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A Study on Estimating Flammability Limits in Oxygen

Chan-Cheng Chen*

Department of Safety, Health and Environmental Engineering, National Kaohsiung First University of Science and Technology,
2 Jhuoyue Road, Nanzih, Kaohsiung City 811, Taiwan, Republic of China

ABSTRACT: In many process units, for example, chemical reactors, flammable gases are operated with pure oxygen, and the data of flammability limits in oxygen are crucial to persons who operate such units. Although the data of flammability limits in oxygen are desirable, there is a significant gap between the demand for such data and their availability. In this regard, an effective method for estimating flammability limits in oxygen is indispensable. In this article, formulations based on a thermodynamic approach are proposed to estimate both the upper flammability limit (UFL) and lower flammability limit (LFL) of pure flammable gases in oxygen at atmospheric pressure and room temperature. The proposed formulations are applicable for flammable gases under constant-pressure combustion. These formulations were then examined by an experimental data set of 21 flammable gases. For these investigated gases, average predictive errors are found to be of 4.94% and 6.67% for predicting LFL and UFL in oxygen, respectively. It is also elucidated that for a flammable gas, which tends to decompose or gives rise to a cool flame, the proposed method may result in larger predictive errors because under such conditions the combustion process should be better explained by the chain theory instead of the thermal theory; it is also shown that if the adiabatic flame temperature is higher than 1850 K, the proposed method also may result in larger predictive errors because of the dissociation of burnt products.

1. INTRODUCTION

Because a gas mixture of a flammable gas and an oxidant could be ignited only if the concentration of the flammable gas lies within a given range known as flammability limits, the data of flammability limits are thus crucial to people who develop safe practices for handling flammable gases. For this reason, many studies have explored flammability limits of flammable gases either by an experimental approach^{1,2} or by a theoretical approach.^{3–11} Although studies on estimating flammability limits of flammable gases are active in the literature, most of them have focused on flammability limits in air rather than flammability limits in oxygen. Moreover, the experimental data of flammability limits in oxygen are also much less than those in air.¹ For example, in Coward and Jones' work, flammability limits in air were reported for 41 hydrocarbons, but flammability limits in oxygen were given only for 10 of them; flammability limits in air were given for 14 ethers, but flammability limits in oxygen were available only for four of them; flammability limits in air were found for 10 alcohols, but flammability limits in oxygen were given for none of these alcohols; flammability limits in air were reported for seven ketones, but flammability limits in oxygen were available for none of them. However, in practical applications, flammable gases may be operated with pure oxygen in many process units (for example, chemical reactors), and the data of flammability limits in oxygen are crucial to persons who operate these units. In this regard, the development of reliable predictive methods to estimate flammability limits in oxygen is indispensable.

However, to the author's best knowledge, studies to predict flammability limits in oxygen for flammable gases are also very rare in the literature.^{12,13} Kong et al. have suggested that the lower flammability limit (LFL) in oxygen for a flammable vapor could be estimated by its flash point in oxygen.¹² Because the data of the flash point in oxygen are also very rare in the literature, practical applications of their method should be very limited.

Moreover, their approach did not address the prediction of the upper flammability limit (UFL) in oxygen, so it cannot afford complete flammability characterization of a given flammable gas. Recently, Hansen and Crowl have proposed a method to estimate both the UFL LFL in oxygen by a thermodynamics approach.¹³ They validated their method by using an 11-compound data set consisting of carbon monoxide and 10 pure hydrocarbons. An empirical method was also proposed by them to extend the applicability of their method to include nonhydrocarbons. The parameters in their empirical equations are obtained by regression from an experimental data set of 16 compounds, which include nonhydrocarbons such as ethers and chlorinated compounds. Because parameters in their empirical equations are directly regressed from experimental data, the predictive performance of their method is still arguable, especially extrapolating it to compounds not included in the original data set, because a regression model has very limited extrapolation capability.

Because for the flammable gases the experimental data of flammability limits in air are much easier to obtain and many effective methods to predict flammability limits in air have also been reported in the literature, this work aims at developing a method that could estimate flammability limits in oxygen of a flammable gas from its flammability limits in air. This article is organized as follows. The developments for the proposed method are elucidated in section 2, and the predictive performance of the proposed formulations is examined by an experimental data set of 21 flammable gases in section 3. Section 4 discusses assumptions employed in the development procedures

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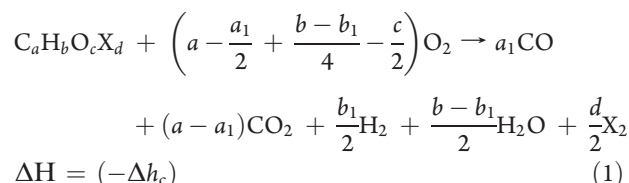
and limitations for the proposed formulations. Finally, we conclude this work in section 5.

2. FORMULATIONS

It should be first noted that the LFL and UFL of a flammable gas are usually expressed in volume percentage (vol %) in the literature; however, at atmospheric pressure, most flammable gases (vapors) could be considered as ideal gases, so the LFL and UFL could be explained as the mole fractions of the flammable gas in the mixture of the flammable gas and the oxidant. In present study, the unit of flammability limits is elucidated as mole fraction.

