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Nitrogen dilution effect on the flammability limits for hydrocarbons

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ABSTRACT

Theoretical models to predict the upper/lower flammability limits of hydrocarbons diluted with inert nitrogen gas are proposed in this study. It is found that there are linear relations between the reciprocal of the upper/lower flammability limits and the reciprocal of the molar fraction of hydrocarbon in the hydrocarbon/inert nitrogen mixture. Such linearity is examined by experimental data reported in the literature, which include the cases of methane, propane, ethylene and propylene. The *R*-squared values (R^2) of the regression lines of the cases explored are all greater than 0.989 for upper flammability limit (UFL). The theoretical slope of the predictive line for lower flammability limit (LFL) is found to be very close to zero for all explored cases; and this result successfully explains the experimental fact that adding inert nitrogen to a flammable material has very limited effect on LFL. Because limit oxygen concentration (LOC) could be taken as the intersectional point of the UFL curve and LFL curve, a LOC-based method is proposed to predict the slope of the UFL curve when experimental data of UFL are not available. This LOC-based method predicts the UFL with average error ranging from 2.17% to 5.84% and maximum error ranging from 8.58% to 12.18% for the cases explored. The predictive models for inert gas of nitrogen are also extended to the case of inert gas other than nitrogen. Through the extended models, it was found that the inert ability of an inert gas depends on its mean molar heat capacity at the adiabatic flame temperature. Theoretical calculation shows that the inert abilities of carbon dioxide, steam, nitrogen and helium are in the following order: carbon dioxide > steam > nitrogen > helium; and this sequence conforms to the existing experimental data reported in the literature.

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1. Introduction

Many manufacturing processes involve flammable chemicals, and an accident involving a fire or an explosion can occur in storage or process equipment if a flammable chemical exists inside it or if a loss of containment of flammable chemicals occurs. Because the gas mixture of a flammable substance could be ignited only if the concentration of the flammable substance lied within a given range known as the flammability limits, the flammability limits are one of the important features in the development of safe practices for handling a flammable vapor or gas. For this reason, they constitute a crucial issue in research on processing and storing flammable chemicals safely. In the literature, different methods have been proposed to predict the flammability limits of a flammable chemical, especially the lower flammability limit (LFL) of a pure flammable chemical [1,2].

Industry works with mixtures under many situations, for example, in a reactor or in a distillation column. The Le Chatelier equation is widely adopted to estimate the flammability limits of a mixture composed of flammable gases [3–6]. However, complex mixtures composed of flammable gases and nonflammable gases are also formed in process industries, for example, the inerting procedure. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion [7,8]. In process industries, the inert gas is usually nitrogen or carbon dioxide, although sometimes steam may be used.

As the inert gas does not take part in the reaction mechanism, the method of "calculated adiabatic flame temperatures" is usually applied to estimate the flammability limits of a mixture of fuel and inert gas in the literature. Vidal et al. [9] concluded that the method of "calculated adiabatic flame temperatures" is a powerful tool to estimate the LFL of a gas mixture composed of fuel and inert gas, and an adiabatic flame temperature of approximately 1400 K will yield the most desirable results for both methane and ethylene when the predicted results are compared to existing experimental data. Shebeko et al. [10] pointed that there exist two rival reaction mechanisms in a combustion system involving $H_2/CO/O_2/N_2$: (1) if the HO_2 free radical reacts to generate an OH free radical or an O free radical,

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the combustion reaction will sustain; and (2) if the HO_2 free radical reacts to generate O_2, the combustion reaction will terminate. Consequently, the combustion reaction does not proceed unless the temperature is above a specific threshold temperature (T_{cr}) at which the reaction rate of mechanism (1) will prevail over that of mechanism (2). The flammability limits of a flammable material are the conditions under which the produced reaction heat can just raise the temperature of the system to such a threshold, which is usually expressed as the adiabatic flame temperature of the combustion system. Therefore, through the calculation of this threshold temperature, the flammability limits of a mixture of flammable gas and inert gas could be obtained. However, prediction models based on adiabatic flame temperature theories typically produce satisfactory results in forecasting LFL, but this is not the case in predicting the upper flammability limit (UFL).

Because the procedure of diluting a combustible gas with inert gas could be also taken as a mixing process of flammable gas and inert gas, Kondo et al. [11,12] have attempted to modify the Le Chatelier equation so that it could be extended to the case of a mixture of flammable gases and inert gases. The following assumptions were included in their work: (K1) at LFL, the heat of combustion per mole of a mixture composed of fuel gas and inert gas is equal to the heat of combustion per mole of pure fuel gas times the molar fraction of the fuel gas in the mixture (i.e., adding inert gas to fuel gas does not change the reaction mechanism at LFL); (K2) the heat release is the same for all limit mixtures at LFL; (K3) the fuel gas would react completely when combustion takes place at LFL; (K4) at UFL, the ratio of the number of moles of oxygen required to burn one mole of the mixture of fuel gas and inert gas to the number of moles of oxygen required to burn one mole of pure fuel gas equals the molar fraction of the fuel gas in the mixture (i.e., adding the inert gas to the fuel gas does not change the reaction mechanism at UFL); (K5) oxygen would react completely when combustion takes place at UFL; (K6) the heat release is the same for all limit mixtures at UFL. Under these assumptions, they reached the following formulations:

$$L = L_1 \tag{1}$$

$$\frac{xn_1}{1 - U/x} = \frac{xn_1}{1 - U_1} \tag{2}$$

where L and U are the LFL and UFL (in molar fraction) of a flammable gas diluted with inert gas, respectively; L_1 and U_1, the LFL and UFL of the pure flammable gas; x, the molar fraction of the flammable gas in the mixture (flammable gas and inert gas, but no air) and n_1 is the number of moles of oxygen required to burn one mole of pure fuel gas at UFL. However, because Eqs. (1) and (2) did not fit their experimental data very well, they proposed the following empirical formula in power-series form to increase the accuracy of the prediction:

$$\frac{x}{L} = \frac{x}{L_1} + p(1 - x) \tag{3}$$

$$\frac{xn_1}{1 - U/x} = \frac{xn_1}{1 - U_1} + q(1 - x) + r(1 - x)^2 + s(1 - x)^3 \tag{4}$$

where p, q, r, and s are parameters that depend on the kind of fuel gas; their values must be determined from experimental data. Usually, Eqs. (3) and (4) fit the experimental data with good accuracy. However, because these two models are of empirical, a considerable amount of experimental data is required to estimate the parameters in the corresponding model for more reliable predictions. Thus, for those flammable gases with little reported experimental data, how to estimate parameters in their model with a sufficient degree of accuracy for prediction is still a challenge.

Recently, theoretical models to predict both UFL and LFL of a hydrocarbon diluted with carbon dioxide were proposed by Chen et al. [13]. It was found in their work that there are linear relations between the reciprocals of the upper/lower flammability limits and the reciprocal of the molar fraction of the hydrocarbon in the hydrocarbon/carbon dioxide mixture (free from air); and experimental data of methane, propane, ethylene and propylene showed that the coefficient of determination (R^2) of the theoretical lines for UFL/LFL are all larger than 0.980/0.967 for these four cases. To explore whether such a result could be extend to the case of inert nitrogen, this article is organized as follows. First, models to predict the change in UFL/LFL of a hydrocarbon diluted with inert nitrogen is explored using mass balance and energy balance theoretically; and the proposed models are then examined by experimental data reported in the literature. In Section 4, the proposed models are extended to the case of inert gas other than nitrogen; moreover, inert abilities between different inert gases are then studied based on this extended model. Finally, main results of present work are discussed in the Section 5.

