



Carbon dioxide dilution effect on flammability limits for hydrocarbons

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ABSTRACT

Theoretical models to predict the upper/lower flammability limits of a mixture composed of hydrocarbon and inert carbon dioxide are proposed in this study. It is found theoretically 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 gas mixture. These theoretical linear relations are examined by existing experimental results reported in the literature, which include the cases of methane, propane, ethylene, and propylene. The coefficients of determination (R^2) of the regression lines are found to be larger than 0.959 for all aforementioned cases. Thus, the proposed models are highly supported by existing experimental results. A preliminary study also shows the conclusions in present work have the possibility to extend to non-hydrocarbon flammable materials or to inert gas other than carbon dioxide. It is coincident that the theoretical model for the lower flammability limit (LFL) in present work is the same as the empirical model conjectured by Kondo et al.

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1. Introduction

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 organic matter safely. Different methods have been proposed to predict the flammability limits, especially the lower flammability limit (LFL), for pure flammable gases [1,2]. Complex gaseous mixtures, for which the Le Chatelier equation is regularly used to estimate the flammability limits, are also consumed or formed in normal and emergency situations in process industries [3–6]. Such complex mixtures could be also formed in the inert procedure in process industries. 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]. 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 applied to estimate the flammability limits of a mixture of fuel and inert gas in the literature [9,10]. Vidal et al. pointed that the method of calculated adiabatic flame temperatures is a powerful tool to esti-

mate 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 the existing experimental data [9]. Shebeko et al. 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, 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 continue 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 [10]. Therefore, through the calculation of this threshold temperature, the flammability limits of a mixture composed of fuel and inert gas can be obtained. Prediction models based on adiabatic flame temperature theories typically produce satisfactory results in forecasting LFL; however, 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 fuel and inert gas, Kondo et al. have attempted to modify the famous Le Chatelier equation so that it could be applied to predict the flammability limits of a mixture composed of fuel and inert gas [11,12]. The following assumptions were included in their work: (K_1) at LFL, the

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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); (K_2) the heat release is the same for all limit mixtures at LFL; (K_3) the fuel gas would react completely when combustion takes place at LFL; (K_4) 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); (K_5) oxygen would react completely when combustion takes place at UFL; (K_6) the heat release is the same for all limit mixtures at UFL. Under aforementioned assumptions, they reached the following conclusion:

$$L = L_1 \quad (1)$$

$$\frac{xn_1}{1 - U/x} = \frac{xn_1}{1 - U_1} \quad (2)$$

where L and U are the LFL and UFL (in molar fraction) of a fuel gas diluted with inert gas, respectively; L_1 and U_1 , the LFL and UFL of the pure fuel gas; x , the molar fraction of the fuel gas in the mixture (fuel and inert gas, but no air); n_1 , 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 the experimental data very well, the following two empirical formulas in power-series form were suggested by them to increase the precision of the prediction:

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

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

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 both of them are empirical models, a considerable amount of experimental data is required to estimate aforementioned parameters for more reliable predictions. Thus, for flammable materials with little reported experimental results, how to estimate these parameters with a sufficient degree of precision for prediction is still a challenge.

As the inert gas does not take part in the combustion kinetics, it seems possible that we could explain the inert gas dilution effects on the flammability limits from the viewpoint of physical principles only. In this study, the carbon dioxide dilution effects on the flammability limits for pure hydrocarbons are explored. Theoretical models for predicting both UFL and LFL are developed on the basis of mass balance and energy balance. The experimental results reported in the literature are also used to examine the feasibility of the proposed model.

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, LFL and UFL could be also 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 carbon dioxide (no air); (3) total mixture—the mixture composed of the blended gas and air. The following notations are also adopted in formulation: (1) x ,

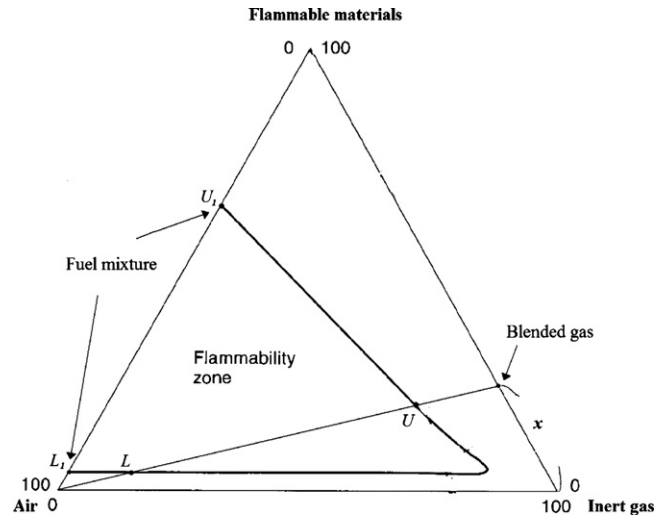
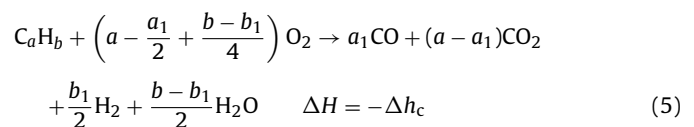