2.1. UFL in Oxygen. Combustion is very complex in a rich condition; soot and many free radicals may be produced, while organic compounds are burned in such a condition. However, Shebeko et al. had pointed out that combustion does not continue unless the temperature is above a specific threshold temperature, at which the reaction rate of propagation prevails over that of termination.¹⁴ Thus, combustion occurring at UFL is the one of this threshold temperature and is a low-temperature combustion process, while it is compared with combustion processes occurring in other rich conditions. This argument was also indicated by other researchers.^{15,16} Moreover, Morehart et al.'s experimental observations clearly indicated that radiation from soot in the reaction zone became imperceptible for combustion near the limit of flammability.¹⁷ Thus, the heat effects of soot and other minor chemicals are usually ignored in the literature, while we estimate flammability limits through the adiabatic flame temperature approach.^{3–11,13,14,16}

For the purpose of estimating the UFL, the combustion reaction at UFL could be adequately described by a simple chemical reaction equation if the investigated flammable gas does not tend to decompose or give rise to a cool flame and the burnt products do not dissociate. For flammable gases, the combustion reaction, however, will not be complete at UFL, and the degree of combustion might be different for separate flammable gases. Thus, we assume that a_1 mol of CO and $b_1/2$ mol of H_2 are formed while burning 1 mol of the flammable gas ($C_aH_bO_cX_d$), in which X means the halogen atom. Obviously, parameters a_1 and b_1 are introduced here to express different degrees of combustion for separate flammable gases. In general, the stoichiometry of a combustion reaction occurring at the UFL could be described as follows:^{15,16,18}



where $-\Delta h_c$ is the heat of reaction for the burning of 1 mol of the investigated flammable gas according to the stoichiometry described by eq 1. Besides this assumption of a simple reaction equation, the following assumptions are also presumed true in subsequent formulations: (U1) the oxygen in the reactants will react completely at the UFL whether the combustion reaction occurs in air or in oxygen; (U2) the stoichiometric coefficients of the combustion reaction occurring at the UFL are the same regardless of the reaction occurring in air or in oxygen; (U3) the adiabatic temperature increases of limiting mixtures at the UFL are the same regardless of the reaction occurring in air or in

Table 1. Mass Balance for the Burning of a Flammable Gas at the UFL in Oxygen (Basis: a 1 mol Mixture of the Investigated Gas and Oxygen)

compound name	no. of moles in the reactants	no. of moles in the burnt products
flammable gas	U	$U - k(1 - U)$
oxygen (O_2)	$1 - U$	0
nitrogen (N_2)	0	0
carbon monoxide (CO)	0	$q(1 - U)$
carbon dioxide (CO_2)	0	$r(1 - U)$
hydrogen (H_2)	0	$s(1 - U)$
steam (H_2O)	0	$t(1 - U)$
halogen gas (X_2)	0	$w(1 - U)$

oxygen. It should be emphasized that the aforementioned arguments are claimed only for combustion reactions occurring at the UFL in air and in oxygen and not for combustions occurring in other rich conditions. Discussions on these assumptions will be postponed until section 4.

Now, let us first consider the case of the burning of a 1 mol mixture of flammable gas and oxygen at the UFL. Let U be the UFL in oxygen of the investigated gas, and then the combustible mixture at the UFL consists of U moles of the investigated flammable gas and $1 - U$ moles of oxygen. Because oxygen is required to be completely consumed at the UFL by assumption U1, the quantities of all burnt products can be obtained according to the stoichiometry given in eq 1. The results of the mass balance for the burning of a flammable gas at the UFL in oxygen are summarized in Table 1 on the basis of a 1 mol mixture of the investigated gas and oxygen. For brevity in notation, the following notations are adopted in Table 1 and this subsection.

$$k \equiv \frac{1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \quad q \equiv \frac{a_1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}}$$

$$r \equiv \frac{a - a_1}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \quad s \equiv \frac{b_1/2}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}}$$

$$t \equiv \frac{(b - b_1)/2}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}} \quad w \equiv \frac{d/2}{a - \frac{a_1}{2} + \frac{b - b_1}{4} - \frac{c}{2}}$$

The heat released on the burning of the 1 mol mixture described in Table 1 is

$$\Delta h = k(1 - U)(-\Delta h_c) \quad (2)$$

and the mean (from room temperature to the specified adiabatic flame temperature) heat capacity of the burnt products is

$$C_p = [U - k(1 - U)]\hat{C}_{p_f} + q(1 - U)\hat{C}_{p_{CO}} + r(1 - U)\hat{C}_{p_{CO_2}} + s(1 - U)\hat{C}_{p_{H_2}} + t(1 - U)\hat{C}_{p_{H_2O}} + w(1 - U)\hat{C}_{p_{X_2}} \quad (3)$$

where \hat{C}_{p_f} , $\hat{C}_{p_{N_2}}$, $\hat{C}_{p_{CO}}$, $\hat{C}_{p_{CO_2}}$, $\hat{C}_{p_{H_2}}$, $\hat{C}_{p_{H_2O}}$, and $\hat{C}_{p_{X_2}}$ are the mean molar heat capacities of flammable gas, nitrogen, carbon monoxide, carbon dioxide, hydrogen, steam, and halogen gas, respectively. After some manipulations, eq 3 could be

Table 2. Mass Balance for the Burning of a Flammable Gas at the UFL in Air (Basis: a 1 mol Mixture of the Investigated Gas and Air)

compound name	no. of moles in the reactants	no. of moles in the burnt products
flammable gas	U_1	$U_1 - 0.21k(1 - U_1)$
oxygen (O_2)	$0.21(1 - U_1)$	0
nitrogen (N_2)	$0.79(1 - U_1)$	$0.79(1 - U_1)$
carbon monoxide (CO)	0	$0.21q(1 - U_1)$
carbon dioxide (CO_2)	0	$0.21r(1 - U_1)$
hydrogen (H_2)	0	$0.21s(1 - U_1)$
steam (H_2O)	0	$0.21t(1 - U_1)$
halogen gas (X_2)	0	$0.21w(1 - U_1)$

rewritten as

$$C_p = U(\hat{C}_{p_f} + P_1) - P_1 \quad (4)$$

where P_1 is defined as follows:

$$P_1 \equiv k\hat{C}_{p_f} - q\hat{C}_{p_{CO}} - r\hat{C}_{p_{CO_2}} - s\hat{C}_{p_{H_2}} - t\hat{C}_{p_{H_2O}} - w\hat{C}_{p_{X_2}} \quad (5)$$

