a$ | 1719.69 | Toluene | 41 | (Si)–O– | 2347.17 | Octamethyltrisiloxane |
| 14 | $C_aH$ | 1731.92 | Phenol | 42 | Si–(Cl) | 1062.27 | Monochlorosilane |
| 15 | OH–(C) | 786.14 | 1-Methylcyclohexanol | 43 | $Si-(Cl_2)$ | 554.54 | Dichlorosilane |
| 16 | OH–(CH) | 1508.33 | Isopropanol | 44 | $Si-(Cl_3)$ | −34.35 | Methyl trichlorosilane |
| 17 | OH–(CH2) | 1397.73 | Butanol | 45 | $F_2-(C)$ | 2556.15 | 1,1-Difluoroethane |
| 18 | $OH-(C_a)$ | 1337.25 | Phenol | 46 | $F_2-(C=C)$ | 2088.23 | 1,1-Difluoroethylene |
| 19 | OH–(CC≡C) | 2209.35 | Propargyl alcohol | 47 | $F_3-(C)$ | 2451.95 | 3,3,3-Trifluoropropene |
| 20 | O=C | 1532.45 | 3-Pentanone | 48 | F–(C) | 1841.54 | Methyl fluoride |
| 21 | $O=C_R$ | 954.03 | Cyclohexanone | 49 | F–(C=C) | 1477.04 | Vinyl fluoride |
| 22 | O=C–C=C | 1761.66 | Methacrolein | 50 | $Cl_2-(C)$ | 2882.45 | Dichloromethane |
| 23 | O=COC | 1492.23 | Hexyl formate | 51 | $Cl_2(C=C)$ | 2956.55 | 1,1-Dichloroethylene |
| 24 | (C)O(C) | 1325.57 | Diethylene glycol | 52 | $Cl_3-(C)$ | 3046.39 | 1,1,1-Trichloroethane |
| 25 | COOH | 1252.38 | Formic acid | 53 | Cl–(C) | 1948.51 | Isopropylchloride |
| 26 | $O_R$ | 1402.11 | Furan | 54 | Cl–(C=C) | 2294.79 | Chloropropene |
| 27 | O–O | −728.23 | Cumene | 55 | Cl–(C=C–Cl) | 3257.79 | o-Dichlorobenzene |
| 28 | N | 1442.71 | Triethylamine | 56 | Br– | 3389.83 | Methyl bromide |

Subscripts a and R indicate an aromatic atom and an atom in a non-aromatic ring, respectively.

**Table 3**
Accuracy of published methods for estimating the LFL at a single temperature compared with the proposed method.

| Method | AAD (%) | | |
|---|---|---|---|
| | Combined sets | Training set | Test set |
| Proposed method | 10.67 | 10.61 | 10.76 |
| Correlations for general organic compounds | AAD (%) combined sets (509 points) | | |
| Pintar [35] | 14.21 | | |
| Spakowski [41] | 15.28 | | |
| Dalmazzone [20] | 15.79 | | |
| Goto [23] | 16.07 | | |
| Hshieh [26] | 16.83 | | |
| Affens [15] | 17.06 | | |
| Hanley [24] | 18.66 | | |
| Shebeko [38] | 20.37 | | |
| Britton [18] | 20.94 | | |
| Jones [27,46] | 21.93 | | |
| Kondo [11,28,29] | 23.86 | | |
| Shimy [39] | 24.54 | | |
| Solovev–Baratov [40] | 25.04 | | |
| Thornton [44] | 26.18 | | |
| Oehley [34] | 27.38 | | |
| Monakhov [17,38] | 29.42 | | |
| Funk [22] | 32.84 | | |
| Suzuki-Ishida [43] | 39.54 | | |
| Miloshev [32] | 40.31 | | |
| Suzuki [42] | 42.90 | | |
| Chemical equilibrium methods | $T_{ad}$ criterion | AAD (%) combined sets (509 points) | |
| Mashuga-Crowl [30]/Ervin et al. [21] | 1200 K | 34.42 | |
| Melhelm [31] | 1000 K | 50.80 | |
| Shebeko et al. [37]/Vidal et al. [45] | 1600 K | 18.39 | |
| Correlations applicable to select compounds | Applicable points | AAD (%) combined sets | |
| Albahri [16] | 104 | 9.71 | |
| Hilado [25] | 445 | 17.88 | |
| Möller [33] | 383 | 20.55 | |
| Seaton [36] | 287 | 19.53 | |
| Zatsepin [47] | 352 | 16.66 | |
| Zatsepin from $T_{ad}$ [48] | 462 | 12.74 | |

