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Effects of inert steam on upper explosion limit for oxygenated hydrocarbons

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Abstract Explosion limits are crucial information for people who handle/operate flammable vapors or gases. It was reported in our previous studies that there is a theoretical linear relation between the reciprocal of the explosion limits and the reciprocal of the molar fraction of hydrocarbons diluted with inert carbon dioxide or nitrogen. In this work, oxygenated hydrocarbons were inertized by inert steam, and the relation of the upper explosion limit and the extent of the inertization was explored. With the assumption that the adiabatic flame temperatures are the same for all limit mixtures, it was found that the aforementioned linear relation still holds in case the inert gas is of steam and the flammable material is of oxygenated hydrocarbons. Experimental work was carried out in a 20-L-Apparatus at 101 kPa and 423 K to measure the upper explosion limit of methyl alcohol, acetone, and methyl formate diluted with steam, respectively. It was found that experimental results fit the theoretical model very well.

Keywords Adiabatic flame temperatures · Explosion limits · Flammable vapors or gases · Inert steam · Oxygenated hydrocarbons

Abbreviations

AFT	Adiabatic flame temperatures (K)
CAFT	Calculated adiabatic flame temperatures (K)
LEL	Lower explosion limit (mol.%)
UEL	Upper explosion limit (mol.%)

List of symbols

Δh_c	Heat of reaction for burning 1 mol of oxygenated hydrocarbon (cal mol^{-1})
Cp_{CO}	Mean molar heat capacities of the carbon monoxide (J mol^{-1} K^{-1})
Cp_{CO_2}	Mean molar heat capacities of the carbon dioxide (J mol^{-1} K^{-1})
Cp_{H_2O}	Mean molar heat capacities of the water (J mol^{-1} K^{-1})
Cp_{H_2}	Mean molar heat capacities of the hydrogen (J mol^{-1} K^{-1})
Cp_{N_2}	Mean molar heat capacities of the nitrogen (J mol^{-1} K^{-1})
Cp_f	Mean molar heat capacities of the oxygenated hydrocarbons (J mol^{-1} K^{-1})
x	Mole fraction of the inertized mixture in an air-free basis
U	Upper flammability limit for inertized mixture (mol.%)
U_1	Upper flammability limit for pure flammable gas (mol.%)

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Introduction

Flammability limits [lower flammability limit (LFL) and upper flammability limit (UFL)], which are also referred to as explosion limits [lower explosion limit (LEL) and upper explosion limit (UEL)] [1], are one of the most important characteristics of chemical substances for safety considerations in preparation, storage, processing, and handling. For this reason, they constitute a crucial issue in research on processing and storing organic matter safely. In order to reduce the explosion hazards, inerting is the most common practice in the 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 combustion explosion [2]. The inert gases frequently seen in the process industries are nitrogen, carbon dioxide, and steam [3, 4].

Many methods have been proposed to predict the flammability limits of pure flammable chemical, which include structural group contribution [5], thumb relation [2, 6], and calculated adiabatic flame temperatures (CAFT) [7]. However, for mixtures of flammable gases, the Le Chatelier's equation is regularly used to estimate mixture's flammability limits.

Recently, Kondo et al. attempted to modify the Le Chatelier's equation so that it could be extended to the case of a mixture of flammable gases and inert gases [8–10]. As inert gas does not take part in reaction mechanism, some methods based on the fact that CAFT is the same for flammable gas and the inertized mixture are also reported in the literature [11–13]. However, these studies focus on the inert gases of nitrogen and carbon dioxide only. In this study, we explored the dilution effect of inert steam on UEL for oxygenated hydrocarbons.

Theory

Usually, the explosion limit of a combustible material is expressed in volume percentage (vol.%) in the literature; however, as the oxygenated hydrocarbons gas could be taken as an ideal gas at atmospheric pressure, the explosion limit could also be explained as the molar fraction, which is the expression adopted in this study. In order to avoid misleading the meaning in formulation, three terminologies are defined here: (1) fuel mixture—the mixture composed of oxygenated hydrocarbons and air (no inert gas); (2) blended gas—the mixture composed of oxygenated hydrocarbons and inert steam (no air); and (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 oxygenated hydrocarbons in the blended gas, i.e., x = oxygenated hydrocarbons/(oxygenated hydrocarbons + inert steam); (2) U, the molar fraction of oxygenated hydrocarbons in the total mixture at UEL, i.e., U = oxygenated hydrocarbons/(oxygenated hydrocarbons + inert steam + air) at UEL; and (3) U_1, the molar fraction of oxygenated hydrocarbons in the fuel mixture at UEL, i.e., U_1 = oxygenated hydrocarbons/(oxygenated hydrocarbons + air) at UEL.