Now, let us turn to the case of the burning of a 1 mol mixture of the investigated gas and air at the UFL. Suppose U_1 is the UFL in air of the investigated gas. It should be noted that assumption U1 requires the oxygen in the reactants to be completely consumed, even the oxidant in air, and assumption U2 requires that the stoichiometries are the same for the burning of a flammable gas at the UFL in air and in oxygen. Therefore, the reaction equation described in eq 1 could also be used to calculate the numbers of moles of burnt products while the combustion process occurs at the UFL in air. Table 2 summarizes the results of the mass balance on the basis of a 1 mol mixture of the investigated gas and air.

The heat released upon the burning of a 1 mol mixture described in Table 2 is

$$(\Delta h)_1 = 0.21k(1 - U_1)(-\Delta h_c) \quad (6)$$

and the mean heat capacity of the burnt products for this burning condition is

$$\begin{aligned} C_{p_1} = & [U_1 - 0.21k(1 - U_1)]\hat{C}_{p_f} + 0.79(1 - U_1)\hat{C}_{p_{N_2}} \\ & + 0.21q(1 - U_1)\hat{C}_{p_{CO}} + 0.21r(1 - U_1)\hat{C}_{p_{CO_2}} \\ & + 0.21s(1 - U_1)\hat{C}_{p_{H_2}} + 0.21t(1 - U_1)\hat{C}_{p_{H_2O}} \\ & + 0.21w(1 - U_1)\hat{C}_{p_{X_2}} \end{aligned} \quad (7)$$

Combining all terms having U_1 in eq 7 and substituting eq 5 into the resulting equation will give

$$\begin{aligned} C_{p_1} = & U_1(\hat{C}_{p_f} + 0.21P_1 - 0.79\hat{C}_{p_{N_2}}) \\ & - (0.21P_1 - 0.79\hat{C}_{p_{N_2}}) \end{aligned} \quad (8)$$

Compare the heat released at the UFL in oxygen with that at the UFL in air, and note that burnt products are heated by these heats. Thus, we can obtain the following relationship:

$$\frac{\Delta h}{(\Delta h)_1} = \frac{C_p \Delta T}{C_{p_1} \Delta T_1} = \frac{C_p}{C_{p_1}} \quad (9)$$

where ΔT and ΔT_1 are the temperature increases for the burning of a flammable gas at the UFL in oxygen and in air, respectively. Because assumption U3 requires these two temperature increases to be of the same value, they are then canceled out in eq 9. Substituting eqs 2, 4, 6, and 8 into the corresponding terms in eq 9 will give

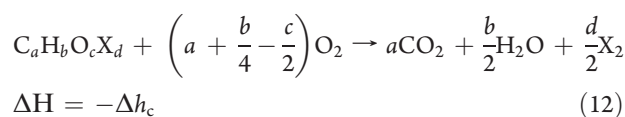
$$\begin{aligned} & \frac{k(1 - U)(-\Delta h_c)}{0.21k(1 - U_1)(-\Delta h_c)} \\ & = \frac{U(\hat{C}_{p_f} + P_1) - P_1}{U_1(C_{p_f} + 0.21P_1 - 0.79\hat{C}_{p_{N_2}}) - (0.21P_1 - 0.79\hat{C}_{p_{N_2}})} \end{aligned} \quad (10)$$

By canceling out $k(-\Delta h_c)$ and combining all terms having U , we rearrange this equation as follows:

$$U = \frac{U_1\hat{C}_{p_f} + 0.79(1 - U_1)\hat{C}_{p_{N_2}}}{0.79U_1(\hat{C}_{p_f} - \hat{C}_{p_{N_2}}) + (0.21\hat{C}_{p_f} + 0.79\hat{C}_{p_{N_2}})} \quad (11)$$

Equation 11 gives us a method to estimate the UFL in oxygen for a flammable gas, while its UFL in air is available. It is worth noting here that eq 11 shows that the UFL in oxygen does not explicitly depend on the parameters a_1 and b_1 in eq 1. Nevertheless, altering these two parameters will change the heat effects, which will vary the calculated adiabatic flame temperature, and this will affect all mean molar heat capacities in eq 11. For most compounds, the mean molar heat capacities usually weakly depend on the specified temperature range;⁹ it could be expected that the estimated UFL in oxygen will also weakly depend on these two parameters. It is also found in eq 11 that only the mean molar heat capacities of the investigated gas and nitrogen appear in eq 11. The mean molar heat capacities of other burnt products, such as carbon dioxide, carbon monoxide, steam, etc., do not appear in eq 11, and this also clearly indicates that the true burnt products have very limited effects on the estimated UFL in oxygen. In the next section, eq 11 will be examined by the existing experimental data to see whether or not it could predict the UFL in oxygen with reasonable accuracy.