2. Theory

Usually the LFL and UFL of a combustible material are expressed in volume percentage (vol%) in the literature; however, as the hydrocarbon gas could be taken as an ideal gas at atmospheric pressure, the LFL and UFL could also be explained as the molar fraction, which is the expression adopted in this study. To avoid misleading the meaning in formulation, three terminologies are defined here: (1) fuel mixture – the mixture composed of hydrocarbon and air (no inert gas); (2) blended gas – the mixture composed of hydrocarbon and inert nitrogen (no air); (3) total mixture – the mixture composed of the blended gas and air. The following notation are also adopted in formulation: (1) x, the molar fraction of hydrocarbon in the blended gas, that is, x = hydrocarbon/(hydrocarbon + inert nitrogen); (2) U, be the molar fraction of hydrocarbon in the total mixture at UFL, that is, U = hydrocarbon/(hydrocarbon + inert nitrogen + air) at UFL, and similarly, let L be the molar fraction of hydrocarbon in the total mixture at LFL; (3) U_1, the molar fraction of hydrocarbon in the fuel mixture at UFL, that is, U_1 = hydrocarbon/(hydrocarbon + air) at UFL, and similarly, let L_1 be the molar fraction of hydrocarbon in the fuel mixture at LFL.

2.1. Assumptions

The assumptions presumed true in formulation are listed as follows.

(U1) oxygen gas reacts completely at UFL.
(U2) the stoichiometric relation of a combustion reaction occurring at UFL does not change by the presence of inert gas.
(U3) the adiabatic temperature rises are the same for all limit mixtures at UFL.
(L1) the hydrocarbon reacts completely at LFL.
(L2) the stoichiometric relation of a combustion reaction occurring at LFL does not change by the presence of inert gas;
(L3) the adiabatic temperature rises are the same for all limit mixtures at LFL.

It is well known that the flammable material is the lean reactant when combustion occurs at LFL, while oxygen gas is the lean reactant when combustion occurs at UFL. Thus, assumptions U1 and L1 merely stated that the lean component will be consumed completely in a burning process occurring at flammability limits. These two assumptions are widely accepted in the literature [1–3,9,10] and they are the same as assumptions K3 and K5 in the work by Kondo et al. [11,12].

Assumptions U2 and L2 stated that the stoichiometry of the combustion reaction at both lower/upper flammability limits does not change by the presence of inert gas. With the aids of these two assumptions, we could estimate the heat released for the blended gas from the heat of combustion of pure hydrocarbon. These two assumptions are popular assumptions for those works which use the calculated adiabatic flame temperatures to estimate the flammability limits in the literature [9,10]; and they are also equivalent to assumptions K1 and K4 in the work by Kondo et al. [11,12]. It should be addressed here that although these two assumptions are very popular in the literature, experimental results do show that the stoichiometry of a combustion reaction occurring at flammability limits might change in the presence of inert gas. The change in stoichiometry could be easily understood from the fact that if an inert gas was added to hydrocarbon/oxidant mixture, the range of concentrations between the UFL and LFL would considerably narrow down and finally converge to a point which is usually known as the inertization point. As earlier mentioned, the lean reactant of a combustion reaction occurring at UFL is different from that of a combustion occurring at LFL; therefore, the stoichiometry of a combustion reaction must change by adding inert gas, because these two flammability limits finally converge to the inertization point. However, it is also obvious that assumptions U2 and L2 are true when the concentration of inert gas is low.

As earlier mentioned, it was reported in the literature that a combustion reaction would continue only if the heat released by the combustion reaction can raise the temperature of the unburned materials to beyond a temperature threshold; and this temperature threshold was usually expressed as the adiabatic flame temperature rise of the combustion system. The energy released at flammability limits is deemed to be the one just sufficient to make the temperature of the combustion system reach this temperature threshold [10]. It is widely accepted that inert gas is not involved in the reaction mechanism of a combustion reaction, so it seems reasonable to assume that this temperature threshold (i.e., the adiabatic flame temperature rise) does not change by adding inert gas. Moreover, it was also reported that the calculated adiabatic flame temperature of LFL was found be around 1400 K at different concentrations of inert nitrogen for some hydrocarbons [9]. Bases on aforementioned facts, it seems reasonable to assume that the adiabatic flame temperature does not change as inert gas is added to a flammable hydrocarbon, thus assumptions L3 and U3 are adopted in this study. It should be noted here that these two assumptions are those that differentiate this study from the work by Kondo et al. [11,12]. In their works, the heat released was assumed to be the same for all limit mixtures.

Table 1
Mole balance for burning one mole of total mixture at UFL.

Compound name	No. of moles before burning	No. of moles after burning
Hydrocarbon	U	$U-0.21k\left(1-\frac{U}{x}\right)$
Air		
Nitrogen	$0.79\left(1-\frac{U}{x}\right)$	$0.79\left(1-\frac{U}{x}\right)$
Oxygen	$0.21\left(1-\frac{U}{x}\right)$	0
Inert nitrogen	$\frac{U}{x}(1-x)$	$\frac{U}{x}(1-x)$
Carbon monoxide	0	$0.21q\left(1-\frac{U}{x}\right)$
Carbon dioxide	0	$0.21r\left(1-\frac{U}{x}\right)$
Hydrogen	0	$0.21s\left(1-\frac{U}{x}\right)$
Steam	0	$0.21t\left(1-\frac{U}{x}\right)$

2.2. Upper flammability limit

As a flammable material will not undergo complete combustion at UFL, we assume that a_1 moles of CO and $b_1/2$ moles of H_2 are formed by burning one mole of the hydrocarbon compound (C_aH_b) at its UFL. Thus, the corresponding stoichiometry of such a combustion reaction could be expressed as follows:

$$C_aH_b + \left(a - \frac{a_1}{2} + \frac{b-b_1}{4}\right)O_2 \rightarrow a_1CO + (a-a_1)CO_2 + \frac{b_1}{2}H_2 + \frac{b-b_1}{2}H_2O \quad \Delta H = (-\Delta h_c) \tag{5}$$

where $(-\Delta h_c)$ is the heat of reaction for burning one mole of hydrocarbon according to the stoichiometry shown in Eq. (5). For brevity in notation, the following notations are defined in this subsection:

$$k \equiv \frac{1}{a-(a_1/2)+((b-b_1)/4)}$$
$$q \equiv \frac{a_1}{a-(a_1/2)+((b-b_1)/4)}$$
$$r \equiv \frac{a-a_1}{a-(a_1/2)+((b-b_1)/4)}$$
$$s \equiv \frac{b_1/2}{a-(a_1/2)+((b-b_1)/4)}$$
$$t \equiv \frac{(b-b_1)/2}{a-(a_1/2)+((b-b_1)/4)}$$

Now, let us consider the case of burning one mole of the total mixture at UFL. Based on assumptions U1 and U2, we could write down the number of moles of reactants and products before and after the combustion reaction. Before the combustion reaction, there are U moles of hydrocarbon, U/x moles of blended gas, $(U/x-U)$ moles of inert nitrogen, and $1-U/x$ moles of air. After the combustion reaction, the oxygen should be of zero moles because assumption U1 requires oxygen gas reacts completely at UFL. Assumption U2 requires the stoichiometric relation of a combustion reaction does not change by the presence of the inert gas, so the quantities of all burnt products could be calculated according to the stoichiometric relation shown in Eq. (5). Table 1 summarizes the number of moles for all materials involved in the combustion reaction before and after burning one mole of the total mixture at its UFL.