As a flammable material will not undergo complete combustion at UEL, we assume that a_1 moles of CO and $b_1/2$ moles of H_2 are formed by burning 1 mol of the oxygenated hydrocarbon compound ($C_aH_bO_c$) at its UEL. Thus, the corresponding stoichiometry of such a combustion reaction could be expressed as follows:

$$\begin{aligned} &C_aH_bO_c + \left(a - \frac{a_1 + c}{2} + \frac{b - b_1}{4}\right) O_2 \rightarrow a_1\,CO \\ &+ (a - a_1)\,CO_2 + \frac{b_1}{2}H_2 + \frac{b - b_1}{2}\,H_2O \\ &\Delta H = -\Delta h_c \end{aligned} \tag{1}$$

where $-\Delta h_c$ is the heat of reaction for burning 1 mol of oxygenated hydrocarbon according to the stoichiometry shown in Eq. 1. For brevity in notation, the following notations are defined in this subsection:

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

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

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

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

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

The assumptions presumed true in this subsection include: (U_1) oxygen reacts completely at UEL; (U_2) the stoichiometric relation in Eq. 1 does not change by the presence of the inert gas; and (U_3) the adiabatic temperature rises are the same for all limit mixtures at UEL.

Now, let us consider the case of burning 1 mol of the total mixture at UEL. 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 oxygenated hydrocarbons, U/x moles of blended gas, $(U/x - U)$ moles of inert steam, and $(1 - U/x)$ moles of air. After the combustion, the oxygen should be of 0 mol because assumption U_1 requires oxygen reacts completely at UEL. 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

Table 1 Mole balance for burning 1 mol of total mixture at UEL

Compound name	No. of moles before burning	No. of moles after burning
Oxygenated 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	0	$0.21r\left(1 - \frac{U}{x}\right)$
Water	$\frac{U}{x}(1 - x)$	$0.21s\left(1 - \frac{U}{x}\right) + \frac{U}{x}(1 - x)$
Hydrogen	0	$0.21t\left(1 - \frac{U}{x}\right)$

calculated according to stoichiometric relation shown in Eq. 1. Table 1 summarizes the number of moles for all the materials involved in the combustion reaction before and after burning 1 mol of the total mixture at its UEL.

As oxygen is assumed to be consumed completely, the heat released on burning 1 mol of the total mixture at UEL can be calculated as follows:

$$\Delta h = 0.21k\left(1 - \frac{U}{x}\right)(-\Delta h_c) \tag{2}$$

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

$$\begin{aligned} Cp = {} & \left(U - 0.21k\left(1 - \frac{U}{x}\right)\right)Cp_f + 0.79\left(1 - \frac{U}{x}\right)Cp_{N_2} \\ & + 0.21q\left(1 - \frac{U}{x}\right)Cp_{CO} + 0.21r\left(1 - \frac{U}{x}\right)Cp_{CO_2} \\ & + \left[0.21s\left(1 - \frac{U}{x}\right) + \frac{U}{x}(1 - x)\right]Cp_{H_2O} \\ & + 0.21t\left(1 - \frac{U}{x}\right)Cp_{H_2} \end{aligned} \tag{3}$$

where Cp is the total heat capacity of the burnt products, Cp_f, Cp_{N_2}, Cp_{CO}, Cp_{CO_2}, Cp_{H_2O}, and Cp_{H_2} are the molar heat capacities of oxygenated hydrocarbons, nitrogen, carbon monoxide, carbon dioxide, water, and hydrogen, respectively.

Combining all terms having U in Eq. 3 together gives the following equation:

$$\begin{aligned} Cp = {} & U\left(Cp_f + 0.21\frac{k}{x}Cp_f - \frac{0.79}{x}Cp_{N_2} - 0.21\frac{q}{x}Cp_{CO}\right. \\ & - 0.21\frac{r}{x}Cp_{CO_2} + Cp_{H_2O}\left(\frac{1}{x} - 1\right) \\ & \left. - 0.21\frac{s}{x}Cp_{H_2O} - 0.21\frac{t}{x}Cp_{H_2}\right) \\ & - \left(0.21kCp_f - 0.79Cp_{N_2} - 0.21qCp_{CO}\right. \\ & \left. - 0.21rCp_{CO_2} - 0.21sCp_{H_2O} - 0.21tCp_{H_2}\right) \end{aligned} \tag{4}$$