Fig. 1. Illustration of the terminologies and notations.

the molar fraction of hydrocarbon in the blended gas, that is, $x = \text{hydrocarbon}/(\text{hydrocarbon} + \text{inert carbon dioxide})$; (2) U , the molar fraction of hydrocarbon in the total mixture at UFL, that is, $U = \text{hydrocarbon}/(\text{hydrocarbon} + \text{inert carbon dioxide} + \text{air})$ 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, $U_1 = \text{hydrocarbon}/(\text{hydrocarbon} + \text{air})$ at UFL, and similarly, let L_1 be the molar fraction of hydrocarbon in the fuel mixture at LFL. To make a clear understanding of aforementioned notations, they are summarized in Fig. 1.

2.1. 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:



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:

$$k = \frac{1}{a - (a_1/2) + (b - b_1)/4}$$

$$q = \frac{a_1}{a - (a_1/2) + (b - b_1)/4}$$

$$r = \frac{a - a_1}{a - (a_1/2) + (b - b_1)/4}$$

$$s = \frac{(b - b_1)/2}{a - (a_1/2) + (b - b_1)/4}$$

$$t = \frac{b_1/2}{a - (a_1/2) + (b - b_1)/4}$$

The assumptions presumed true in this subsection include: (U_1) oxygen reacts completely at UFL; (U_2) the stoichiometric relation in Eq. (5) does not change by the presence of the inert gas; (U_3) the adiabatic temperature rises are the same for all limit mixtures at UFL. Detailed discussions on these assumptions are deferred until Section 4.

Now, let us consider the case of burning one mole of the total mixture at UFL. Based on assumptions U_1 and U_2 , the number of moles of all the reactants and products before and after the combustion reaction could be calculated. Before the combustion, there are U moles of hydrocarbon, U/x moles of blended gas, $(U/x - U)$ moles of inert carbon dioxide, and $(1 - U/x)$ moles of air. After the combustion, the oxygen should be of zero moles because assumption U_1 requires oxygen reacts completely at UFL. As assumption U_2 requires the stoichiometric relation of a combustion reaction does not change by the presence of the inert gas, the quantities of all burnt products could be calculated according to stoichiometric relation shown in Eq. (5). Table 1 summarizes the number of moles for all the materials involved in the combustion reaction before and after burning one mole of the total mixture at its UFL.

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

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

Moreover, the total heat capacity of the burnt products (including the unburned reactants) is then calculated as

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

where C_p is the total heat capacity of the burnt products; and C_{p_f} , $C_{p_{N_2}}$, $C_{p_{CO}}$, $C_{p_{CO_2}}$, $C_{p_{H_2O}}$ and $C_{p_{H_2}}$ are the molar heat capacities of hydrocarbon, nitrogen, carbon monoxide, carbon dioxide, water and hydrogen, respectively.

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

$$\begin{aligned} C_p = & U \left(C_{p_f} + 0.21 \frac{k}{x} C_{p_f} - \frac{0.79}{x} C_{p_{N_2}} - 0.21 \frac{q}{x} C_{p_{CO}} - 0.21 \frac{r}{x} C_{p_{CO_2}} \right. \\ & \left. + C_{p_{CO_2}} \left(\frac{1}{x} - 1\right) - 0.21 \frac{s}{x} C_{p_{H_2O}} - 0.21 \frac{t}{x} C_{p_{H_2}} \right) \\ & - (0.21k C_{p_f} - 0.79 C_{p_{N_2}} - 0.21q C_{p_{CO}} - 0.21r C_{p_{CO_2}} \\ & - 0.21s C_{p_{H_2O}} - 0.21t C_{p_{H_2}}) \end{aligned} \quad (8)$$

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
Carbon monoxide	0	$0.21q \left(1 - \frac{U}{x}\right)$
Carbon dioxide	$\frac{U}{x}(1-x)$	$\frac{U}{x}(1-x) + 0.21r \left(1 - \frac{U}{x}\right)$
Water	0	$0.21s \left(1 - \frac{U}{x}\right)$
Hydrogen	0	$0.21t \left(1 - \frac{U}{x}\right)$