2.2. LFL in Oxygen. Because the amount of oxygen present is sufficient for perfect combustion at the LFL, the combustion process will completely undergo while we burn a flammable gas at the LFL. Thus, if the investigated flammable gas does not tend to decompose or give rise to a cool flame and the burnt products do not dissociate, the following simple reaction equation could adequately describe the combustion process occurring at the LFL:^{15,16,18}



where $-\Delta h_c$ is the heat of reaction for the burning of 1 mol of flammable gas according to the stoichiometry described in eq 12. Besides this assumption of a simple reaction equation, assumptions also presumed true in the subsequent formulation are as follows: (L1) a flammable gas will react completely at the LFL either in oxygen or in air; (L2) the stoichiometries of combustion processes occurring at the LFL in oxygen and in air are the same; (L3) the adiabatic temperature increases of limiting mixtures at the LFL are the same regardless of the reaction occurring in air or

Table 3. Mass Balance for the Burning of a Flammable Gas at the LFL in Oxygen (Basis: a 1 mol Mixture of the Investigated Gas and Oxygen)

compound name	no. of moles in the reactants	no. of moles in the burnt products
flammable gas	L	0
oxygen (O_2)	$1 - L$	$(1 - L) - kL$
nitrogen (N_2)	0	0
carbon dioxide (CO_2)	0	qL
steam (H_2O)	0	rL
halogen gas (X_2)	0	sL

in oxygen. It should be noted here that the aforementioned assumptions are claimed only for combustion processes occurring at the LFL in oxygen and in air and not for combustion processes occurring in any other lean conditions. Discussions on these assumptions will also be postponed to section 4.

Now, consider the case of the burning of a 1 mol mixture of a flammable gas and oxygen at the LFL. Let L be the LFL in oxygen of the investigated gas, so the combustible mixture at the LFL in oxygen contains L moles of the investigated gas and $1 - L$ moles of oxygen. Because assumption L1 requires the investigated gas to be completely consumed at the LFL, the quantities of all burnt products can then be obtained from the stoichiometry described in eq 12. The numbers of moles for all burnt products are summarized in Table 3 on the basis of a 1 mol mixture of the investigated gas and oxygen. For brevity in notation, the following notations are adopted in Table 3 and this subsection.

$$k \equiv a + \frac{b}{4} - \frac{c}{2}; \quad q \equiv a; \quad r \equiv \frac{b}{2}; \quad s \equiv \frac{d}{2}$$

The heat released upon the burning of a 1 mol mixture described in Table 3 is

$$\Delta h = L(-\Delta h_c) \quad (13)$$

and the mean (from room temperature to the specified adiabatic flame temperature) heat capacity of the burnt products is

$$C_p = (1 - L - kL)\hat{C}_{p_{O_2}} + qL\hat{C}_{p_{CO_2}} + rL\hat{C}_{p_{H_2O}} + sL\hat{C}_{p_{X_2}} \quad (14)$$

Let us define P_2 as follows:

$$P_2 \equiv -k\hat{C}_{p_{O_2}} + q\hat{C}_{p_{CO_2}} + r\hat{C}_{p_{H_2O}} + s\hat{C}_{p_{X_2}} \quad (15)$$

Equation 14 could be rewritten as

$$C_p = L(P_2 - \hat{C}_{p_{O_2}}) + \hat{C}_{p_{O_2}} \quad (16)$$

Let us now turn to the case of the burning of a 1 mol mixture of a flammable gas and air at the LFL. Let L_1 be the LFL in air of the investigated gas. Assumption L1 requires that the investigated gas be completely consumed at the LFL in air, and assumption L2 requires that the stoichiometries are the same for the burning of a flammable gas at the LFL in oxygen and in air. Thus, the number of moles of all burnt products could be written down according to eq 12. Table 4 summarizes the results of such a mass balance on the basis of a 1 mol mixture of the investigated gas and air.

Table 4. Mass Balance for the Burning of a Flammable Gas at the LFL in Air (Basis: a 1 mol Mixture of the Investigated Gas and Air)

compound name	no. of moles in the reactants	no. of moles in the burnt products
flammable substance	L_1	0
oxygen (O_2)	$0.21(1 - L_1)$	$0.21(1 - L_1) - kL$
nitrogen (N_2)	$0.79(1 - L_1)$	$0.79(1 - L_1)$
carbon dioxide (CO_2)	0	qL_1
steam (H_2O)	0	rL_1
halogen gas (X_2)	0	sL_1

The heat released upon the burning of the 1 mol mixture described in Table 4 is

$$\Delta h_1 = L_1(-\Delta h_c) \quad (17)$$

and the mean heat capacity of the burnt products is

$$C_{p_1} = [0.21(1 - L_1) - kL_1]\hat{C}_{p_{O_2}} + 0.79(1 - L_1)\hat{C}_{p_{N_2}} + qL_1\hat{C}_{p_{CO_2}} + rL_1\hat{C}_{p_{H_2O}} + sL_1\hat{C}_{p_{X_2}} \quad (18)$$

When all terms containing L_1 in eq 18 are combined and eq 15 is substituted into it, eq 18 will be reduced to the following eq 19.

$$C_{p_1} = L_1[P_2 - (0.21\hat{C}_{p_{O_2}} + 0.79\hat{C}_{p_{N_2}})] + (0.21\hat{C}_{p_{O_2}} + 0.79\hat{C}_{p_{N_2}}) \quad (19)$$

Now let us compare the heat released at the LFL in oxygen with in air, and note that the burnt products are heated by these heats. Thus, we could obtain the following eq 20.