Table 2 Mole balance for burning 1 mol of fuel mixture at UEL

Compound name	No. of moles before burning	No. of moles after burning
Oxygenated 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:

$$\begin{aligned} P_1 \equiv {} & 0.21kCp_f - 0.79Cp_{N_2} - 0.21qCp_{CO} \\ & - 0.21rCp_{CO_2} - 0.21sCp_{H_2O} - 0.21tCp_{H_2} \end{aligned} \tag{5}$$

Substituting Eq. 5 into Eq. 4 and rearranging gives

$$Cp = U\left(Cp_f - Cp_{H_2O}\right) + \frac{U}{x}\left(P_1 + Cp_{H_2O}\right) - P_1 \tag{6}$$

Now, let us consider the case of burning 1 mol of fuel mixture at UEL. 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 1 mol of fuel mixture at UEL is

$$(\Delta h)_1 = 0.21k(1 - U_1)(-\Delta h_c) \tag{7}$$

The total heat capacity of the burnt products for burning 1 mol of the fuel mixture is then calculated as follows:

$$\begin{aligned} Cp_1 = {} & (U_1 - 0.21k(1 - U_1))Cp_f + (0.79(1 - U_1))Cp_{N_2} \\ & + (0.21q(1 - U_1))Cp_{CO} + 0.21r(1 - U_1)Cp_{CO_2} \\ & + 0.21s(1 - U_1)Cp_{H_2O} + 0.21t(1 - U_1)Cp_{H_2} \end{aligned} \tag{8}$$

Combining all terms having U_1 in Eq. 8 together and substituting Eq. 5 into it will give

$$\begin{aligned} Cp_1 & = U_1\left(Cp_f + P_1\right) - P_1 \\ & = U_1\left(Cp_f - Cp_{H_2O}\right) + U_1\left(Cp_f + Cp_{H_2O}\right) - P_1 \end{aligned} \tag{9}$$

Now, let us compare the heat released on burning 1 mol of the total mixture and 1 mol of the fuel mixture at the corresponding UEL. The following result is a direct conclusion from assumption U_3.

$$\frac{\Delta h}{(\Delta h)_1} = \frac{Cp\Delta T}{Cp_1\Delta T_1} = \frac{Cp}{Cp_1} \tag{10}$$

where ΔT and ΔT_1 are the adiabatic temperature rises for burning the total mixture and fuel mixture at the corresponding UEL, respectively. Substituting Eqs. 2, 6, 7, and 9 into the corresponding terms in Eq. 10 gives

$$\frac{0.21k(1-U/x)(-\Delta h_c)}{0.21k(1-U_1)(-\Delta h_c)} = \frac{U\left(Cp_f - Cp_{\mathrm{H_2O}}\right) + (U/x)(P_1 + Cp_{\mathrm{H_2O}}) - P_1}{U_1\left(Cp_f + P_1\right) - P_1} \qquad (11)$$

Dropping $-\Delta h_c$ from Eq. 11 and combining all terms having U together will reach the following relation:

$$\frac{1}{U} = \frac{U_1 Cp_f + (1-U_1)Cp_{\mathrm{H_2O}}}{U_1 Cp_f}\frac{1}{x} + \frac{(1-U_1)\left(Cp_f - Cp_{\mathrm{H_2O}}\right)}{U_1 Cp_f} \qquad (12)$$

On rearranging Eq. 12 gives,

$$\frac{1}{U} = \frac{1}{U_1} + \frac{U_1 Cp_f + (1-U_1)Cp_{\mathrm{H_2O}}}{U_1 Cp_f}\left(\frac{1}{x} - 1\right) \qquad (13)$$

It can be easily understood from Eq. 13 that the coefficient of the $((1/x) - 1)$ term is a constant for a given oxygenated hydrocarbons compound. Now, let us define ϕ_U as follows:

$$\phi_U \equiv \frac{U_1 Cp_f + (1-U_1)Cp_{\mathrm{H_2O}}}{U_1 Cp_f} \qquad (14)$$

Thus, Eq. 13 can be expressed in a more compact form as follows:

$$\frac{1}{U} = \frac{1}{U_1} + \phi_U\left(\frac{1}{x} - 1\right) \qquad (15)$$

Equation 15 is the theoretical model for predicting the UEL of a oxygenated hydrocarbons diluted with steam. It states that if $((1/U) - (1/U_1))$ was plotted against $((1/x) - 1)$, then we will obtain a straight line passing through the origin. We have examined whether this conclusion is supported by the existing "Experimental method" section or in "Results" and "Discussion" sections.