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	$0.21r(1 - U_1)$
Water	0	$0.21s(1 - U_1)$
Hydrogen	0	$0.21t(1 - U_1)$

For brevity in notation, let us define the P_1 as follows:

$$\begin{aligned} P_1 = & 0.21k C_{p_f} - 0.79 C_{p_{N_2}} - 0.21q C_{p_{CO}} - 0.21r C_{p_{CO_2}} \\ & - 0.21s C_{p_{H_2O}} - 0.21t C_{p_{H_2}} \end{aligned} \quad (9)$$

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

$$C_p = U(C_{p_f} - C_{p_{CO_2}}) + \frac{U}{x}(P_1 + C_{p_{CO_2}}) - P_1 \quad (10)$$

Now, let us consider the case of burning one mole of fuel mixture at UFL. With assumptions U_1 and U_2 , the number of moles of each material involved in this combustion reaction before and after this burning process could be calculated. The results of calculation 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 total heat capacity of the burnt products for burning one mole of the fuel mixture is then calculated as follows:

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

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

$$C_{p_1} = U_1(C_{p_f} + P_1) - P_1 = U_1(C_{p_f} - C_{p_{CO_2}}) + U_1(P_1 + C_{p_{CO_2}}) - P_1 \quad (13)$$

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 U_3 .

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

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

$$\frac{0.21k(1 - (U/x))(-\Delta h_c)}{0.21k(1 - U_1)(-\Delta h_c)} = \frac{U(C_{p_f} - C_{p_{CO_2}}) + (U/x)(P_1 + C_{p_{CO_2}}) - P_1}{U_1(C_{p_f} + P_1) - P_1} \quad (15)$$

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

$$\frac{1}{U} = \frac{U_1 C_{p_f} + (1 - U_1)C_{p_{CO_2}}}{U_1 C_{p_f}} \frac{1}{x} + \frac{(1 - U_1)(C_{p_f} - C_{p_{CO_2}})}{U_1 C_{p_f}} \quad (16)$$

On rearranging Eq. (16) gives,

$$\frac{1}{U} = \frac{1}{U_1} + \frac{U_1 C_{p_f} + (1 - U_1) C_{p_{CO_2}}}{U_1 C_{p_f}} \left(\frac{1}{x} - 1 \right) \quad (17)$$

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

$$\phi_U \equiv \frac{U_1 C_{p_f} + (1 - U_1) C_{p_{CO_2}}}{U_1 C_{p_f}} \quad (18)$$

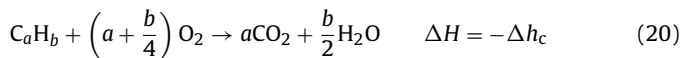
Thus, Eq. (17) can be expressed in a more compact form as follows:

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

Eq. (19) is the theoretical model for predicting the UFL of a hydrocarbon diluted with carbon dioxide. 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. We will examine whether this conclusion is supported by the existing experimental results or not in next section.

2.2. Lower flammability limit

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



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 through this subsection:

$$k \equiv a + \frac{b}{4}$$

$$r \equiv a$$

$$s \equiv \frac{b}{2}$$

Before beginning our deduction, the main assumptions employed in this subsection were listed here: (L_1) the hydrocarbon reacts completely at LFL; (L_2) the stoichiometric relation of Eq. (20) does not change by the presence of the inert gas; (L_3) the adiabatic temperature rises are the same for all limit mixtures at LFL. Discussions on these assumptions will be presented in Section 4.

First, let us consider the case of burning one mole of the total mixture at LFL. Based on assumptions L_1 and L_2 , 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.

Table 3
Mole balance for burning one mole of 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	$0.21 \left(1 - \frac{L}{x} \right)$	$0.21 \left(1 - \frac{L}{x} \right) - kL$
Carbon dioxide	$\frac{L}{x} (1 - x)$	$\frac{L}{x} (1 - x) + rL$
Water	0	sL

Table 4
Mole balance for burning one molar 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

As the hydrocarbon is the lean material of the combustion reaction and it reacts completely at LFL, the heat released for burning one mole of the total mixture at LFL could be calculated as follows:

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

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

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

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

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

For brevity in notation, let us define the following:

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

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

$$C_p = L(-k C_{p_{O_2}} - C_{p_{CO_2}} + r C_{p_{CO_2}} + s C_{p_{H_2O}}) + (-P_2 + C_{p_{CO_2}}) \frac{L}{x} + P_2 \quad (25)$$