$$\frac{\Delta h}{\Delta h_1} = \frac{C_p \Delta T}{C_{p_1} \Delta T_1} = \frac{C_p}{C_{p_1}} \quad (20)$$

where ΔT and ΔT_1 are the temperature increases for the burning of a flammable gas at the LFL in oxygen and in air, respectively. According to assumption L3, these two temperature increases should be equal to each other, so they are then canceled out in eq 20. Substituting eqs 13, 16, 17, and 19 into the corresponding terms in eq 20 gives

$$\begin{aligned} & \frac{L(-\Delta h_c)}{L_1(-\Delta h_c)} \\ &= \frac{L(P_2 - \hat{C}_{p_{O_2}}) + \hat{C}_{p_{O_2}}}{L_1[P_2 - (0.21\hat{C}_{p_{O_2}} + 0.79\hat{C}_{p_{N_2}})] + (0.21\hat{C}_{p_{O_2}} + 0.79\hat{C}_{p_{N_2}})} \end{aligned} \quad (21)$$

By canceling out $-\Delta h_c$ and then combining all terms having L , we could rearrange eq 21 as

$$L = \frac{L_1\hat{C}_{p_{O_2}}}{L_1\hat{C}_{p_{O_2}} + (1 - L_1)(0.21\hat{C}_{p_{O_2}} + 0.79\hat{C}_{p_{N_2}})} \quad (22)$$

Equation 22 gives us a method to estimate the LFL in oxygen of a flammable gas, while its LFL in air is available. It should be noted that the estimated LFL in oxygen explicitly depends on the mean molar heat capacities of oxygen and nitrogen, but the mean molar heat capacities of the flammable gas and other burnt products have no explicit effect on the estimated LFL in oxygen. Whether or not the estimated result by means of eq 22 coincides

Table 5. Reported Flammability Limits for the Selected Flammable Gases^a

compound name	formula	LFL in air	UFL in air	LFL in oxygen	UFL in oxygen
methane	CH ₄	0.053	0.140	0.051	0.610
ethane	C ₂ H ₆	0.030	0.125	0.030	0.660
propane	C ₃ H ₈	0.022	0.095	0.023	0.550
butane	C ₄ H ₁₀	0.019	0.085	0.018	0.490
isobutane	C ₄ H ₁₀	0.018	0.084	0.018	0.480
ethylene	C ₂ H ₄	0.031	0.320	0.030	0.800
propylene	C ₃ H ₆	0.020	0.103	0.021	0.530
butene-1	C ₄ H ₈	0.016	0.093	0.018	0.580
butene-2	C ₄ H ₈	0.018	0.097	0.017	0.550
cyclopropane	C ₃ H ₆	0.024	0.104	0.025	0.600
methyl ether	C ₂ H ₆ O	0.034	0.270	0.039	0.610
ethyl ether	C ₄ H ₁₀ O	0.019	0.480	0.021	0.820
ethyl <i>n</i> -propyl ether	C ₅ H ₁₂ O	0.019	0.240	0.020	0.780
vinyl ether	C ₄ H ₈ O	0.017	0.280	0.018	0.850
acetaldehyde	C ₂ H ₄ O	0.041	0.550	0.040	0.930
methyl chloride	CH ₃ Cl	0.076	0.190	0.080	0.660
ethyl chloride	C ₂ H ₅ Cl	0.038	0.154	0.040	0.670
vinyl chloride	C ₂ H ₃ Cl	0.040	0.220	0.040	0.700
2-chloropropene	C ₃ H ₃ Cl	0.045	0.160	0.045	0.540
hydrogen	H ₂	0.040	0.750	0.040	0.940
carbon monoxide	CO	0.125	0.740	0.155	0.940

^aData in this table are collected from ref 1.

with the existing experimental data will be explored in the next section.

3. EXAMINING THE PROPOSED METHOD WITH EXPERIMENTAL DATA

An experimental data set of 21 compounds is used to assess the predictive performance for the proposed formulations. These data are collected from the work of U.S. Bureau of Mines by Coward and Jones¹ and are summarized in Table 5. It can be seen from Table 5 that there are 10 hydrocarbons, four ethers, one aldehyde, four chlorinated derivatives, and two inorganic compounds. According to descriptions in the original work, these flammability limit data were observed with upward propagation of the flame in larger vessels, opened at their ends. Recently, the experimental data of the LFL in air were reexamined by using a 20 L or bigger vessel for some flammable gases, and these new results were found to be generally in agreement with the results of the U.S. Bureau of Mines with the one exception of 1,2-dichloroethane.^{19,20} It should be also noted here that all collected data in the present work are those measured at atmospheric pressure and room temperature. Because the mean molar heat capacities of the investigated gas, nitrogen, and oxygen are also required to implement the proposed formulations, they are obtained from the DIPPR database supported by the American Institute of Chemical Engineers.²¹

The required adiabatic flame temperatures are first calculated from the LFL in air and the UFL in air, and the calculated results are summarized in Table 6. In Table 6, the column with the column heading of “ T_{ad} at the LFL” shows the calculated adiabatic flame temperatures for the LFL, and the column with the column heading of “ T_{ad} at the UFL” shows the case of the UFL. It should be noted here that, in the calculation of T_{ad}

at the UFL, all carbon atoms contained in the investigated gas are assumed to completely convert into carbon monoxide (i.e., $a_1 = a$ in eq 1) and all hydrogen atoms contained in the investigated gas are assumed to completely convert into steam (i.e., $b_1 = 0$ in eq 1).¹³ However, there is one exception for this rule; if the investigated gas is carbon monoxide, then it is assumed that carbon monoxide is completely reacted with oxygen to form carbon dioxide even if combustion occurs at the UFL.