Experimental method

In this study, the experimental materials were methyl alcohol, acetone, and methyl formate. These substances were chosen because they are flammable material of oxygenated hydrocarbons and they are commonly used solvents. According to their functional structure, they could be divided into three categories: alcohol (methyl alcohol), ketone (acetone), and ester (methyl formate).

Materials

Water was purified using a Milli-Q plus system. Methyl alcohol (99.9%) and acetone (99.8%) were purchased from Mallinckrodt, USA, and were of ACS specifications. Methyl formate (97.0%) was from Alfa Aesar.

Initial conditions

The initial pressure and temperature were set at 101 kPa (1 atm) and 423 K, respectively. The initial temperature of 423 K, instead of the room temperature, was chosen to ensure a good mixing state in the gas phase, as this temperature is higher than the normal boiling point for all test materials.

Methods, procedures, and parameters

It is well known that explosion limits (flammability limits) depend on the experimental apparatus and conditions used for measurement. In this study, we adopted the 20-L-Apparatus (or so-called 20-L spherical explosion vessel) to measure the explosion limits. It was manufactured by Adolf Kühner AG (Switzerland) and appearance was shown in Fig. 1. The test chamber is a stainless steel hollow sphere with a personal computer interface. The top of the cover contains holes for the lead wires to the ignition system. The opening provides for ignition by a condenser discharging with an auxiliary spark gap, which is controlled by a KSEP 320 unit of the 20-L-Apparatus. The KSEP 332 unit uses piezoelectric pressure sensors to measure the pressure as function of time. A comprehensive software package KSEP 6.0 was available, which allowed safe operation of the test equipment and an optimum evaluation of the explosion test results [14].

In this study, the experimental procedure is complied with the ASTM E 681-04 [1], E 918-83 [15], and E 2079 [16]. In our study, the procedures have divided into three stages. First, according to ASTM E 681-04, the system is evacuated and flushed with air to ensure removal of

Fig. 1 Twenty liter spherical explosion vessel (20-L-Apparatus) for this study

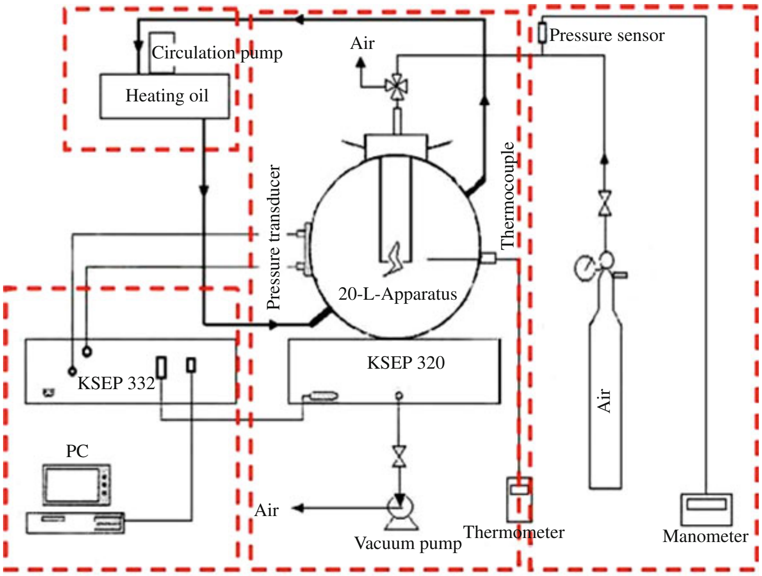

Fig. 2 Schematic diagram of the experimental set-up and its control system [15]

residual volatile materials that may be present as a result of cleaning or prior tests. As many three flush cycles may be required to ensure complete removal combustion products between tests. In second stage, the fuel is added before inert, and then air is loading into vessel until reach initial condition (101 kPa) in sequence. In final stage, we must determine whether or not an explosion occurs at this specific composition. According to E 918-83, a pressure rise greater than or equal to 7% of the initial test pressure is taken to be explosive. In addition, providing ignition energy of about 10 J by E 2079 criterion was recommend. Figure 2 displays its schematic diagram of the experimental set-up and the corresponding control system [17].

Results

The experimental results of UEL at different degrees of inerting are listed in Tables 3, 4, and 5, which show the results of methyl alcohol/steam, acetone/steam, and methyl formate/steam system, respectively.