Eq. (6) is easily solved for the LFL if heat capacities are assumed to be independent of temperature, and $T^o$ is assumed to be close to 298 K:

$$LFL(298\,K) = \frac{100}{1 + \nu}, \tag{9}$$

where

$$\nu = \frac{H^o_{fuel} - \sum_{products} n_i H_i(T_{ad}) + \beta H_{O_2}(T_{ad})}{H_{air}(T_{ad})}, \tag{10}$$

$H^o_{fuel}$ is the ideal gas heat of formation of the fuel, and the enthalpy of each species relative to the ideal gas enthalpy of formation at
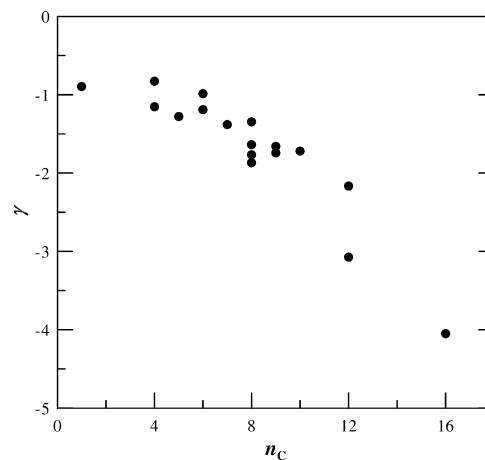


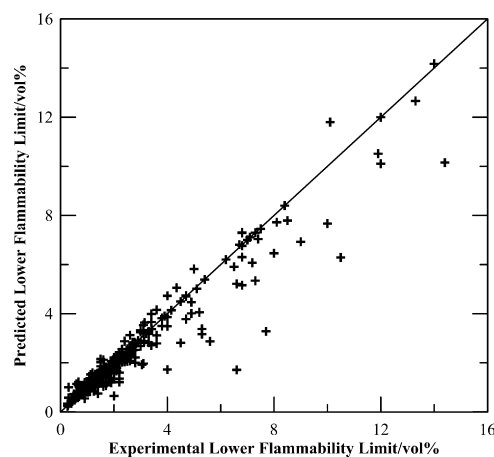**Fig. 1.** Slope of the adiabatic flame temperature, $\gamma$, as a function of carbon number, nC.



**Fig. 2.** Comparison of predicted and reported LFL values.

298 K, $H^o_i$, is found using

$$H_i(T_{ad}) = H^o_i + C_{p,i}(T_{ad} - 298\,K). \tag{11}$$

Enthalpy of formation and heat capacity values were taken from the DIPPR® database, and are listed in Table 1.
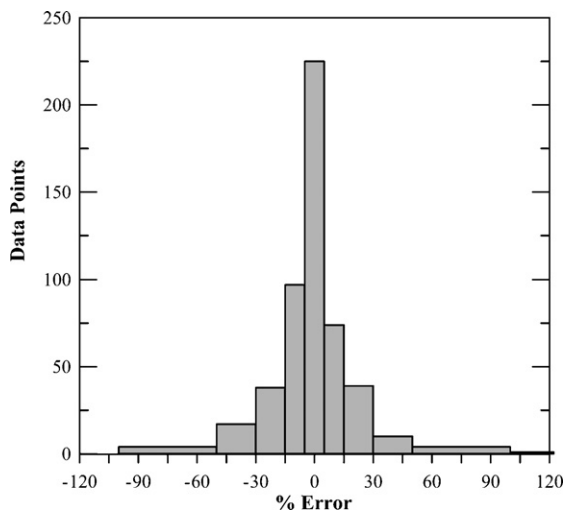


**Fig. 3.** Distribution of the deviations of the predicted LFL using the proposed method from experimental data in the DIPPR® 801 database.