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 total heat capacity of the burnt products for burning one mole of fuel mixture at its LFL is calculated as follows:

$$C_{p_1} = 0.79(1 - L_1) C_{p_{N_2}} + (0.21(1 - L_1) - kL_1) C_{p_{O_2}} + rL_1 C_{p_{CO_2}} + sL_1 C_{p_{H_2O}} \quad (27)$$

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

$$C_{p_1} = L_1(-0.79 C_{p_{N_2}} - 0.21 C_{p_{O_2}} - k C_{p_{O_2}} + r C_{p_{CO_2}} + s C_{p_{H_2O}}) + (0.79 C_{p_{N_2}} + 0.21 C_{p_{O_2}}) \quad (28)$$

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

$$C_{p_1} = L_1(-P_2 - k C_{p_{O_2}} + r C_{p_{CO_2}} + s C_{p_{H_2O}}) + P_2 \quad (29)$$

Now, let us compare the heat released on burning one mole of the total mixture and one mole of the fuel mixture at LFL. The

following relation is a direct conclusion from assumption L_3 .

$$\frac{\Delta h}{(\Delta h)_1} = \frac{C_p \Delta T}{C_{p1} \Delta T_1} = \frac{C_p}{C_{p1}} \quad (30)$$

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

$$\begin{aligned} & \frac{L(-\Delta h_c)}{L_1(-\Delta h_c)} \\ &= \frac{L(-kC_{pO_2} - C_{pCO_2} + rC_{pCO_2} + sC_{pH_2O}) + (-P_2 + C_{pCO_2})\frac{L}{x} + P_2}{L_1(-P_2 - kC_{pO_2} + rC_{pCO_2} + sC_{pH_2O}) + P_2} \end{aligned} \quad (31)$$

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

$$\frac{1}{L} = \frac{1}{L_1} + \frac{-C_{pCO_2} + 0.79C_{pN_2} + 0.21C_{pO_2}}{0.79C_{pN_2} + 0.21C_{pO_2}} \left(\frac{1}{x} - 1 \right) \quad (32)$$

Now, let us define ϕ_L as follows:

$$\phi_L \equiv \frac{-C_{pCO_2} + 0.79C_{pN_2} + 0.21C_{pO_2}}{0.79C_{pN_2} + 0.21C_{pO_2}} = \frac{-C_{pCO_2} + P_2}{P_2} \quad (33)$$

Then, Eq. (33) could be expressed in 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 model for predicting the LFL of a hydrocarbon diluted with carbon dioxide. 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 this conclusion through existing experimental results in the next section. Before ending this section, it is worth noting here that although the hydrocarbon is the lean material at LFL and 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 conditions used for measurement. To enhance the consistency and reliability of experimental data, the experimental data reported in a recent work by Kondo et al. are adopted in present study [12]. The cases adopted to examine the proposed model include methane, propane, ethylene, and propylene.

As earlier mentioned, it could be concluded from Eq. (19) that if we plot $((1/U) - (1/U_1))$ against $((1/x) - 1)$, we will have a straight line passing through the origin. To examine this linearity, linear regression was performed on experimental results with a linear model passing through the origin. Figs. 2–5 show the regression results for the cases of methane, propane, ethylene, and propylene, respectively. It could be found from these figures that the experimental results fit a straight line passing through the origin very well for every case. Table 5 lists the coefficients of determination

Table 5
Regression results of four hydrocarbons at UFL

Compound name	R^2	Slope (experimental)
Methane	0.9940	2.2836
Propane	0.9923	2.1741
Ethylene	0.9796	2.1970
Propylene	0.9918	2.1300

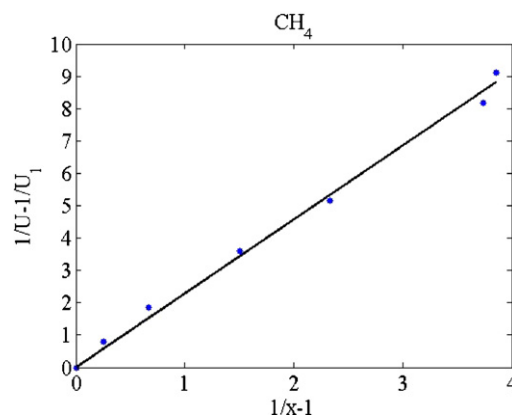


Fig. 2. Regression line of methane at UFL: round point—experimental data; solid line—regression line.