Because the oxygen gas is consumed completely, the heat released on burning one mole of the total mixture at UFL can be calculated as follows:

$$(\Delta h) = 0.21k\left(1-\frac{U}{x}\right)(-\Delta h_c). \tag{6}$$

Moreover, the mean (from room temperature to the adiabatic flame temperature) total heat capacity of the burnt products (including the unburned reactants) is then calculated as:

$$C_p = \left(U-0.21k\left(1-\frac{U}{x}\right)\right)C_{p_f} + \left(0.21q\left(1-\frac{U}{x}\right)\right)C_{p_{CO}} + \left(0.21r\left(1-\frac{U}{x}\right)\right)C_{p_{CO_2}} + \left(0.21s\left(1-\frac{U}{x}\right)\right)C_{p_{H_2}} + \left(0.21t\left(1-\frac{U}{x}\right)\right)C_{p_{H_2O}} + \left(0.79\left(1-\frac{U}{x}\right)+\frac{U}{x}(1-x)\right)C_{p_{N_2}} \tag{7}$$

where C_{p_f}, $C_{p_{N_2}}$, $C_{p_{CO}}$, $C_{p_{CO_2}}$, $C_{p_{H_2}}$ and $C_{p_{H_2O}}$ are mean molar heat capacities of hydrocarbon, nitrogen, carbon monoxide, carbon dioxide, hydrogen and steam, respectively.

Table 2
Mole balance for burning one mole of fuel mixture at UFL.

Compound name	No. of moles before burning	No. of moles after burning
Hydrocarbon	U_1	$U_1 - 0.21k(1-U_1)$
Air		
Nitrogen	$0.79(1-U_1)$	$0.79(1-U_1)$
Oxygen	$0.21(1-U_1)$	0
Carbon monoxide	0	$0.21q(1-U_1)$
Carbon dioxide	0	$0.21r(1-U_1)$
Hydrogen	0	$0.21s(1-U_1)$
Steam	0	$0.21t(1-U_1)$

Combining all terms having U in Eq. (7) together gives the following equation:

$$C_p = U\left(C_{p_f} + 0.21\frac{k}{x}C_{p_f} - 0.21\frac{q}{x}C_{p_{CO}} - 0.21\frac{r}{x}C_{p_{CO_2}} - 0.21\frac{s}{x}C_{p_{H_2}} - 0.21\frac{t}{x}C_{p_{H_2O}} - \frac{0.79}{x}C_{p_{N_2}} + C_{p_{N_2}}\left(\frac{1}{x}-1\right)\right) - \left(0.21kC_{p_f} - 0.21qC_{p_{CO}} - 0.21rC_{p_{CO_2}} - 0.21sC_{p_{H_2}} - 0.21tC_{p_{H_2O}} - 0.79C_{p_{N_2}}\right) \quad (8)$$

For brevity in notation, let us define P_1 as follows.

$$P_1 \equiv 0.21kC_{p_f} - 0.21qC_{p_{CO}} - 0.21rC_{p_{CO_2}} - 0.21sC_{p_{H_2}} - 0.21tC_{p_{H_2O}} - 0.79C_{p_{N_2}} \quad (9)$$

Substituting Eq. (9) into Eq. (8) and rearranging gives:

$$C_p = U\left(C_{p_f} - C_{p_{N_2}}\right) + \frac{U}{x}\left(P_1 + C_{p_{N_2}}\right) - P_1 \quad (10)$$

Now, let us turn to the case of burning one mole of fuel mixture at UFL. With the aids of assumptions U1 and U2, the number of moles of each material involved in the combustion before and after the burning process could be written down. The results are summarized in Table 2.

According to Table 2, the heat released on burning one mole of fuel mixture at UFL is:

$$(\Delta h)_1 = 0.21k(1-U_1)(-\Delta h_c) \quad (11)$$

The mean total heat capacity of the burnt products for burning one mole of fuel mixture is then calculated as follows:

$$C_{p_1} = (U_1 - 0.21k(1-U_1))C_{p_f} + (0.21q(1-U_1))C_{p_{CO}} + (0.21r(1-U_1))C_{p_{CO_2}} + (0.21s(1-U_1))C_{p_{H_2}} + (0.21t(1-U_1))C_{p_{H_2O}} + (0.79(1-U_1))C_{p_{N_2}} \quad (12)$$

Combining all terms having U_1 in Eq. (12) together and substituting Eq. (9) into it will give

$$C_{p_1} = U_1(C_{p_f} + P_1) - P_1 = U_1(C_{p_f} - C_{p_{N_2}}) + (P_1 + C_{p_{N_2}})U_1 - P_1 \quad (13)$$

Now, let us compare the heat released on burning one mole of the total mixture and one mole of the fuel mixture at the corresponding UFLs. The following result is a direct conclusion from assumption U3.

$$\frac{(\Delta h)}{(\Delta h)_1} = \frac{C_p \Delta T}{C_{p_1}\Delta T_1} = \frac{C_p}{C_{p_1}} \quad (14)$$

where ΔT and ΔT_1 are the adiabatic flame temperature rises for burning total mixture and fuel mixture at their UFL, respectively. Substituting Eqs. (6), (10), (11) and (13) into the corresponding terms in Eq. (14) gives:

$$\frac{0.21k(1-(U/x))(-\Delta h_c)}{0.21k(1-U_1)(-\Delta h_c)} = \frac{U(C_{p_f} - C_{p_{N_2}}) + (P_1 + C_{p_{N_2}})(U/x) - P_1}{U_1(C_{p_f} + P_1) - P_1} \quad (15)$$

Dropping $0.21k(-\Delta h_c)$ from Eq. (15) and combining all terms having U together will reach the following relation:

$$\frac{1}{U} = \frac{U_1C_{p_f} + (1-U_1)C_{p_{N_2}}}{U_1C_{p_f}}\frac{1}{x} + \frac{(1-U_1)(C_{p_f} - C_{p_{N_2}})}{U_1C_{p_f}} \quad (16)$$

On rearranging Eq. (16) gives,

$$\frac{1}{U} = \frac{1}{U_1} + \frac{U_1C_{p_f} + (1-U_1)C_{p_{N_2}}}{U_1C_{p_f}}\left(\frac{1}{x} - 1\right) \quad (17)$$

It can be easily understood from Eq. (17) that the coefficient of the $((1/x)-1)$ term is a constant for a given hydrocarbon. Now, let us define ϕ_U as follows:

$$\phi_U \equiv \frac{U_1C_{p_f} + (1-U_1)C_{p_{N_2}}}{U_1C_{p_f}} \quad (18)$$

Thus, Eq. (17) can be expressed in a more compact form as follows:

$$\frac{1}{U} = \frac{1}{U_1} + \phi_U\left(\frac{1}{x} - 1\right) \quad (19)$$

Eq. (19) is the theoretical model for predicting the UFL of a hydrocarbon diluted with inert nitrogen. It states that if $1/U - 1/U_1$ was plotted against $1/x - 1$, then we will get a straight line passing through the origin. In next section, we will examine whether this deduction is supported by existing experimental data or not.

2.3. Lower flammability limit

At LFL, the amount of oxygen present is sufficient for perfect combustion of hydrocarbons; thus, the stoichiometry of a combustion reaction occurring at LFL could be expressed as follows.

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O \quad \Delta H = (-\Delta h_c) \quad (20)$$

where $(-\Delta h_c)$ is the heat of reaction for burning one mole of the hydrocarbon compound according to Eq. (20). For brevity in notation, the following terms are defined and adopted throughout this subsection:

$$k \equiv a + \frac{b}{4}$$
$$r \equiv a$$
$$s \equiv \frac{b}{2}$$

Now, let us consider the case of burning one mole of the total mixture at LFL. Based on assumptions L1 and L2, we could write down the number of moles of all the reactants and products before and after the combustion reaction. Table 3 lists the number of moles of each material involved in the combustion reaction before and after burning one mole of the total mixture at its LFL.

Because assumption L1 requires the hydrocarbon to be completely consumed at LFL, the heat released on burning one mole of the total mixture at LFL could be calculated as follows:

$$(\Delta h) = L(-\Delta h_c) \quad (21)$$

Table 3
Mole balance for burning one mole of the total mixture at LFL.