**Table 4**
Absolute deviations exceeding 30% when the lower flammability limit is predicted using the proposed method (Eq. (9)).

| Compound | Pred. LFL (vol%) | Deviation (%) | Compound | Pred. LFL (vol%) | Deviation (%) |
|---|---|---|---|---|---|
| Diacetone alcohol | 1.25 | −30.44 | Pentafluoroethyl methyl ether | 6.29 | −40.13 |
| n-Methylpiperidin | 1.19 | 31.79 | cis-1,3-Dichloropropene | 3.16 | −40.32 |
| 4-Formylmorpholine | 1.59 | 32.31 | 1,4-Dichloro-trans-2-butene | 2.15 | 43.36 |
| Methacrylic acid | 2.12 | 32.62 | Hexamethylenediamine | 1.01 | 44.88 |
| Diethylenetriamine | 1.34 | −32.90 | Dopropylene glycol | 1.21 | −45.00 |
| Triethylene glycol | 1.20 | 33.56 | 1-Dodecene | 0.58 | 45.21 |
| Dichlorodiethylsilane | 1.52 | 34.73 | α-Terpineol | 0.73 | 45.38 |
| n-Ethylaniline | 1.04 | −34.74 | Benzidine | 0.75 | −46.39 |
| 1,4-Dichlorobutane | 2.03 | 35.05 | Hydrogen cyanide | 2.87 | −48.70 |
| Methyl isocyanate | 3.38 | −36.30 | Piperazine | 1.72 | −56.94 |
| Propionitrile | 1.97 | −36.42 | 1,1,2,2,3-Pentafluoropropane | 3.28 | −57.42 |
| Propylene glycol 1-tert-butyl | 1.07 | −36.86 | Cylcohexylamine | 1.10 | 66.06 |
| Acrylonitrile | 1.29 | −36.88 | Tris(2-methoxyethoxy)vinylsilane | 0.65 | 67.66 |
| 3-(n, n-Dimethylamino) propylamine | 1.19 | −37.27 | Cyanogen | 1.71 | −74.04 |
| 2-Chloropropene | 2.81 | −37.52 | 2-Propanol-1-methoxy-propanoate | 1.14 | 89.62 |
| Vinylacetylene | 1.36 | −38.21 | m-Divinylbenzene | 0.58 | 92.13 |
| Decamethyltetrasilaoxane | 0.55 | −39.16 | Methylglutaronitrile | 1.00 | 234.74 |

$T_{ad}$ may be estimated using the structural contributions that were found to minimize the AAD from the experimental data in the DIPPR® 801 database. The relationship between $T_{ad}$ and these structural contributions is given by

$$T_{ad} = \frac{\sum_j ng_j \cdot \Delta T_j}{\sum_k ng_k}, \quad (12)$$

where $ng$ is the occurrences of the $j$ th structural contribution, $\Delta T$, given in Table 2, and the sum in the denominator represents the total number of structural contributions used to represent the fuel. Note that the value of $T_{ad}$ in Eq. (12) will differ from $T_{ad}$ calculated at the lower flammability limit using chemical equilibrium calculators due to the simplifying assumptions made in deriving Eq. (10). Because the structural contributions were fit to adiabatic flame temperatures calculated with consistent assumptions, these assumptions do not largely affect the accuracy of the method but make the method simple to implement.

## 2.2. Estimation of temperature dependence

Assuming heat capacities are independent of temperature, Eq. (6) may be rewritten as

$$LFL(T) \cdot (-\Delta H_c^o) + \bar{C}_{p,fuel-air}(T - 298\,K) = \bar{C}_{p,prod}(T_{ad} - 298\,K), \quad (13)$$

where $\bar{C}_{p,prod}$ is the constant pressure total heat capacity of the combustion product mixtures (including excess air) formed by combustion of LFL moles of fuel in 100-LFL moles of air, and $\Delta H_c^o$ is the heat of combustion for the gaseous reactant, which may be found from the standard state enthalpies of combustion and formation ($H_{std}$) by:

$$\Delta H_c^o = \Delta H_c + H_{std} - H^o. \quad (14)$$

It should be noted that the enthalpy of combustion used in this work is consistent with the definition used by DIPPR which assumes the gaseous products of Eq. (7) except for crystalline $SiO_2$.