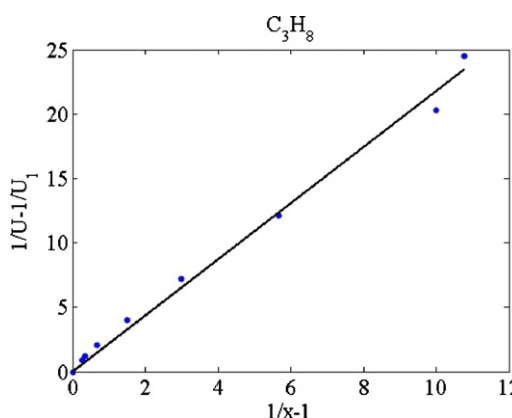


Fig. 3. Regression line of propane at UFL: round point—experimental data; solid line—regression line.

(R^2) and the slopes of the regression lines for these four cases. As shown in Table 5, the R^2 -values for these four hydrocarbons are all larger than 0.979. With these facts, it might be reasonable to conclude that the proposed Eq. (19) effectively explains the change in UFL when carbon dioxide is added to flammable hydrocarbons.

It is obvious from Eq. (34) that if $((1/L) - (1/L_1))$ is plotted against $((1/x) - 1)$, we could get a straight line passing through the origin. To examine whether this linearity was also supported by experimental results or not, we once again perform linear regression on the existing experimental results with a linear model passing

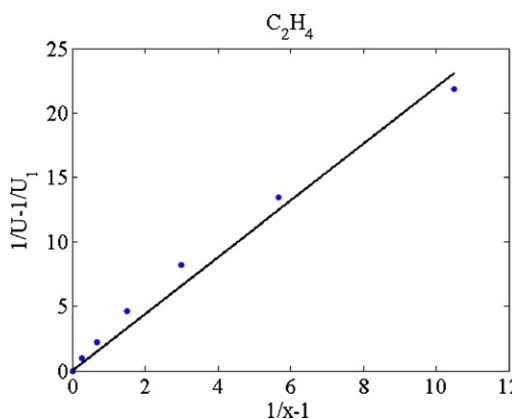


Fig. 4. Regression line of ethylene at UFL: round point—experimental data; solid line—regression line.

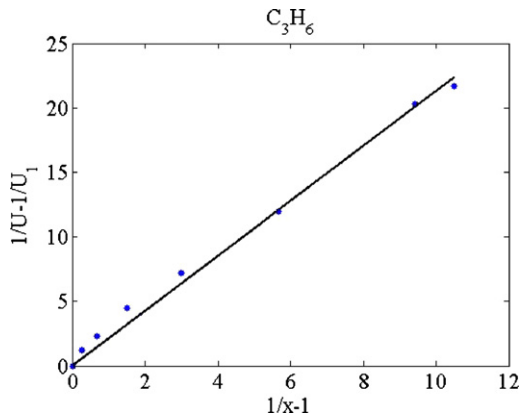


Fig. 5. Regression line of propylene at UFL: round point—experimental data; solid line—regression line.

through the origin. Figs. 6–9 show the regression results for the cases of methane, propane, ethylene, and propylene, respectively. Table 6 lists the coefficients of determination (R^2) and the slopes of the regression lines for these four hydrocarbons. It should be noted here that the fuel inertization point (FIP), which is defined in Kondo et al.'s work, is not considered in the regression for LFL in this study. Discussions about this issue will be deferred until Section 4. It could be found from these figures that if the FIP is excluded from the experimental data, the regression line fits the experimental data very well in these four cases. Moreover, as shown in Table 6,

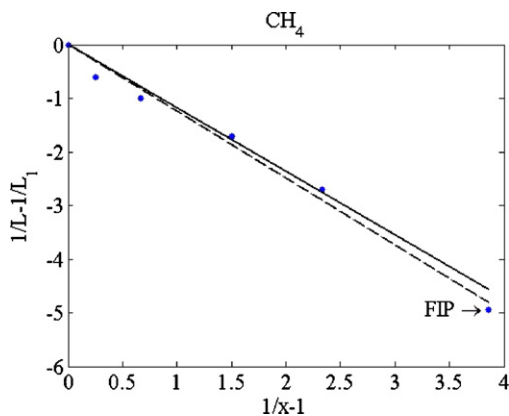


Fig. 6. Regression line of methane at LFL: round point—experimental data; solid line—regression line excluding FIP; dashed line—regression line including FIP.