Compound name	No. of moles before burning	No. of moles after burning
Hydrocarbon	L	0
Air		
Nitrogen	$0.79\left(1-\frac{L}{x}\right)$	$0.79\left(1-\frac{L}{x}\right)$
Oxygen	$0.21\left(1-\frac{L}{x}\right)$	$0.21\left(1-\frac{L}{x}\right)-kL$
Inert nitrogen	$\frac{L}{x}(1-x)$	$\frac{L}{x}(1-x)$
Carbon dioxide	0	rL
Water	0	sL

According to Table 3, the mean total heat capacity of the burnt products could be calculated as follows:

$$C_p = \left(\frac{L}{x}(1-x)+0.79\left(1-\frac{L}{x}\right)\right)C_{p_{N_2}} + \left(0.21\left(1-\frac{L}{x}\right)-kL\right)C_{p_{O_2}} + rLC_{p_{CO_2}} + sLC_{p_{H_2O}} \quad (22)$$

Combining all terms having L in Eq. (22) together gives

$$C_p = L\left(-\frac{0.21}{x}C_{p_{O_2}} - kLC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}} - \frac{0.79}{x}C_{p_{N_2}} + C_{p_{N_2}}\left(\frac{1}{x}-1\right)\right) + \left(0.21C_{p_{O_2}} + 0.79C_{p_{N_2}}\right) \quad (23)$$

For brevity in notation, let us define P_2 as follows:

$$P_2 \equiv 0.79C_{p_{N_2}} + 0.21C_{p_{O_2}} \quad (24)$$

Substituting Eq. (24) into Eq. (23), we obtain

$$C_p = L(-kC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}} - C_{p_{N_2}}) + (-P_2 + C_{p_{N_2}})\frac{L}{x} + P_2 \quad (25)$$

Now, let us turn to the case of burning one mole of the fuel mixture at LFL. Table 4 summarizes the number of moles of each material involved in this combustion reaction before and after this burning process.

According to Table 4, the heat released on burning one mole of the fuel mixture at LFL can be calculated as follows:

$$(\Delta h)_1 = L_1(-\Delta h_c) \quad (26)$$

The mean total heat capacity of the burnt products for burning one mole of fuel mixture at LFL is then derived as follows:

$$C_{p_1} = 0.79(1-L_1)C_{p_{N_2}} + (0.21(1-L_1)-kL_1)C_{p_{O_2}} + rL_1C_{p_{CO_2}} + sL_1C_{p_{H_2O}} \quad (27)$$

Combining all terms having L_1 in Eq. (27) together, we get,

$$C_{p_1} = L_1(-0.79C_{p_{N_2}} - 0.21C_{p_{O_2}} - kC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}}) + (0.79C_{p_{N_2}} + 0.21C_{p_{O_2}}) \quad (28)$$

Table 4
Mole balance for burning one mole of the fuel mixture at LFL.

Compound name	No. of moles before burning	No. of moles after burning
Hydrocarbon	L_1	0
Air		
Nitrogen	$0.79(1-L_1)$	$0.79(1-L_1)$
Oxygen	$0.21(1-L_1)$	$0.21(1-L_1)-kL_1$
Carbon dioxide	0	rL_1
Water	0	sL_1

Substituting P_2 in Eq. (24) into Eq. (28), we get,

$$C_{p_1} = L_1(-P_2 - kC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}}) + P_2 \quad (29)$$

Now, let us compare the heat released on burning one mole of the total mixture and one mole of the fuel mixture at their corresponding LFLs. Assumption L3 deduces the following relation:

$$\frac{(\Delta h)}{(\Delta h)_1} = \frac{C_p\Delta T}{C_{p_1}\Delta T_1} = \frac{C_p}{C_{p_1}} \quad (30)$$

where ΔT and ΔT_1 are the adiabatic flame temperature rises for the total mixture and the fuel mixture at their LFLs, respectively. Substituting Eqs. (21), (25), (26) and (29) into the corresponding terms in Eq. (30) will reach the following result:

$$\frac{L(-\Delta h_c)}{L_1(-\Delta h_c)} = \frac{L\left(-kC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}} - C_{p_{N_2}}\right) + \left(-P_2 + C_{p_{N_2}}\right)(L/x) + P_2}{L_1\left(-P_2 - kC_{p_{O_2}} + rC_{p_{CO_2}} + sC_{p_{H_2O}}\right) + P_2} \quad (31)$$

Dropping $(-\Delta h_c)$ from Eq. (31) and combining all terms having L will give the following relation:

$$\frac{1}{L} = \frac{1}{L_1} + \frac{-C_{p_{N2}} + P_2}{P_2}\left(\frac{1}{x}-1\right) \quad (32)$$

Now, let us define ϕ_L as follows:

$$\phi_L \equiv \frac{-C_{p_{N_2}} + 0.79C_{p_{N_2}} + 0.21C_{p_{O_2}}}{0.79C_{p_{N_2}} + 0.21C_{p_{O_2}}} = \frac{-C_{p_{N_2}} + P_2}{P_2} \quad (33)$$

Then, we will reach a more compact form as follows:

$$\frac{1}{L} = \frac{1}{L_1} + \phi_L\left(\frac{1}{x}-1\right) \quad (34)$$

Eq. (34) is the theoretical model for predicting the LFL of a hydrocarbon diluted with inert nitrogen. It states that if $1/L-1/L_1$ was plotted against $1/x-1$, then we will get a straight line passing through the origin. We will examine where this deduction is supported by existing experimental data or not in next section.

Before ending this section, it is worth noting here that although the hydrocarbon is the lean material at LFL while oxygen is the lean material at UFL, Eq. (19) for UFL and Eq. (34) for LFL are of similar form.

3. Examining the theoretical model with experimental data

It is well known that the reported values of flammability limits depend on the experimental apparatus and condition used for measurement. To enhance the consistency and reliability of experimental data, the data reported in a recent work by Kondo et al. [11] are adopted in present study. The cases employed to examine the proposed models include the compounds of methane, propane, ethylene and propylene.

As Eq. (19) shows, if $((1/U)-(1/U_1))$ was plotted against $((1/x)-1)$, we will obtain a straight line passing through the origin. To examine this linearity, linear regression was performed on experimental data with a linear model passing through the origin. Figs. 1–4 show the regression results for the cases of methane, propane, ethylene and propylene respectively. It could be seen from these figures that the experimental data fit a straight line passing through the origin very well for every case. To make quantitative description, R^2-values and the slopes of the regression lines for these four cases are summarized in Table 5. As shown in Table 5, all the R^2-values for these four hydrocarbons are larger than 0.991. With these facts, it might be reasonable to conclude that the proposed model for UFL could effectively explain these experimental data.

It is obvious that if assumptions U1–U3 well described the burning conditions of a reaction occurring at UFL, the value of

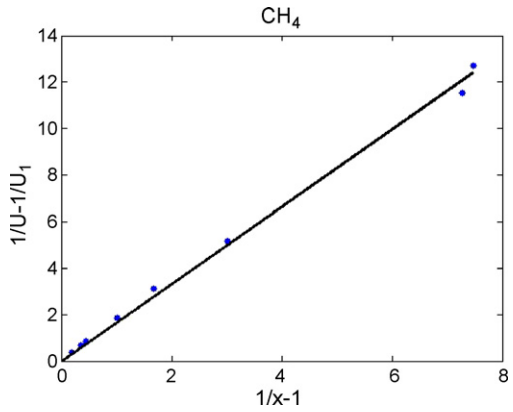

Fig. 1. Regression line of methane at UFL: round point – experimental data; solid line – regression line

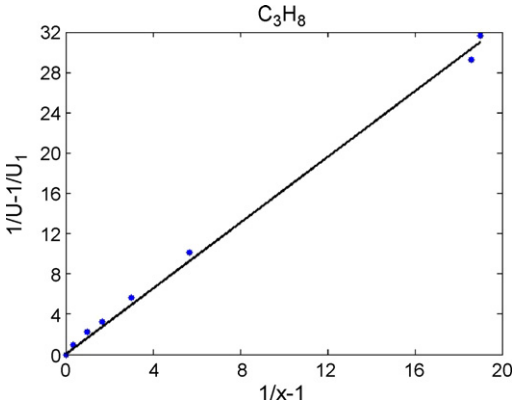

Fig. 2. Regression line of propane at UFL: round point – experimental data; solid line – regression line.