Equating Eq. (13) for two different temperatures and solving for the lower flammability limit at temperature $T_2$ yields

$$LFL(T_2) = LFL(T_1) + \frac{\bar{C}_{p,fuel-air}(T_1 - T_2) - \bar{C}_{p,prod}(T_{ad}(T_1) - T_{ad}(T_2))}{(-\Delta H_c^o)}. \quad (15)$$

It was previously shown that the adiabatic flame temperature decreases linearly with initial test temperature [51]. If a simple slope–intercept equation is substituted for the adiabatic flame temperature in Eq. (15), i.e.,
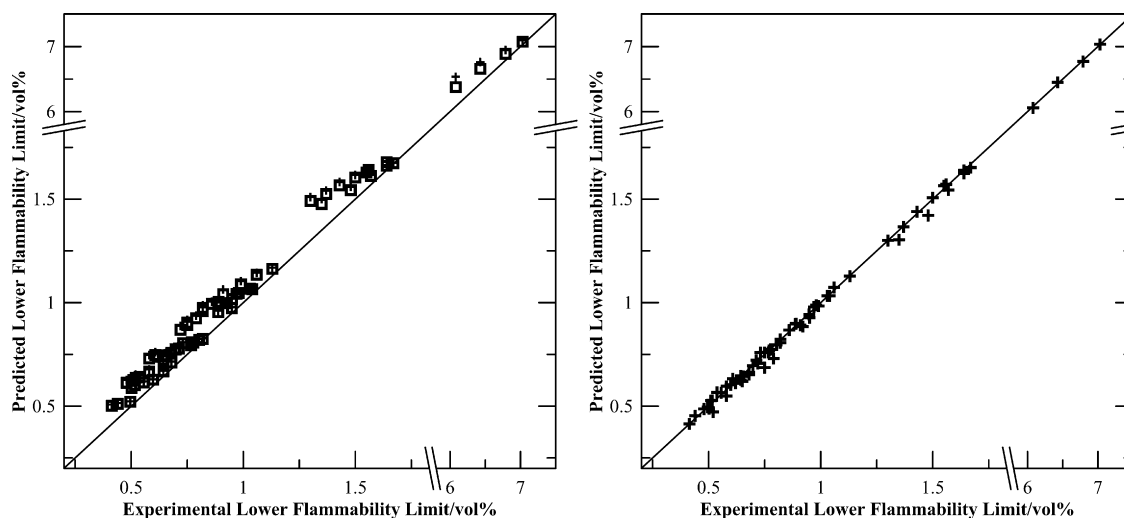
$$T_{ad} = \gamma T + b, \quad (16)$$



**Fig. 4.** Comparison of the estimated temperature dependence of the LFL, as calculated by (left) the method of Britton and Frurip (Eq. (2), □), the modified Burgess–Wheeler law (Eq. (1), +), and (right) the proposed method (Eq. (17)).
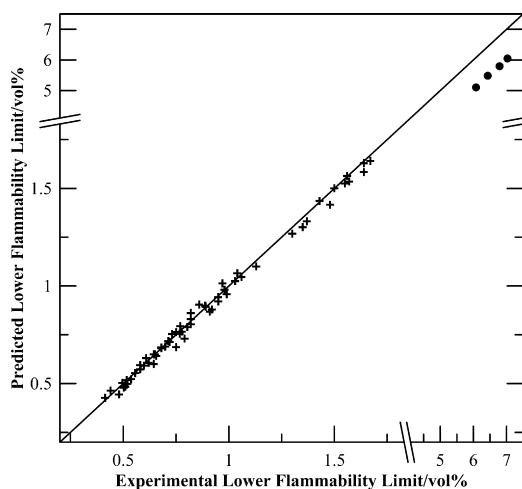
**Fig. 5.** Combined estimation of temperature-dependent LFL values using the proposed method compared with data from [51]. Data for methanol are shown by solid circles.

and the total heat capacity of the products are assumed to be roughly equal to the total heat capacity of the fuel–air mixture, then the expression is greatly simplified:

$$\text{LFL}(T_2) = \text{LFL}(T_1) - \frac{(1-\gamma)\bar{C}_{p,\text{fuel-air}}}{(-\Delta H_c^{\circ})}(T_2 - T_1). \tag{17}$$

The value of the total heat capacity is assumed to be the value at the reference temperature, $T_1$, calculated from

$$\bar{C}_{p,\text{fuel-air}} = \text{LFL}(T_1)\,C_{p,\text{fuel}} + (100 - \text{LFL}(T_1))\,C_{p,\text{air}}. \tag{18}$$