The mean molar heat capacities of the investigated gas, nitrogen, and oxygen are then calculated from 298 K to the adiabatic flame temperatures listed in Table 6 for each flammable gas. These calculated mean molar heat capacities are then substituted into eq 11 to estimate the UFL in oxygen and into eq 22 to estimate the LFL in oxygen. Because this approach requires calculation of the individual adiabatic flame temperature for each flammable gas, we call this approach “the rigorous approach”. The estimated UFL in oxygen and the LFL in oxygen by this approach are summarized in Table 6. The experimental flammability limits for each flammable gas are also included in Table 6 for convenience in comparison. Because experimental flammability limits are usually reported to be of three decimal places in the literature, the estimated flammability limits are also rounded to three decimal places in Table 6. The predictive error in the percentage for each of the investigated gases is also listed in this table. It is observed from Table 6 that, in the case of the prediction of the LFL in oxygen, the predictive error is less than 10% in 17 of the 21 selected compounds, and the maximum predictive error is 16.13% for the prediction of the LFL in oxygen of carbon monoxide. For the case of the prediction of the UFL in oxygen, the predictive error in 14 of the 21 selected compounds is less than 10%, and the maximum predictive error is 19.67% for the prediction of the UFL in oxygen of methyl ether. To more quantitatively illustrate the predictive performance of the

Table 6. Predictive Results with the Rigorous Approach

compound name	T_{ad} at the LFL ^a	LFL exptl ^a	LFL estim. ^a	error (%) ^b	T_{ad} at the UFL ^a	UFL exptl ^a	UFL estim. ^a	error (%) ^b
methane	1541	0.051	0.055	7.84	1947	0.610	0.711	16.56
ethane	1537	0.030	0.031	3.33	1840	0.660	0.632	4.24
propane	1582	0.023	0.023	0.00	1830	0.550	0.551	0.18
butane	1709	0.018	0.020	11.11	1776	0.490	0.502	2.45
isobutane	1643	0.018	0.019	5.56	1777	0.480	0.500	4.17
ethylene	1509	0.030	0.032	6.67	1483	0.800	0.785	1.88
propylene	1435	0.021	0.021	0.00	1928	0.530	0.587	10.75
butene-1	1484	0.018	0.017	5.56	1813	0.580	0.532	8.28
butene-2	1605	0.017	0.019	11.76	1825	0.550	0.540	1.82
cyclopropane	1647	0.025	0.025	0.00	1955	0.600	0.585	2.50
methyl ether	1572	0.039	0.035	10.26	1455	0.610	0.730	19.67
ethyl ether	1640	0.021	0.020	4.76	801	0.820	0.834	1.71
ethyl n-propyl ether	1898	0.020	0.020	0.00	1075	0.780	0.666	14.62
vinyl ether	1437	0.018	0.018	0.00	1284	0.850	0.722	15.06
acetaldehyde	1584	0.040	0.043	7.50	966	0.930	0.877	5.70
methyl chloride	1716	0.080	0.079	1.25	1638	0.660	0.734	11.21
ethyl chloride	1658	0.040	0.040	0.00	1575	0.670	0.650	2.99
vinyl chloride	1646	0.040	0.042	5.00	1609	0.700	0.723	3.29
2-chloropropene	2338	0.045	0.047	4.44	1565	0.540	0.637	17.96
hydrogen	626	0.040	0.041	2.50	1158	0.940	0.948	0.85
carbon monoxide	1389	0.155	0.130	16.13	1282	0.940	0.945	0.53

^a All temperatures are in Kelvin, and all flammability limits are in mole fraction. ^b Error = |estimated value — experimental value|/experimental value.

Table 7. Predictive Performance for the 21-Compound Data Set

case		max error (%)	avg error (%)
rigorous approach	LFL	16.13	4.94
	UFL	19.67	6.67
simplification approach	LFL	16.13	4.99
	UFL	19.18	7.01

proposed formulations, the average predictive error and maximum predictive error for all of the collected data are summarized in Table 7. It can be observed from Table 7 that the average predictive errors for all of the collected data are 4.94% and 6.67% for the prediction of the LFL and UFL in oxygen, respectively. While these errors are compared with the reported experimental reproducibility, the proposed formulations obviously predict the results with acceptable accuracy. Discussions on the flammable gases with larger predictive errors will be given in the next section.

It is known that the mean molar heat capacity of a compound does not significantly vary if the temperature range considered does not vary very much. For example, the mean molar heat capacity of nitrogen varies from 7.4705 to 7.6123 cal/(mol K), while the specified temperature range changes from 298–1200 to 298–1500 K.⁹ Thus, it is straightforward to realize that the estimated flammability limits in oxygen rather weakly depend on the calculated adiabatic flame temperature. Moreover, it is also observed from Table 6 that for most hydrocarbons the adiabatic flame temperatures for the LFL and UFL are around 1500 and 1800 K, respectively. Thus, it seems possible that we could set the adiabatic flame temperature to be the same for all investigated flammable gases rather than calculate their individual adiabatic flame temperatures one by one.

To explore the feasibility of such a simplification approach, we must first realize how much error will be introduced while this simplification approach is adopted. For this purpose, the LFLs in oxygen are estimated by changing the adiabatic flame temperature from 1300 to 1800 K, and the results are summarized in Table 8. For convenience in comparison, the estimated LFLs in oxygen are reported as four decimal places in this table, although the experimental results are usually reported as three decimal places in the literature. It is observed from this table that for all investigated gases the difference in the predicted values of the LFL in oxygen is, as expected, very minor. In most cases, these differences are even below the reported experimental precision.

In Table 9, the estimated UFLs in oxygen are listed for all investigated gases with the adiabatic flame temperature varied from 1500 to 2000 K. It is also found from Table 9 that for all investigated gases the difference in the estimated UFLs is also very limited. Aforementioned observations suggested that, for all investigated gases, we could predict the LFL in oxygen and the UFL in oxygen with acceptable accuracy by using unified adiabatic flame temperatures for the LFL and UFL. In the present study, this approach is called as a simplification approach, and the unified adiabatic flame temperatures are suggested to be 1500 and 1800 K for calculation of the LFL and UFL in oxygen, respectively. It should be noted that these two adiabatic flame temperatures are not intended to express the real flame temperatures at flammability limits for any flammable gas. They were adopted to estimate the flammability limits in the present work just because the heat effects have rather weak effects on the estimation of flammability limits in oxygen.