In order to examine the proposed theory, we plotted $((1/U) - (1/U_1))$ versus $((1/x) - 1)$ for aforementioned systems, and the results are shown in Figs. 3, 4, and 5. As these figures show, experimental data fit a line passing through the origin very well. In order to quantitatively examine this linearity, linear regression was performed on

Table 3 Experimental UEL of inertized mixture of methyl alcohol and steam

Mole fraction (x)	UEL/mol.%
0.130	6.7638
0.150	8.1512
0.170	8.6715
0.200	10.0590
0.250	13.5276
0.500	21.6788
0.750	31.0441
1.000	41.1030

Table 4 Experimental UEL of inertized mixture of acetone and steam

Mole fraction (x)	UEL/mol.%
0.080	3.4686
0.090	3.9889
0.100	4.1623
0.250	7.6309
0.500	10.5793
0.750	12.8339
1.000	13.8744

Table 5 Experimental UEL of inertized mixture of methyl formate and steam

Mole fraction (x)	UEL/mol.%
0.125	6.7638
0.150	7.8044
0.250	11.2730
0.500	17.8633
0.750	23.0663
0.900	25.8411
1.000	28.4426

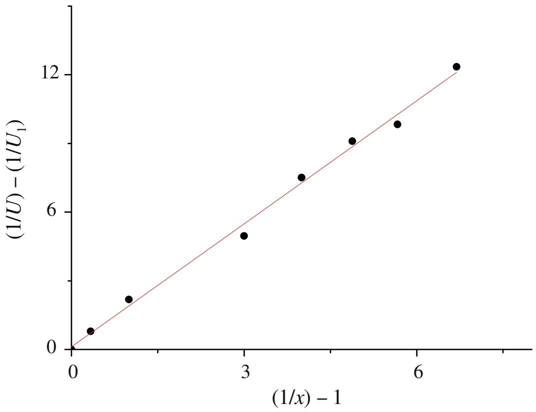

Fig. 3 Regression line of methyl alcohol at UEL: *filled circle* experimental data; *solid line* regression line

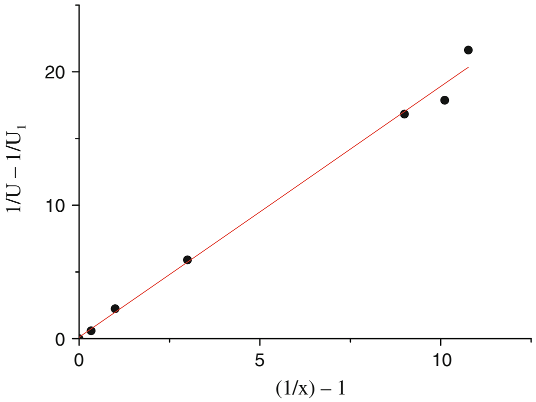

Fig. 4 Regression line of acetone at UEL: *filled circle* experimental data; *solid line* regression line

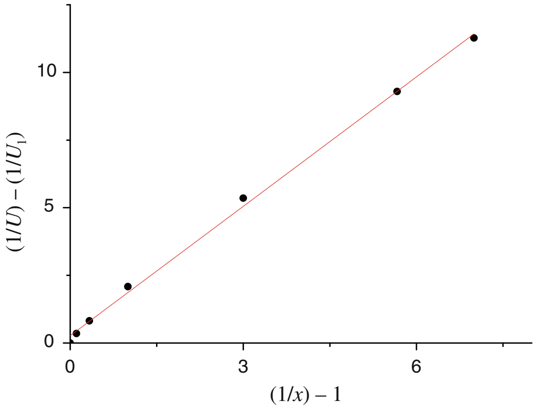

Fig. 5 Regression line of methyl formate at UEL: *filled circle* experimental data; *solid line* regression line

experimental data with a linear model passing through the origin. Table 6 lists the coefficients of determination (R^2) and the slopes of the regression lines for these three cases. From this table, we could observe that all the R^2 values for these systems are >0.9920. Thus, it might be reasonable to conclude that the proposed Eq. 15 effectively explains the change in UEL when steam is added to flammable oxygenated hydrocarbons.