Eq. (17) may be easily modified to estimate the temperature dependence of the lower flammability limit obtained in different apparatuses by adjusting $\gamma$. For example, in small-diameter apparatuses, White [54] and Zabetakis et al. [50] found that the adiabatic flame temperature was constant with initial test temperature, i.e., $\gamma$ equals 0. In such a case, Eq. (17) reduces to the modified Burgess–Wheeler law for gases. For data determined in the large diameter ASHRAE-style vessel used in [51], the slope of the adiabatic flame temperature, $\gamma$, appears to be a strong function of the number of carbon atoms in the fuel for fuels containing C, H, O, and

N atoms (Fig. 1). Through linear regression of data from [51], the slope of the adiabatic temperature as a function of carbon number was found to be

$$\gamma = -0.0125 \cdot n_C^2 - 0.779, \tag{19}$$

with a coefficient of determination ($R^2$) equal to 0.917.

## 3. Results and discussion

### 3.1. Estimation of magnitude

A comparison of the accuracy of the proposed method (based on AAD) with some previously reported methods is given in Table 3. The proposed method returns a lower AAD than the other estimation methods in Table 3 that are applicable to general organic compounds, predicting close to, if not within, experimental error. The difference between the AAD of the regression and test sets is less than 0.5%, indicating that the method has high predictive potential.

Gharagheizi [55,56] also proposed a method of estimating the LFL at 298 K based on structural contributions and fit to LFL values in the DIPPR® 801 database. He reports an AAD under 5% for more than 1000 compounds. However, this method was excluded from the comparison in Table 3 because the DIPPR® 801 database indicates that the bulk of the LFL values used in developing and testing the method are actually values predicted using other methods. The AADs of the proposed method and the other methods listed in Table 3, on the other hand, are based only on data in the DIPPR® 801 database thought to be experimental. If the AADs of each method are compared using only the values of the 260 compounds common between the dataset of Gharagheizi and the data used in this work, the method of Gharagheizi results in an AAD of about 7.7% while the proposed method exhibits an AAD of 6.9%.

The predicted values of the LFL using the proposed method are compared with the 509 DIPPR® database values used to develop and validate the method in Fig. 2. Although the bulk of the predicted values agree well with the reported values, there are several significant outliers. This can also be seen from the distribution of deviations of the predicted values (Fig. 3). Table 4 lists the points for which the absolute deviation from this method exceeds 30%.

Most of the deviations listed in Table 4 are for lower flammability limit data of questionable accuracy. In fact, 24 of the 33 points with absolute deviations larger than 30% had only one
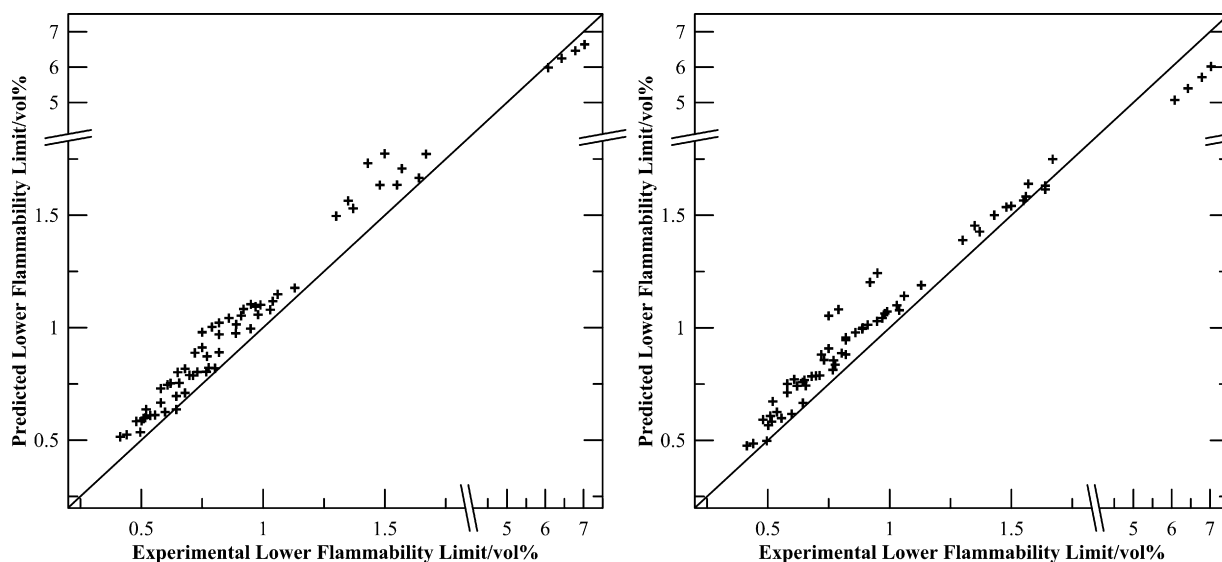