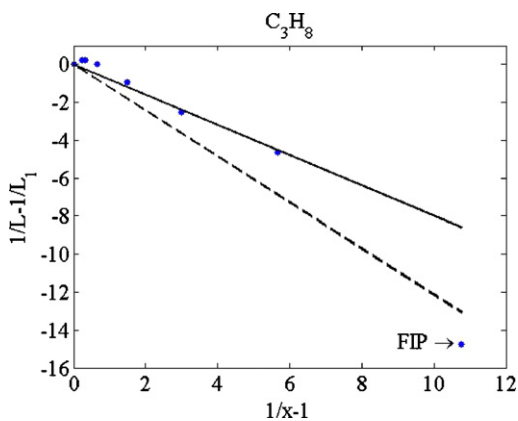


Fig. 7. Regression line of propane at LFL: round point—experimental data; solid line—regression line excluding FIP; dashed line—regression line including FIP.

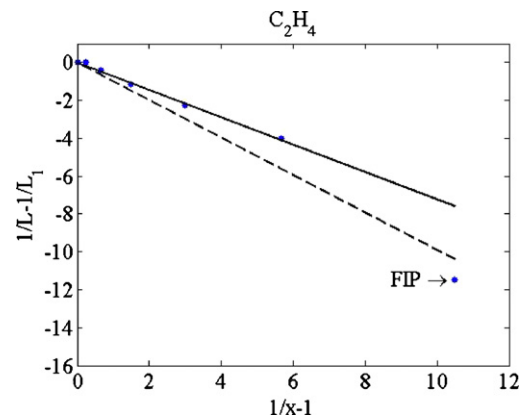


Fig. 8. Regression line of ethylene at LFL: round point—experimental data; solid line—regression line excluding FIP; dashed line—regression line including FIP.

Table 6

Regression results of four hydrocarbons at LFL^a

Compound name	R^2	Slope (experimental)
Methane	0.9673	-1.1837
Propane	0.9596	-0.7970
Ethylene	0.9955	-0.7200
Propylene	0.9888	-0.9490

^a FIP data is not included in the regression.

the R^2 -values for these four cases are all larger than 0.959. Thus, it is reasonable to conclude that the proposed Eq. (34) can effectively explain the change in LFL when carbon dioxide is added to flammable hydrocarbons.

4. Discussions

It is well known that the flammable material is the lean reactant when combustion occurs at LFL, while oxygen is the lean material when combustion occurs at UFL. Assumptions L_1 and U_1 merely state that the lean component will be consumed completely in a burning process. These two assumptions are widely accepted in the literature [1–3,9–12] and they are the same as assumptions K_3 and K_5 in the work by Kondo et al.

The assumptions L_2 and U_2 state 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

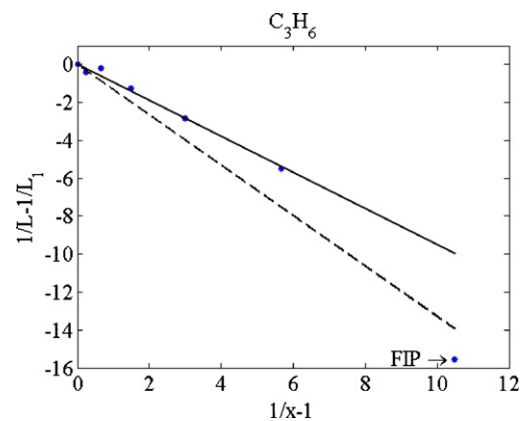


Fig. 9. Regression line of propylene at LFL: round point—experimental data; solid line—regression line excluding FIP; dashed line—regression line including FIP.

Table 7
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 ₃ H ₈	31.4246	32.8829	34.2243	35.4488	36.5564	37.5471	38.4210
C ₂ H ₄	17.3583	18.0909	18.7652	19.3814	19.9395	20.4393	20.8810
C ₃ H 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 ₂ O	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

^a Unit: cal/gmole K.

for 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 [9,10]; and they are also equivalent to assumptions K_1 and K_4 in the work by Kondo et al. [11,12]. It should be emphasized 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 the inert gas. The change in the stoichiometry of a combustion reaction occurring at the flammability limits could be easily understood from the fact that if an inert gas was added to the hydrocarbon/oxidant mixture, the range of concentrations between the lower flammability limit and upper flammability limit 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 reaction occurring at LFL; therefore, the stoichiometry of a combustion reaction must change by adding inert gas as these two limits will finally converge to the inertization point.