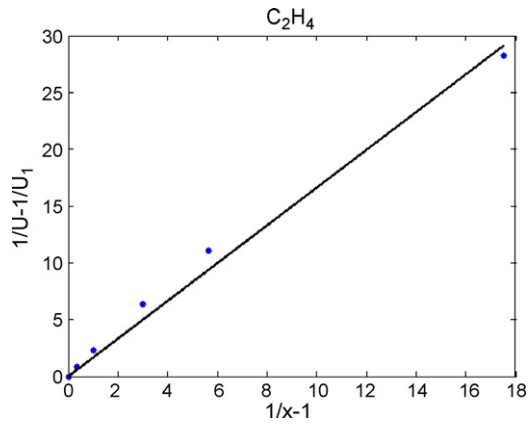

Fig. 3. Regression line of ethylene at UFL: round point – experimental data; solid line – regression line.

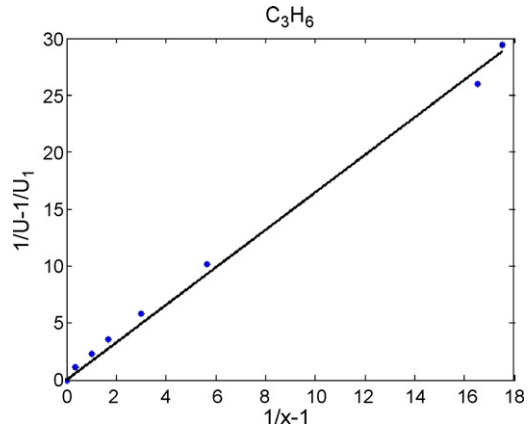

Fig. 4. Regression line of propylene at UFL: round point – experimental data; solid line – regression line.

Table 5
Regression results of four hydrocarbons at UFL.

Compound name	R^2	ϕ_U (experimental)
Methane	0.9968	1.6592
Propane	0.9965	1.6321
Ethylene	0.9897	1.6608
Propylene	0.9950	1.6435

ϕ_U estimated by Eq. (18) should match the one regressed by experimental data. As earlier discussion, because the fact that UFL curve and LFL curve finally converge to the inertization point, the real burning conditions always deviate from our assumptions, especially, assumption U2, in some degree. To illustrative this point, let us compare the ϕ_U calculated from Eq. (18) and obtained by the experimental data. As Eq. (18) shows, two types of information are needed to theoretically calculate ϕ_U: (1) the information of mean molar heat capacities for the flammable hydrocarbon and inert nitrogen; (2) the adiabatic flame temperature for calculation. For convenience, Table 6 summaries the mean molar heat capacities of the materials involved in the combustion reaction from the room temperature (298 K) to the given temperature shown in that table. This table was constructed from the specific heat capacity—temperature dependency for compounds provided in a textbook by Smith and Van Ness [14]. However, the choice for the adiabatic flame temperature of a hydrocarbon is not unified in the literature. Some researchers agree that this temperature is around 1550 K [10] or 1200 K [15], while others believe that this temperature is in the range of 1000–1500 K [16]. In a recent work, the experiment data of methane and ethylene were found to be

Table 6
Mean molar heat capacities between 298 K and temperature listed[a].

Compound	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
CH_4	13.1038	13.6623	14.1921	14.6933	15.1658	15.6096	16.0247
C_3H_8	31.4246	32.8829	34.2243	35.4488	36.5564	37.5471	38.4210
C_2H_4	17.3583	18.0909	18.7652	19.3814	19.9395	20.4393	20.8810
C_3H_6	26.1817	27.3392	28.4052	29.3795	30.2622	31.0533	31.7528
CO	7.3891	7.4415	7.4933	7.5446	7.5957	7.6464	7.6969
CO_2	11.2416	11.4095	11.5668	11.7161	11.8591	11.9970	12.1309
N_2	7.3738	7.4225	7.4705	7.5181	7.5653	7.6123	7.6589
H_2O	8.8965	9.0195	9.1425	9.2655	9.3885	9.5115	9.6345
O_2	7.6748	7.7370	7.7971	7.8557	7.9131	7.9695	8.0251
He	4.9688	4.9688	4.9688	4.9688	4.9688	4.9688	4.9688

[a] Unit: cal/gmole K.

Table 7
Theoretical ϕ_U calculated at different adiabatic flame temperatures.

Compound name	1000K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
Methane	3.9988	3.8952	3.8052	3.7268	3.6584	3.5988	3.5470
Propane	3.1119	3.0315	2.9645	2.9088	2.8625	2.8246	2.7941
Ethylene	1.9238	1.8922	1.8657	1.8435	1.8251	1.8099	1.7976
Propylene	3.2787	3.1966	3.1279	3.0704	3.0227	2.9834	2.9516

fitted theoretical LFL well at a temperature of approximately 1400 K [9]. Detailed discussions about the issue for choosing the adiabatic flame temperature for calculating flammability limits could be found in the work by Vidal et al. [9] and the references therein.

As the reported adiabatic flame temperatures for most hydrocarbons ranging from 1000 K to 1600 K, the values of ϕ_U are calculated for adiabatic flame temperatures in this temperature range for the explored compounds in present work; and the results are summarized in Table 7. It could be found from Tables 5 and 7 that these theoretical values of ϕ_U do not match the experimental one very well. For example, ϕ_U from regression on experimental data is found to be of 1.6321 for the case of propane, but the predictive values range from 3.1119 to 2.7941 as the adiabatic flame temperature ranges from 1000 K to 1600 K.

Moreover, it was found in Figs. 1–4 that experimental data show positive deviations from the regression lines in the region adjacent to $((1/x)-1)\rightarrow 0$ in all explored cases. In regression analysis, such a systematic error might result from the fact that the experimental data of UFL at high concentration of inert gas, i.e., large value of $((1/x)-1)$, is lower than the one predicted by the regression line. It is well known that the UFL curve will fall down and finally intersect with the LFL curve as the concentration of inert gas increases. Thus, it seems reasonable that the experimental data of UFL at high concentration of inert gas will be lower than the one predicted by the regression line; and this result conforms to previous observations.

If the conjecture that the inconsistence between the theoretical ϕ_U and experimental ϕ_U comes from the violation of assumption U2 is true, the experimental ϕ_U estimated from the experimental data at low concentrations of inert nitrogen must be more close to the theoretical one than the ϕ_U estimated from whole experimental data because assumption U2 must be true when the concentration of inert nitrogen is low. To estimate the limit value of ϕ_U for low concentration of inert nitrogen, we calculate it from the set of whole experimental data, the set of the lowest three concentrations of inert gas and the set of the lowest two concentrations of inert gas, respectively. In Table 8, we summarized the values of ϕ_U estimated by different subsets of experimental data for the four compounds explored.

It could be seen from Table 8 that the values of ϕ_U obtained from the subset containing only the data at low concentrations of inert gas are closer to the theoretical one than those estimated from the set of whole experimental data. Moreover, it could be also found that the value of ϕ_U determined by the two-point subset for propane is of 2.967 and this value is within those theoretically predicted with the adiabatic flame temperature ranging from 1000 K to 1600 K. For the cases of other compounds in this table, although the values of ϕ_U estimated from the subset of the data at low concentrations of inert gas are not within those predicted by the theoretical adiabatic flame temperatures, they are much closer to the theoretical one than that estimated by the set of whole experimental data. Thus, this conjecture is positively supported by existing experimental data.

Table 8
ϕ_U estimated by different set of experimental data.