**Fig. 6.** Comparison of temperature-dependent LFL data from [51] with value predicted using the methods of Britton and Frurip (left) and Catoire and Naudet (right).

lower flammability limit value reported, and of uncertain origin. 23 of the compounds had flash point values that suggest that the lower flammability limit should be shifted towards the predicted value. For example, the reported lower flammability limit of *m*-divinylbenzene corresponds to a lower temperature limit ($T_L$) of 319 K, calculated from the vapor pressure, $P^*$, using

$$LFL = \frac{P^*(T_L)}{101.3 \, \text{kPa}} \times 100. \tag{20}$$

The recommended flash point for this compound is 340 K. The large difference between the flash point and the calculated lower temperature limit suggests the LFL may be too low. The predicted LFL (0.58 vol%) corresponds to a lower temperature limit of 331 K, which agrees reasonably well with the recommended flash point. However, not all deviations between the predicted and experimental values are a result of inaccurate lower flammability limit data. Legitimately large absolute deviations occur for highly halogenated compounds, and compounds at the beginning of a chemical series, e.g., hydrogen cyanide, cyanogen, and ethylene.

### 3.2. Estimation of temperature dependence

A direct comparison of Eq. (17), the method proposed by Britton and Frurip (Eq. (2)) and the modified Burgess–Wheeler law (Eq. (1)) is given in Fig. 4 for data from the large-diameter vessel in [51]. The lower flammability limit at the lower temperature limit was used as the reference point for all three methods to provide an unbiased analysis of the estimated temperature-dependence from each method. The modified Burgess–Wheeler law and the method proposed by Britton and Frurip are nearly identical, because both methods are based on the assumption of a constant adiabatic flame temperature along the lower flammability limit curve. These methods clearly under-estimate the temperature dependence of the lower flammability limit when determined in large-diameter vessels. Eq. (17) reproduces the temperature dependence of the lower flammability limit quite accurately, slightly overestimating the temperature dependence for just a few compounds. Direct comparison with the temperature dependence proposed by Catoire and Naudet is not possible because the temperature-dependence aspect of the method is not separable from Eq. (3).

### 3.3. Combined estimation

Combined magnitude and temperature-dependence estimation of the lower flammability limit is performed by first predicting the LFL($T_1$) using Eq. (9). Because LFL data for liquids are typically measured at some temperature above 298 K, assumed to be at $T_L$ in this work, $T_L$ is then approximated from the vapor pressure curve using Eq. (20). If the estimated $T_L$ is less than 298 K, then the reference temperature $T_1$ in Eq. (17) is 298 K, otherwise $T_1$ is $T_L$. Once the LFL at $T_1$ is known, subsequent LFL points may then be calculated using Eq. (17). Fig. 5 is a plot of the predicted values versus the experimental data from [51].

The largest deviation, as shown in Fig. 5, is a result of the magnitude estimation for methanol. The AAD for the 65 points from 17 compounds was 3.29%, and the max absolute deviation (MAD) was 16.07% (methanol at 420 K). The predicted values using the proposed method are significantly more consistent with experimental data than the method of Britton and Frurip (AAD = 13.18%, MAD = 30.64%), and the method developed by Catoire and Naudet (AAD = 12.93%, MAD = 40.37%), though the Britton method approximates the lower flammability limit of methanol more accurately (Fig. 6.).

## 4. Conclusions

This work shows that the LFL of general organic compounds may be accurately estimated from structural contributions and the heat of formation of the fuel. This method of estimating the LFL results in a lower average deviation than any previously published single-point method. A new expression for the temperature dependence of the LFL has also been proposed that accurately reproduces temperature-dependent LFL data from large-diameter vessels. The expression may be applied to smaller vessels as well, by adjusting the parameter $\gamma$. Simultaneous prediction of the LFL and its dependence on temperature shows excellent agreement with experimental data obtained in an ASHRAE-style apparatus.

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