The predictive performance of this simplification approach is summarized in Table 7 in the row with the row heading of “simplification approach”. It could be found that for the

Table 8. Estimated LFLs in Oxygen with the Adiabatic Flame Temperature Ranging from 1300 to 1800 K

compound name	1300 K	1400 K	1500 K	1600 K	1700 K	1800 K
methane (CH ₄)	0.0553	0.0553	0.0552	0.0552	0.0552	0.0551
ethane (C ₂ H ₆)	0.0313	0.0313	0.0313	0.0313	0.0313	0.0312
propane (C ₃ H ₈)	0.0230	0.0230	0.0230	0.0229	0.0229	0.0229
butane (C ₄ H ₁₀)	0.0198	0.0198	0.0198	0.0198	0.0198	0.0198
isobutane (C ₄ H ₁₀)	0.0188	0.0188	0.0188	0.0188	0.0188	0.0188
ethylene (C ₂ H ₄)	0.0324	0.0324	0.0323	0.0323	0.0323	0.0323
propylene (C ₃ H ₆)	0.0209	0.0209	0.0209	0.0209	0.0208	0.0208
butene-1 (C ₄ H ₈)	0.0167	0.0167	0.0167	0.0167	0.0167	0.0167
butene-2 (C ₄ H ₈)	0.0188	0.0188	0.0188	0.0188	0.0188	0.0188
cyclopropane (C ₃ H ₆)	0.0251	0.0251	0.0250	0.0250	0.0250	0.0250
methyl ether (C ₂ H ₆ O)	0.0355	0.0355	0.0355	0.0354	0.0354	0.0354
ethyl ether (C ₄ H ₁₀ O)	0.0198	0.0198	0.0198	0.0198	0.0198	0.0198
ethyl <i>n</i> -propyl ether (C ₅ H ₁₂ O)	0.0198	0.0198	0.0198	0.0198	0.0198	0.0198
vinyl ether (C ₄ H ₆ O)	0.0178	0.0178	0.0177	0.0177	0.0177	0.0177
acetaldehyde (C ₂ H ₄ O)	0.0428	0.0428	0.0427	0.0427	0.0427	0.0427
methyl chloride (CH ₃ Cl)	0.0792	0.0792	0.0791	0.0791	0.0790	0.0790
ethyl chloride (C ₂ H ₅ Cl)	0.0397	0.0396	0.0396	0.0396	0.0396	0.0396
vinyl chloride (C ₂ H ₃ Cl)	0.0417	0.0417	0.0417	0.0417	0.0417	0.0416
2-chloropropene (C ₃ H ₅ Cl)	0.0470	0.0469	0.0469	0.0469	0.0469	0.0468
hydrogen (H ₂)	0.0417	0.0417	0.0417	0.0417	0.0417	0.0416
carbon monoxide (CO)	0.1299	0.1299	0.1298	0.1298	0.1297	0.1296

Table 9. Estimated UFLs in Oxygen with the Adiabatic Flame Temperature Ranging from 1500 to 2000 K

compound name	1500 K	1600 K	1700 K	1800 K	1900 K	2000 K
methane (CH ₄)	0.7220	0.7192	0.7166	0.7142	0.7120	0.7101
ethane (C ₂ H ₆)	0.6393	0.6368	0.6345	0.6326	0.6308	0.6294
propane (C ₃ H ₈)	0.5588	0.5562	0.5540	0.5520	0.5503	0.5488
butane (C ₄ H ₁₀)	0.5073	0.5050	0.5030	0.5012	0.4997	0.4984
isobutane (C ₄ H ₁₀)	0.5054	0.5031	0.5011	0.4993	0.4978	0.4965
ethylene (C ₂ H ₄)	0.7849	0.7839	0.7830	0.7822	0.7815	0.7809
propylene (C ₃ H ₆)	0.5951	0.5927	0.5906	0.5888	0.5872	0.5857
butene-1 (C ₄ H ₈)	0.5387	0.5364	0.5344	0.5325	0.5309	0.5295
butene-2 (C ₄ H ₈)	0.5466	0.5442	0.5420	0.5402	0.5385	0.5371
cyclopropane (C ₃ H ₆)	0.5946	0.5921	0.5898	0.5878	0.5860	0.5844
methyl ether (C ₂ H ₆ O)	0.7298	0.7287	0.7278	0.7269	0.7262	0.7256
ethyl ether (C ₄ H ₁₀ O)	0.8312	0.8310	0.8308	0.8306	0.8304	0.8303
ethyl <i>n</i> -propyl ether (C ₅ H ₁₂ O)	0.6611	0.6604	0.6597	0.6591	0.6585	0.6580
vinyl ether (C ₄ H ₆ O)	0.7201	0.7194	0.7187	0.7181	0.7176	0.7172
acetaldehyde (C ₂ H ₄ O)	0.8749	0.8747	0.8745	0.8743	0.8741	0.8740
methyl chloride (CH ₃ Cl)	0.7358	0.7343	0.7329	0.7317	0.7306	0.7296
ethyl chloride (C ₂ H ₅ Cl)	0.6511	0.6492	0.6475	0.6459	0.6445	0.6432
vinyl chloride (C ₂ H ₃ Cl)	0.7243	0.7233	0.7224	0.7217	0.7210	0.7203
2-chloropropene (C ₃ H ₅ Cl)	0.6382	0.6369	0.6358	0.6348	0.6338	0.6330
hydrogen (H ₂)	0.9481	0.9481	0.9481	0.9481	0.9481	0.9481
carbon monoxide (CO)	0.9453	0.9453	0.9453	0.9453	0.9453	0.9453