Before embarking a discussion on the possible effects for these deviations from assumptions L_2 and U_2 , let us first give a brief discussion on assumption L_3 and U_3 . As mentioned earlier, it is widely accepted 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 the temperature threshold of the combustion reaction; and this temperature threshold was usually expressed in the form of an adiabatic temperature rise. The energy released at the flammability limit is deemed to be just sufficient to make the unburned materials reach this temperature threshold [3,9,10]. Because the inert gas is not involved in the kinetics of the combustion reaction, it seems reasonable to assume that this temperature threshold (i.e., the adiabatic temperature rise) does not change by adding the inert gas. Furthermore, because the adiabatic flame temperatures at the flammability limits for most hydrocarbons are about equal, assumptions L_3 and U_3 are also adopted in Mashuga and Crowl's work to theoretically derive the famous Le Chatelier's mixing rule for the flammability limits [3]. All aforementioned viewpoints give us the reasons why assumptions L_3 and U_3 are adopted in this study. It should be also noted that these two assumptions are those that differentiate this study from the work by Kondo et al. In present study, the adiabatic temperature rises were assumed to be the same for all limit mixtures, but the heat released was assumed to be the same for all limit mixtures in their work [12].

The influence of the fact that the real burning conditions of a combustion reaction occurring at UFL deviate from our assumptions in certain degrees could be understood from the following discussions. It is obvious that if assumptions U_1 – U_3 well describe the burning conditions of a combustion reaction occurring at UFL, the value of ϕ_U calculated by Eq. (18) should match the one deter-

Table 8
Theoretical and experimental values of ϕ_U for different materials

Compound name	ϕ_U (Exp)	ϕ_U (Eq. (18)) ^a
Methane	2.2836	5.1672
Propane	2.1741	3.9197
Ethylene	2.1970	2.2934
Propylene	2.1300	4.1707

^a The mean molar heat capacity is calculated between 298 and 1400 K.

mined from the experimental data. To theoretically calculate ϕ_U , the information of molar heat capacities of all materials involved in the combustion reaction are indispensable. Table 7 summarizes the mean (from 298 K to the temperature shown in the table) molar heat capacities of all the materials involved in the burning process. This table was constructed based on the formula of the temperature effect on specific heat in a textbook by Smith and Van Ness [13]. In addition to the mean molar heat capacities, the adiabatic flame temperature for calculation is also indispensable to calculate ϕ_U . However, such a choice for a hydrocarbon is not unified in the literature. Some researchers agree that this temperature is around 1550 K [10] or 1200 K [14], while others believe that this temperature is in the range of 1000–1500 K [15]. In a recent work, the experiment data of methane and ethylene were found to be fitted LFL well at a temperature of approximately 1400 K. Detailed discussions about the issue for choosing the adiabatic flame temperature may be found in the work by Vidal et al. [9] and the references therein. The adiabatic flame temperature was chosen to be of 1400 K in present study.

The value of ϕ_U calculated from Eq. (18) and the one obtained by regression are listed and compared in Table 8 for four hydrocarbon compounds. As we have mentioned that the real burning conditions of a combustion reaction occurring at UFL might deviate from assumption U_2 , these two values do not match each other very well. However, they remain in the same order of magnitude for all cases and the difference between them is less than 5% for the case of ethylene.

If the burning conditions of a combustion reaction occurring at LFL are well described by assumptions L_1 – L_3 , the value of ϕ_L calculated by Eq. (33) should match the one obtained from the regression. To calculate ϕ_L , the adiabatic flame temperature for calculating is chosen to be of 1400 K here. Table 9 lists and compares the value of ϕ_L calculated from Eq. (33) and the one from regression on experimental data for four hydrocarbon compounds. As we have

Table 9
Theoretical and experimental values of ϕ_L for different materials

Compound name	ϕ_L (excluding FIP)	ϕ_L (including FIP)	ϕ_L (Eq. (33)) ^a
Methane	–1.1837	–1.2489	–0.5526
Propane	–0.7970	–1.2144	–0.5526
Ethylene	–0.7200	–0.9885	–0.5526
Propylene	–0.9490	–1.3284	–0.5526

Table 10
Regression results for four non-hydrocarbon materials at UFL

Compound Name	R^2	Slope (experimental)
Dimethyl ether	0.9565	2.3840
Methyl formate	0.9973	1.8847
1,1-Difluoroethane	0.9916	2.0982
Ammonia	0.9865	4.1833

mentioned, the burning conditions occurring at LFL might deviate from assumption L_2 , so these two values do not match each other well. However, as shown in Table 9, they are in the same order of magnitude in all cases and the difference between these two values is about 25% for ethylene.

The FIP is defined as the point on the envelope of the flammable region in the triangular system of fuel–air–diluent that defines the maximum ratio of fuel to diluent concentration that never produces a flammable mixture whatever the amount of air added or removed from the mixture [12]. According to this definition, it is obvious that the burning conditions of FIP significantly violate both assumptions L_1 and L_2 . This explains why the FIP significantly deviates from the regression line composed of the other experimental data in Figs. 6–9. The regression lines including the FIP are also shown in the form of dashed lines for comparison in Figs. 6–9. It can be seen that these dashed lines obviously deviate from the regression lines excluding FIP (solid lines). The slopes of the regression lines including the FIP are also listed in Table 9 for comparison and it is found that the slopes of the dashed lines deviate from the theoretical values much more than those of the solid lines. Based on the aforementioned facts, the FIP is not recommended to use in determining ϕ_L .