Compound name	ϕ_U (whole data)	ϕ_U (3 points)	ϕ_U (2 points)
Methane	1.6592	2.0299	2.1663
Propane	1.6321	2.2723	2.9670
Ethylene	1.7481	2.2818	2.4762
Propylene	1.6435	2.3794	3.3395

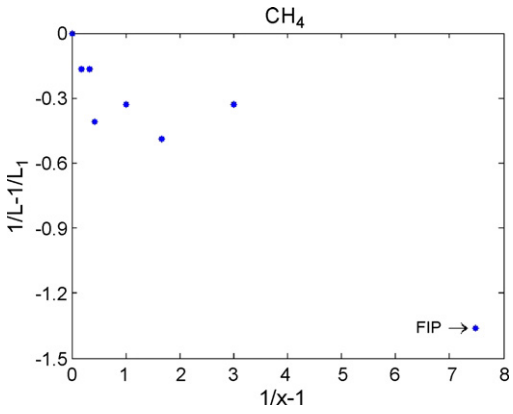

Fig. 5. Experimental results of methane at LFL.

To be an acceptable model for predicting UFL, we need to understand the predictive errors of UFL itself at different concentrations of inert gas. Moreover, as earlier discussion, the values of ϕ_U estimated from different subset of experimental data will somewhat differ with each other in certain degrees, thus a comparison of the predictive errors for this issue should be also addressed. In Table 9, experimental data of UFL for methane at different concentrations of inert nitrogen are compared with the predictive values of UFL calculated from different values of ϕ_U. It could be seen from Table 9 that the ϕ_U estimated from the whole experimental data set gives more accurate predictive result than that of the other two ϕ_Us. For these three different choices of ϕ_U, the average error of prediction ranges from 1.95% to 6.14% and the maximum error ranges from 3.7% to 19.1%. As compared to the known experimental error in UFL, all

Table 9
Predictive errors of UFL in methane for ϕ_U estimated by different sets of experimental data.

x	UFL[a] (exp)	ϕ_U = 1.6592		ϕ_U = 2.0299		ϕ_U = 2.1663	
		UFL (Pred.)	Error (%)	UFL (Pred.)	Error (%)	UFL (Pred.)	Error (%)
1.000	0.1580	0.1580	0.0000	0.1580	0.0000	0.1580	0.0000
0.850	0.1490	0.1510	1.3515	0.1495	0.3601	0.1490	0.0001
0.750	0.1430	0.1453	1.6103	0.1427	−0.1819	0.1418	−0.8255
0.700	0.1394	0.1420	1.8949	0.1389	−0.3538	0.1378	−1.1564
0.500	0.1219	0.1252	2.6931	0.1196	−1.8611	0.1177	−3.4368
0.375	0.1060	0.1100	3.7332	0.1030	−2.8656	0.1006	−5.0872
0.250	0.0870	0.0884	1.6587	0.0805	−7.4448	0.0780	−10.3973
0.121	0.0560	0.0544	−2.8569	0.0474	−15.2696	0.0453	−19.0744
0.118	0.0525	0.0534	1.6907	0.0465	−11.4137	0.0444	−15.4239
		Average	1.9432	Average	4.4167	Average	6.1557

[a] Data in this column were taken from the work by Kondo et al. [11].

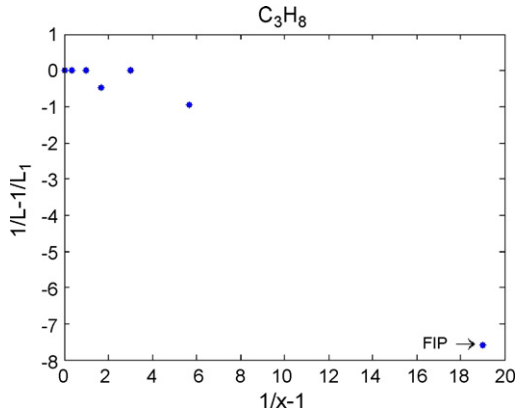

Fig. 6. Experimental results of propane at LFL.

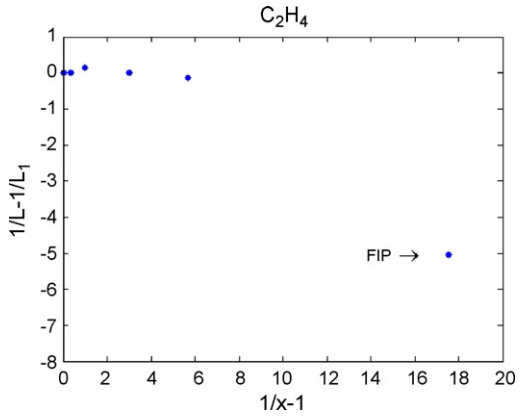

Fig. 7. Experimental results of ethylene at LFL.

these ϕ_Us give satisfactory performance for practical applications. As the precise adiabatic flame temperature is usually unknown for a hydrocarbon, ϕ_U is rarely theoretically calculated from Eq. (18) and experimental data of UFL are indispensable to determine ϕ_U in practice; however, as the proposed model is a linear one, it needs the least experimental data to build up the model.

Now, let us turn to examine the model for LFL. It could be seen from Eq. (34) that if assumptions L1–L3 well described the burning conditions at LFL, we will obtain a straight line passing through the origin when $((1/L)-(1/L_1))$ is plotted against $((1/x)-1)$. In Figs. 5–8, we plot $((1/L)-(1/L_1))$ against $((1/x)-1)$ for the cases of methane, propane, ethylene and propylene, respectively; however, as shown in these figures, the experimental data do not obviously show such

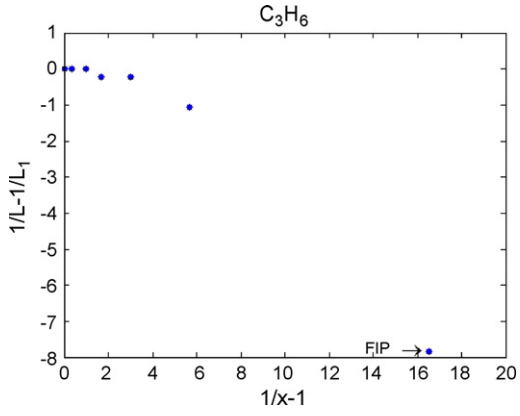

Fig. 8. Experimental results of propylene at LFL.

Table 10
Theoretical ϕ_L for different adiabatic flame temperature.

Compound name	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
Methane	0.0085	0.0088	0.0091	0.0093	0.0096	0.0098	0.0099
Propane	0.0085	0.0088	0.0091	0.0093	0.0096	0.0098	0.0099
Ethylene	0.0085	0.0088	0.0091	0.0093	0.0096	0.0098	0.0099
Propylene	0.0085	0.0088	0.0091	0.0093	0.0096	0.0098	0.0099

linearity. It could be also found from these figures that the experimental data of $((1/L)-(1/L_1))$ seem to be around zero except the fuel inertization point (FIP). The FIP was defined by Kondo et al. [11,12] to be the point on the envelope of flammable region in the triangular system of fuel–air–diluent which defines the maximum ratio of fuel to diluent concentration that never gives flammable mixtures whatever amount of air is added or subtracted from the mixture. According to their definitions, it is obvious that the burning conditions of FIP significantly violate both assumptions L1 and L2. Thus, the burning behavior of FIP is obviously different from that of other experimental data, so we do not consider it in present study.

As the experimental data of $((1/L)-(1/L_1))$ are around zero, this seems to indicate that $((1/L)-(1/L_1))$ is independent of $((1/x)-1)$ when flammable hydrocarbons are diluted with inert nitrogen and this fact seems to be at variance with Eq. (34). To clearly clarify this argument, let us check the theoretical values of ϕ_L calculated from Eq. (33). Table 10 summarized the values of ϕ_L for the four explored cases at the adiabatic flame temperature ranging from 1000 K to 1600 K. According to Eq. (33), ϕ_L is independent of the kind of hydrocarbons involved in the combustion reaction, so the values of ϕ_L are the same if the adiabatic flame temperatures are the same. Thus, as shown in Table 10, these four cases are of the same ϕ_L at the same flame temperature.