investigated data set the average predictive errors are 4.99% and 7.01% for prediction of the LFL and UFL in oxygen, respectively, and the maximum predictive errors are found to be 16.13% and 19.18% for prediction of the LFL and UFL in oxygen, respectively. It could also be observed from Table 7 that the performance of this simplification approach is just a

little bit inferior to that of the rigorous one. Because this simplification approach does not require one to calculate the adiabatic flame temperature case by case, it is easier to implement for most users. Therefore, it is highly recommended that this simplification approach could be considered for practical applications.

4. DISCUSSION

It should be first noted that, because the proposed formulations require the combustion reaction to be adequately described by both eqs 1 and 12, it could be anticipated that the proposed formulations may result in larger predictive errors if the flammable gas tends to decompose or gives rise to a cool flame or the burnt products begin to dissociate. For such flammable gases, ignitability of the limit mixture is better explained by the chain theory instead of the thermal theory employed in the present work. Because halogenated hydrocarbons are found to tend to decompose even in flames of the limit mixture² and ethers are reported to be capable of giving rise to the phenomenon known as a cool flame,¹ it is then expected that the proposed formulations may result in larger predictive errors for compounds that belong to these two categories. In fact, it can be clearly seen from Table 6 that the predictive error for the UFL in oxygen is larger than 14% in three of the four investigated ethers and is larger than 11% in two of the four investigated chlorinated hydrocarbons.

Schmidt and List pointed out that the dissociation effect of the burnt products should be considered if the adiabatic flame temperature is above 2900 °F (about 1850 K).²² The adiabatic flame temperature for the burning of most organics at the LFL is, as can be observed in Table 6, usually much lower than this dissociation temperature. However, there are some cases in which the adiabatic flame temperature at the UFL is higher than this dissociation temperature. It is observed from Table 6 that there are three flammable gases of which T_{ad} values at the UFL are larger than 1850 K, and the predictive errors are found to be larger than 10% in two of these three flammable gases. This observation is in agreement with what it is expected, that the proposed method may result in larger predictive errors while the burnt products begin to dissociate.

The other potential concerns in using the proposed formulations are assumptions U1–U3 and L1–L3 included in deriving eqs 11 and 22. The underlying idea for these assumptions is that nitrogen is an inert gas in a combustion process; thus, adding nitrogen to or extracting nitrogen from a combustible mixture should not affect the reaction mechanism. In fact, these assumptions were adopted in many studies that explored the inert gas dilution effect on the flammability limits through the calculated adiabatic flame temperature approach.^{7–14} Because these assumptions were proven to reasonably describe the chemical reaction mechanism for adding inert nitrogen to a combustible mixture, they should also work for the extraction of inert nitrogen from a combustible mixture.

Some other experimental observations could also be qualitatively explained by the proposed formulations. It could be calculated that the mean molar heat capacities (from 298 to 1500 K) of nitrogen and oxygen are 31.594 and 33.536 kJ/kmol, respectively. Because these two values are very close and the mean molar heat capacity of the flammable gas, \hat{C}_{p_f} , does not appear in eq 22, it could be concluded from eq 22 that the LFL in oxygen must be a little bit larger than the LFL in air for all flammable gases. As is shown in Table 5, this deduction coincides with experimental observations. The following equation could also be easily derived from eq 11.

$$U - U_1 = \frac{0.79(1 - U_1)[U_1\hat{C}_{p_f} + (1 - U_1)\hat{C}_{p_{N_2}}]}{(0.79U_1 + 0.21)\hat{C}_{p_f} + 0.79(1 - U_1)\hat{C}_{p_{N_2}}} \quad (23)$$

Because the UFL in air, i.e., U_1 , must be less than unity, eq 23 requires that the UFL in oxygen, i.e., U , always be larger than U_1 . This deduction also conforms to experimental observations.

5. CONCLUSIONS

In this study, formulations for predicting the upper/LFLs in oxygen of the flammable gases by their flammability limits in air are proposed. These formulations are then examined by 21 flammable gases. For these investigated flammable gases, the proposed formulations give average predictive errors of 4.94% and 6.67% for predicting the LFL and UFL in oxygen, respectively. In addition, the maximum predictive error for the LFL in oxygen is found to be 16.13% for carbon monoxide, and the maximum predictive error for the UFL in oxygen is found to be 19.67% for methyl ether. Because it is found that the estimated flammability limits in oxygen rather weakly depend on the adiabatic flame temperature employed, a simplification approach of setting the adiabatic flame temperatures at the LFL and UFL as 1500 and 1800 K, respectively, is also suggested. It is found that the average predictive errors of this simplification approach are just a little bit larger than those of the rigorous approach. Thus, it is strongly recommended that this simplification approach be considered for practical applications.

The limitations of the proposed formulations are also discussed. It is demonstrated that for a flammable gas, which tends to decompose or gives rise to a cool flame, the proposed method may result in larger predictive errors than the usual cases. Moreover, when the adiabatic flame temperature is higher than 1850 K, the proposed method may also result in larger predictive errors because of dissociation of the burnt products.

AUTHOR INFORMATION

Corresponding Author

*E-mail: chch_chen@ccms.nkfust.edu.tw. Tel: 886-7-6011000 ext. 2311. Fax: 886-7-6011061.

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