As it has been discussed that the real burning conditions of a combustion reaction occurring at the flammability limits somewhat deviate from our assumptions, both ϕ_U and ϕ_L had better be determined from experimental data to increase the accuracy of prediction. As the proposed models are of linear ones, it requires the least number of data to determine these two values. It should be also noted here that the proposed prediction model for LFL (i.e., Eq. (34)), in fact, is the same as Eq. (3) which is the empirical model for LFL conjectured by Kondo et al. [11,12]. Thus, this work also gives a theoretical explanation for their empirical model on LFL.

It is obvious that there are two limitations in present work: (1) the flammable materials are limited to hydrocarbons and (2) the inert gas is limited to carbon dioxide. It seems interesting to investigate whether there is a possibility or not to extend aforementioned conclusions to the case of non-hydrocarbon flammable compounds or the case of inert gas other than carbon dioxide. This question could be possibly understood from the fact that all chemical kinetics of a combustion reaction is listed in the assumptions in present work and the derivation procedure considers only the physical principles of a combustion reaction (i.e., mass balance and energy balance). Thus, it seems reasonable to conjecture that if a combustion system does not heavily deviate from the listed assumptions, the conclusions in this work could apply to that system. To preliminarily examine this conjecture, Table 10 lists the coefficients of determination and the slopes of the regression lines for the cases of four non-hydrocarbons diluted with nitrogen at their UFL. All the results in Table 10 are calculated from the experimental data reported by Kondo et al. [11]. As shown in this table, the values of R^2 , in all cases, are larger than 0.956. Obviously, this result positively supports our conjecture—the conclusions in present work could be extended to non-hydrocarbon flammable compounds and to inert gas other than carbon dioxide. However, a theoretical derivation is still required to examine this conjecture in a future work.

An important point that should be also noted here is that Eq. (18) shows that the value ϕ_U depends on the molar heat capacity of the flammable hydrocarbon, but Eq. (33) shows that the value of ϕ_L is independent of the molar heat capacity of the flammable hydrocarbon involved in the combustion reaction. Possibly, because the degrees by which the burning conditions deviate from our assumptions are different for different kinds of hydrocarbons, the experimental data for hydrocarbons diluted with carbon dioxide do not strongly support this point. However, it is widely accepted that the concentration of inert gas has little effect on LFL for almost all hydrocarbons if nitrogen is chosen as the inert gas, but the UFL changes differently for different kinds of hydrocarbons [3]. Thus, aforementioned theoretical conclusions give a possibility to explain this phenomenon in a future work.

5. Conclusions

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

- (U_1), oxygen reacts completely at UFL.
- (U_2), the stoichiometric relation of the combustion reaction occurring at UFL does not change by the presence of the inert gas.
- (U_3), the adiabatic temperature rises are the same for all limit mixtures at UFL.
- (L_1), the hydrocarbon reacts completely at LFL.
- (L_2), the stoichiometric relation of a combustion reaction occurring at LFL does not change by the presence of the inert gas.
- (L_3), the adiabatic temperature rises are the same for all limit mixtures at LFL.

With aforementioned assumptions, it was derived analytically that there are linear relations between the reciprocals of the UFL/LFL and the reciprocal of the molar fraction of hydrocarbon in the hydrocarbon/carbon dioxide mixture. Experimental data reported in the literature, which include the cases of methane, propane, ethylene, and propylene, were used to examine these theoretical linear relations. The coefficients of determination of the regression lines for these four cases are all larger than 0.959 for both UFL and LFL.

The unique parameter in the proposed model is the slope of the theoretical line. Because the burning conditions of a combustion reaction occurring at flammability limits might somewhat deviate from our assumptions, the slope obtained from the theoretical calculation and the slope obtained from regression on experimental data do not match each other very well. Thus, it is recommended that this parameter should be determined from experimental data to increase the precision of prediction.

As all of the derivation in present study depends on the physical principles only, it is conjectured that a combustion system contains non-hydrocarbon flammable materials or diluted by inert gas other than carbon dioxide still follows the proposed linearity if it does not heavily deviate from the listed assumptions. A preliminary study with four non-hydrocarbon flammable materials diluted by inert nitrogen has been explored to examine this linearity; and the results showed that the linearity is observed for all these four compounds.

Acknowledgments

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