It could be found in Table 6 that the mean molar heat capacities of nitrogen and oxygen are very close to each other at the adiabatic flame temperature ranging from 1000 K to 1600 K, so ϕ_Ls are very close to zero according to Eq. (33). Thus, it is concluded that $((1/L)-(1/L_1))$ is irrelative of $((1/x)-1)$ for most hydrocarbons. This conclusion accords with the experimental fact that the concentration of inert nitrogen has little effect on the LFL for most hydrocarbons [8]. Thus, these experimental data of LFL are effectively explained by the proposed Eq. (34).

4. Discussions

In our notation, x means the molar fraction of hydrocarbon in the blended gas, so $1-x$ means the molar fraction of the inert nitrogen in the blended gas. Thus, the well-known empirical fact that the concentration of inert nitrogen has little effect on the LFL for most hydrocarbons could be mathematically expressed as $dL/(d(1-x)) \approx 0$. When the concentration of inert gas is low, i.e., $x \to 1$, we could reach the following Eq. (35) by doing implicit differentiation on the proposed Eq. (34):

$$\left.\frac{dL}{d(1-x)}\right|_{x\to 1} = -\phi_L L_1^2 \tag{35}$$

Eq. (35) gives the slope of the tangent line of the LFL curve at $x = 1$. As we know, the LFL of most hydrocarbons are less than 0.1 and the ϕ_Ls of organic compounds are about 0.009 for inert nitrogen, thus the numerical values of $\phi_L L_1^2$ for most hydrocarbons are less than 1×10^{-4}. This theoretically explained why the concentration of inert nitrogen has very limited effect on LFL for most hydrocarbons.

Because the concentration of inert nitrogen has very limited effect on LFL, predicting the change in UFL is the only crucial issue to an inerting process with inert nitrogen in process industries. As we have mentioned earlier, it always need experimental data of

Table 11
Errors in UFL for ϕ_U estimated by LOC-based method.

Compound name	ϕ_U (whole data)	ϕ_U (LOC)	Error in ϕ_U (%)	Max. error[a] (%)	Avg. error[a] (%)
Methane	1.6592	1.8175	9.54	8.58	2.17
Propane	1.6321	1.8446	13.02	11.53	3.64
Ethylene	1.7481	1.8392	5.21	9.57	5.84
Propylene	1.6435	1.8655	13.51	12.18	4.56

[a] This error means the difference between the predictive UFL and the experimental UFL reported by Kondo et al. [11].

UFL to establish the predictive model because the precise adiabatic flame temperatures are not clearly defined for most hydrocarbons. However, the fact that LFL does not change with respect to the concentration of inert nitrogen gives the possibility to estimate ϕ_U whenever no experimental data of UFL are available. As the fact that the point of LOC could be approximately taken as the intersection of the UFL curve and LFL curve is a widely accepted practice [8], we could reach the following estimation of ϕ_U from the LOC information:

$$\phi_U = \frac{U_1 - L_1}{U_1(1 - L_1 - \mathrm{LOC}/0.21)} \tag{36}$$

Eq. (36) is recommended as the preferred method to estimate ϕ_U whenever no experimental data of UFL are available. To evaluate the feasibility of Eq. (36), experimental data of the cases of methane, propane, ethylene and propylene are explored. The corresponding LOCs for arforementioned four compounds were taken from a textbook by Crowl and Louvar [8]; and their numerical values are of 0.120, 0.115, 0.100 and 0.115, respectively. The values of ϕ_U are then calculated by Eq. (36), and these results and those determined from the whole experimental data set are compared in Table 11. It could be seen that the errors in ϕ_U range from 5.21% to 13.51% for different compounds. To obtain a more clear insight on the predictive errors for this LOC-based method, the estimated values of ϕ_U are then applied to Eq. (19) to obtain the predicted UFLs at specific concentrations reported in Kondo et al.'s work [11]. These predicted values of UFLs are compared with the experimental data at the corresponding concentrations. For the cases considered, the average errors range from 2.17% to 5.84% and the maximum errors range from 8.58% to 12.18% for these four cases; and the results are also summarized in Table 11. As compared to the known experimental errors of flammability limits, the LOC-based method could afford the predicted values of UFL with reasonable accuracy in practical applications.

In our earlier work [13], it has been shown that if carbon dioxide is served as the inert gas, both Eq. (34) for UFL and Eq. (19) for LFL are valid except that the definitions of ϕ_U and ϕ_L must be somewhat modified. Table 12 compares the definitions of ϕ_U and ϕ_L for both the cases of inert carbon dioxide and inert nitrogen. It could be found from Table 12 that the only difference between them is the mean molar heat capacities of the inert gases employed. In fact, it could be derived that Eq. (34) for UFL and Eq. (19) for LFL will hold for hydrocarbons diluted with any other inert gas, if the definitions of ϕ_U and ϕ_L are modified as follows:

$$\phi_U \equiv \frac{U_1 C_{p_f} + (1 - U_1) C_{p_{\mathrm{inert\,gas}}}}{U_1 C_{p_f}} \tag{37}$$

Table 12
Definitions of ϕ_U and ϕ_L for different inert gas[a].

Inert gas	Carbon dioxide	Nitrogen
ϕ_U	$\phi_U = \frac{U_1 C_{p_f} + (1-U_1) C_{p_{CO_2}}}{U_1 C_{p_f}}$	$\phi_U = \frac{U_1 C_{p_f} + (1-U_1) C_{p_{N_2}}}{U_1 C_{p_f}}$
ϕ_L	$\phi_L = \frac{P_2 - C_{p_{CO_2}}}{P_2}$	$\phi_L = \frac{P_2 - C_{p_{N_2}}}{P_2}$

[a] $P_2 = 0.21 C_{p_{O_2}} + 0.79 C_{p_{N_2}}$.

$$\phi_L \equiv \frac{P_2 - C_{p_{\mathrm{inert\,gas}}}}{P_2} \tag{38}$$

where $C_{p_{\mathrm{inert\,gas}}}$ is the mean molar heat capacity of the inert gas employed. With the aids of these two equations, we could develop a way to theoretically compare the inert ability for different kinds of inert gas. To understand the idea of comparing the inert ability for different kinds of inert gases in present work, the flammability curves of methane diluted with carbon dioxide, steam, nitrogen and helium are shown Fig. 9. This figure is basically reproduced from the experimental data reported in the work of Coward and Jones [17]. Because the experimental data in their work were expressed in graphic form, we read the numerical values from the corresponding graphics and then reproduced them into Fig. 9. It should be noted that the flammability limits were plotted against the concentration of inert gas (i.e., $1-x$) in that figure. It is obvious from Fig. 9 that the flammability curves for a given inert gas were enveloped in the area bounded by the line passing through the point of pure hydrocarbon at LFL with the slope of $(dL/d(1-x))|_{x=1}$ and the line passing through the point of pure hydrocarbon at UFL with the slope of $(dU/d(1-x))|_{x=1}$. So, we could use $(dL/d(1-x))|_{x=1}$ and $(dU/d(1-x))|_{x=1}$ to be the indices to evaluate inert ability for different kinds of inert gases. Referring to proposed models, $(dL/d(1-x))|_{x=1}$ is of the form of Eq. (35) and $(dU/d(1-x))|_{x=1}$ is of the following form:

$$\left.\frac{dU}{d(1-x)}\right|_{x\to 1} = -\phi_U U_1^2 \tag{39}$$

For a given hydrocarbon, the values of L_1 and U_1 are the same to all kinds of inert gases, so the inert ability of an inert gas depends on the numerical values of ϕ_U and ϕ_L. As Fig. 9 shows, the change in UFL is usually more obvious than that in LFL when the inert gas is added, so ϕ_U could be taken as the main index to compare the inert ability for different kinds of inert gases.