Table 6 Regression results of methyl alcohol, acetone, and methyl formate at UEL

Chemical	R^2	Slope, Exp.	Standard error
Methyl alcohol	0.9942	1.7923	0.0520
Acetone	0.9920	1.8801	0.0689
Methyl formate	0.9976	1.6520	0.0307

Discussion

In fact, the slopes of regression lines listed in Table 6 should be equal to the ϕ_U calculated by Eq. 14 if the proposed method is accurate. In order to examine this point, the ϕ_U values for these three cases are theoretically calculated. Table 7 summarizes the mean (from 423 K to the temperature shown in the table) molar heat capacities of all the materials involved in the burning process for the explored cases. This table was constructed based on the formula of the temperature effect on specific heat for the specified compounds reported in DIPPR [18]. Apart from addition to the mean molar heat capacities, the AFT is also indispensable to calculate ϕ_U of specific compound. However, such a choice for a hydrocarbon is not unified in the literature. Some researchers agree that this temperature is around 1,550 K [11] or 1,200 K [19], while others believe that it is in the range of 1,000–1,500 K [20]. Detailed discussion about the issue for choosing the AFT may be found in the work by Vidal et al. [7] and the references therein. The AFT was chosen to be of 1,400 K in present study. The value of ϕ_U calculated from Eq. 14 and the one obtained by regression on experimental are in Table 8. As Table 8 indicates, these three results are close to the theoretical ones regarding the uncertainty in the AFT employed.

As we have mentioned, the proposed model is basically derived from the fact that inert gas does not take part in the reaction mechanism. However, when the quantity of the inert gas increases, experimental results do show deviations from this assumption. This deviation is easily understood from the fact that the UEL and LEL will shrink to a point as the inert gas is added. It should be noted that the lean material in combustion is different in LEL and UEL. Based on this, it is recommended that ϕ_U have better be determined from experimental data to increase the accuracy of prediction. It is obvious that the proposed method requires the least number of experimental data to determine the value of ϕ_U, as it is of linear.

Table 7 Mean molar heat capacities between 423 K and temperature listed [16]

Chemical	1,000 K	1,100 K	1,200 K	1,300 K	1,400 K	1,500 K	1,600 K
Methyl alcohol	12.4528	13.1309	13.8004	14.4506	15.0749	15.6702	16.2349
Acetone	31.9359	33.1061	34.1596	35.1089	35.9659	36.7415	37.4454
Methyl formate	14.9948	15.7994	16.5288	17.1917	17.7953	18.3464	18.8507
Steam	9.0122	9.1599	9.3082	9.4557	9.6011	9.7435	9.8821

Unit: cal g^{-1} mol^{-1} K^{-1}

Table 8 Theoretical and experimental values of ϕ_U for methyl alcohol, acetone, and methyl formate

Chemical	ϕ_U, Exp.	ϕ_U, Eq. 14
Methyl alcohol	1.7923	1.9126
Acetone	1.8801	2.6536
Methyl formate	1.6520	2.3690

It could be also seen from Eq. 14 that inert steam has little effect of inerting if the flammable material is of higher value of UEL. It is obvious from Eq. 14 that if U_1 was approached to be 1 because the $(1 - U_1)$ is equal to zero and the ϕ_U was not effected by Cp_{H_2O}. This argument agrees with the results shown in Figs. 3, 4, and 5.

In our another work, the semi-empirical models for predicating UFL for flammable gases diluted with inert nitrogen and with carbon dioxide are explored for 20 hydrocarbons reported in the literature, respectively. It was found that the diluted model could be derived for each class of compounds instead of individual compound. It was reported that such classes depend on the functional groups of an organic compounds. Thus, the proposed models might apply to the cases of alcohols, ketones, and esters inertized by steam, respectively. However, this argument should be further explored by experimental result in a future work [21].

Conclusions

In this study, a model for predicting the UEL of oxygenated hydrocarbons diluted with steam was proposed. This work extended our earlier work for pure hydrocarbon and inert nitrogen/carbon dioxide to the case of oxygenated hydrocarbons and inert steam. Experiments on alcohol (methyl alcohol), ketone (acetone), and ester (methyl formate) systems were conducted to examine the proposed model. It was found that the linear relation between the reciprocal of the UEL and the reciprocal of the molar fraction of flammable material in the air-free basis still holds in case of oxygenated hydrocarbons and inert steam. Experimental results including alcohol (methyl alcohol), ketone (acetone), and ester (methyl formate) systems showed that the coefficients of determination (R^2) of the regression lines were >0.9920 in all explored cases. The theoretical slopes of the regression lines were also calculated and they were found to be close to those determined by the experimental data. Although the proposed method offers an analytical way to calculate out the slope of the regression line, it is recommended that this value should be found through experimental data regarding the uncertainty in the reported AFT and the fact that AFT will change in some degree as inert steam added.

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