It could be concluded from Eq. (39) that if an inert gas of larger value of ϕ_U is added to hydrocarbons, the UFL will decrease more

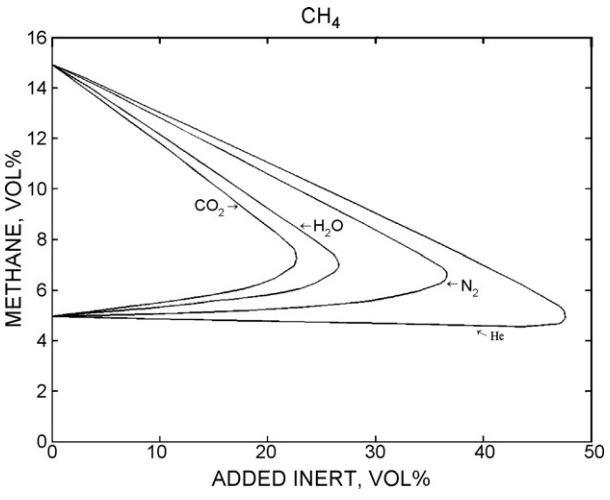

Fig. 9. Flammability curves of methane for different inert gases.

Table 13
Mean molar heat capacities of different inert gases between 298 K and temperature listed[a].

Compound	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
CO_2	11.2416	11.4095	11.5668	11.7161	11.8591	11.9970	12.1309
N_2	7.3738	7.4225	7.4705	7.5181	7.5653	7.6123	7.6589
H_2O	8.8965	9.0195	9.1425	9.2655	9.3885	9.5115	9.6345
He	4.9688	4.9688	4.9688	4.9688	4.9688	4.9688	4.9688

[a] Unit: cal/gmole K.

Table 14
Theoretical ϕ_L of different inert gases for different adiabatic flame temperature ranging from 1000 K to 1600 K.

Compound name	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
Carbon dioxide	−0.5116	−0.5236	−0.5342	−0.5438	−0.5526	−0.5606	−0.5681
Nitrogen	0.0085	0.0088	0.0091	0.0093	0.0096	0.0098	0.0099
Steam	−0.1962	−0.2044	−0.2127	−0.2209	−0.2291	−0.2373	−0.2454
Helium	0.3319	0.3365	0.3409	0.3453	0.3495	0.3536	0.3577

rapidly than an inert gas of smaller value of ϕ_U. As Eq. (37) shows that an inert gas of larger mean molar heat capacity is of larger value of ϕ_U, it is then reached that an inert gas of larger mean molar heat capacity at the specified adiabatic flame temperature is of more excellent ability to inertize flammable hydrocarbons. Table 13 lists the mean molar heat capacities of aforementioned four kinds of inert gases, i.e., carbon dioxide, steam, nitrogen and helium, with the adiabatic flame temperature ranging from 1000 K to 1600 K. It is found from Table 13 that the mean molar heat capacities of these four kinds of inert gases are in the following order: carbon dioxide > steam > nitrogen > helium, so we could conclude that the inert ability of them for diluting methane is of the same order. The experimental data of methane shown in Fig. 9 positively support this conclusion.

According to Eq. (37), an inert gas of larger mean molar heat capacity would lead a larger value of ϕ_U for any given hydrocarbon, and this means that aforementioned order of inert ability is independent of the flammable materials employed, thus aforementioned conclusion could apply to the case other than methane. In fact, existing experimental data of hydrocarbons other than methane still show a flammability limits graphic similar to figure [17].

It could be found in Fig. 9 that when the concentration of inert gas is low, the LFL of the methane/inert gas mixture will increase as the concentration of the inert gas increases if the inert gas is carbon dioxide or steam; the LFL of methane/inert gas mixture seems to be irrelative of the concentration of inert gas if the inert gas is nitrogen; and the LFL of methane/inert gas mixture will decrease as the concentration of inert gas increases if the inert gas is helium. Thus, if our model of LFL is feasible to describe these behaviors, it means that the numerical value of ϕ_L in our model should be negative, zero or positive according to the kind of inert gas employed.

To quantitatively explore this feasibility, theoretical values of ϕ_L for different kinds of inert gases are calculated at adiabatic flame temperature ranging from 1000 K to 1600 K, and the results are summarized in Table 14. As it is shown in Table 14, carbon dioxide and steam are of negative values of ϕ_L, which implies, according to Eq. (35), the values of $(dL/d(1-x))|_{x=1}$ are positive for these two kinds of inert gases, so the LFL will increase if one of these two inert gases is added to hydrocarbons; it could also be found that the value of ϕ_L of helium is positive, so the LFL will decrease if helium is added to flammable hydrocarbons; although the value of ϕ_L of nitrogen is positive, its value is very close to zero and this explains why the experimental data of LFL seems to be irrelative of the concentration of inert nitrogen.

Moreover, it could be seen from Eq. (38) that the value of ϕ_L is independent of the hydrocarbons, thus aforementioned conclusion could be applied to all hydrocarbons, not only limited to methane. In fact, many experimental data other than methane also support this conclusion [17].

5. Conclusions

The development of reliable predictive methods for estimating the flammability limits of combustible gas would reduce significantly the amount of experimental data required for a complete flammability characterization. In this study, theoretical models for predicting the upper/lower flammability limits of pure hydrocarbon diluted with nitrogen were developed. The main assumptions in developing these theoretical models include:

(U1) the oxygen gas reacts completely at UFL.
(U2) the stoichiometric relation of a combustion reaction occurring at UFL does not change by the presence of inert gas.
(U3) the adiabatic temperature rises are the same for all limit mixture at UFL.
(L1) the hydrocarbon reacts completely at LFL.
(L2) the stoichiometric relation of a combustion reaction occurring at LFL does not change by the presence of inert gas;
(L3) the adiabatic temperature rises are the same for all limit mixture at LFL.

Based on aforementioned assumptions, it is derived analytically that there are linear relations between both the reciprocal of the upper/lower flammability limits and the reciprocal of the molar fraction of hydrocarbon in the hydrocarbon/nitrogen mixture (free from air). Experimental data of flammability limits reported in the literature, which include the cases of methane, propane, ethylene and propylene, are used to examine these theoretical linearity. The coefficients of determination (R^2) of the theoretical lines for these four cases are all greater than 0.989 for UFL. The slope of the theoretical line for LFL is found to be very close to zero and this result successfully explains the well known experimental fact that inert nitrogen has little effect on LFL for almost all hydrocarbons. Thus, the proposed linearity at LFL is also positively supported by existing experimental data.

As the precise adiabatic flame temperature is usually unknown for a hydrocarbon, ϕ_U in the proposed model is not recommended to calculate by theoretical method and the experimental data of UFL are indispensable to determine ϕ_U in practice. Because LOC could be taken as a point on the UFL, a LOC-based method is proposed to predict ϕ_U when no other experimental data of UFL are available. For the cases of methane, propane, ethylene and propylene, the average predicted error in UFL and the maximum predicted error in UFL range from 2.17% to 5.84% and from 8.58% to 12.18%, respectively. As compared to the known experimental error in

determining UFL, the LOC-based method could estimate the UFL of a hydrocarbon/nitrogen mixture with reasonable accuracy.

The proposed models are extended to the case of diluting hydrocarbons with inert gas other than nitrogen. Through the extended models, it was found that the inert ability of an inert gas depends on its mean molar heat capacity at the adiabatic flame temperature. Theoretical calculation shows that the inert abilities of carbon dioxide, steam, nitrogen and helium are in the following order: carbon dioxide > steam > nitrogen > helium; and this sequence conforms to the existing experimental data reported in the literature.

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