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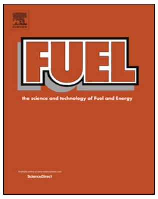

Full Length Article

Method for determination of flammability limits of gaseous compounds diluted with N_2 and CO_2 in air

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ABSTRACT

The present work studies the flammability limits of combustible–diluent–air mixtures at 25 °C and 1 atm pressure. The diluent species, considered in this study, were nitrogen and carbon dioxide. A factor called k_{FL} was obtained from mass and energy conservation, this factor relates the flammability limit of a combustible–air mixture to that of a combustible–diluent–air mixture. The factor k_{FL} varies with diluent concentration. Nevertheless, it was shown that an average value of this factor (k_{FL}^{av}) can represent, with good accuracy, the variation of the flammability limits with diluent concentration.

An empirical method to determine the flammability limits of combustible–diluent–air mixtures was developed. The method approximates k_{FL}^{av} by means of correlations. For the total set of experimental data, it was found that, for dilution with N_2 and CO_2 respectively: (a) at the LFL the Average of the relative errors (AARE) were 4.02% and 7.01%, the squared correlation coefficients (R^2) were 0.9833 and 0.9660; and (b) at the UFL the AAREs were 3.91% and 5.57%, the R^2 were 0.9920 and 0.9792.

At the Fuel Inertization Point (FIP) there is an inert concentration above which the mixture is non-flammable. A method was developed to determine the diluent mole fraction in the combustible–inert mixture at the FIP. The AAREs of 0.82% and 1.95% were obtained for dilution with N_2 and CO_2, respectively.

1. Introduction

The study of flammability limits is relevant to several industrial processes due to safety conditions. The theoretical aspects of the flammability limits (FL) are still being developed. However, their practical implications are very well stablished, and they have to be considered for any combustion application.

The present work deals with the FL of combustible–diluent–air mixtures. In the scope of the studies on flammability limits, it is considered as a diluent any inert species that once added to a combustible–air mixture reduces its flammability. Examples of such species are nitrogen (N_2), carbon dioxide (CO_2), water vapor (H_2O) and Helium (He), among others.

A combustible–diluent–air mixture is flammable when the combustible concentration is within the flammability limits. The lower flammability limit (LFL), for a fixed diluent concentration, is the lowest combustible concentration in the combustible–diluent–air mixture which sustains flame propagation. The upper flammability limit (UFL), for a fixed diluent concentration, is the highest combustible concentration in the combustible–diluent–air mixture which sustains flame propagation. In the case where no inert is present, its fixed concentration would be zero. This applies in general to any combustible–oxidant mixture. For instance, Pfahl et al. [1] determined the FLs of some combustibles using N_2O as oxidant. The earlier works by Zabetakis [2], Coward and Jones [3], and the reviews by Lovachev [4], Macek [5] and Coronado et al. [6] provide insight into this matter.

The FLs of a combustible–air mixture depend on the initial temperature and pressure conditions [7–11]. Also, there are different standard test methods to determine the FL [12]. These methods produce slightly different results for the LFL and sometimes they produce different results for the UFL of some combustibles. For example, Coward and Jones [3] report different values of the UFL of ethylene–air mixtures.

Several methods to calculate the FL of combustible–air mixtures at reference conditions have been developed and validated [13–19]. Although there are some approximations to the determination of the FL of combustible–diluent–air mixtures, there is still room for improvement.

The knowledge of the FL of combustible–diluent–air mixtures can be useful for several combustion applications, for example, Bade Shresta and Karim [20] have studied the performance of internal combustion

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Nomenclature

FL	flammability limit, %
g^0	specific Gibbs free energy at standard pressure in mole basis, kJ/mol
ΔG_T^0	standard state Gibbs function change, kJ/mol
$\bar{h}_i$	specific absolute enthalpy of species i in mole basis, kJ/mol
$\Delta\bar{h}_i$	specific sensible enthalpy of species i in mole basis, kJ/mol
$\bar{h}_{f,i}^0$	formation enthalpy of species i in mole basis at standard pressure, kJ/mol
H_C	heat of combustion of 1 mol of the combustible, kJ
K_{eq}	equilibrium constant for the water–gas homogeneous reaction
k_{FL}	factor which relates the FL of a combustible–air mixture to that of a combustible–inert–air mixture. It can be determined at the LFL and UFL.
k_{FL}^{av}	average value of k_{FL} determined for a particular combustible–inert–air system. It can be determined at the LFL and UFL.
LHV	lower heating value, kJ/g
M_d	representation of the diluent's molecule
n_i	number of moles of species i, mol
n_T	total number of moles of gaseous species in the products, mol
P_{air}	percentage of air in the combustible–diluent–air mixture, %
P_d	percentage of diluent in the combustible–diluent–air mixture,%
R	Universal gas constant, kJ/mol-K
R^2	squared correlation coefficient
s	specific entropy, kJ/mol-K
S	sample standard deviation
T	temperature, K
v_{air}^{FL}	number of moles of oxygen at the flammability limit, mol
v_{air}^{LFL}	number of moles of oxygen at the lower flammability limit, mol
v_{air}^{UFL}	number of moles of oxygen at the upper flammability limit, mol
v_{air}^{FIP}	number of moles of oxygen at the Fuel Inertization Point, mol
v_{air}^{s}	stoichiometric Number of moles of oxygen for y_F moles of combustible, mol
$v_{air,1}^{s}$	stoichiometric Number of moles of oxygen for 1 mol of combustible, mol
x_C	number of moles of carbon in the combustible, mol
x_H	number of moles of monoatomic hydrogen in the combustible, mol
x_O	number of moles of monoatomic oxygen in the combustible, mol
y_d	diluent mole fraction in the combustible–diluent mixture
y_F	combustible mole fraction in the combustible–diluent mixture
θ_d	ratio of adiabatic flame temperatures at LOC and at LFL
ϕ	equivalence ratio

Subscripts and Superscripts

air	air
av	average value
d	variable related to the combustible–diluent–air mixture
F	variable related to the combustible
LFL	variable at the lower flammability limit
FIP	variable at the fuel inertization point
P	products of the combustion process
R	reactants of the combustion process
UFL	variable at the upper flammability limit

Abbreviations

ARE	absolute value of the relative error,%
AARE	average of the absolute values of the relative errors of a set of data,%
FIP	Fuel Inertization Point
FL	flammability limit
LFL	lower flammability limit
UFL	upper flammability limit

engines operating with methane diluted with CO_2 and N_2. Also, the addition of diluents to combustible–air mixtures can reduce NOx emissions in spark ignition engines [21,22] and in diesel engines [23]. The diluents can decrease the constant volume peak combustion pressure and the mass burning rate of a combustible–air mixture as was shown by Zhang et al. [24] for the case of methanol.

The present article deals with the effect on the FL of diluent species as nitrogen and carbon dioxide. The objective is to develop two methods:

a) An empirical method for the determination of the FL of combustible–diluent–air mixtures at reference temperature and atmospheric pressure. This method can be used to determine the variation of the FL with different diluent concentrations.
b) A method to determine the diluent concentration at the fuel inertization point. This method can be used to assess the maximum diluent concentration for which the mixture is still flammable in air.

2. Overview of the effect of diluent species on the flammability limits

This section is divided in two sub-sections. On the first of these sub-sections some definitions, relevant to the present study, are provided together with the mathematical relations among the variables which appear on the study. On the second sub-section, the mathematical relations which can be applied to quantify the effect of the diluents on the FL are introduced.

2.1. Definitions and basic relations

In the present work, the term combustible is used to denote a species which can be flammable in the presence of an oxidant. A diluent could be any species which behaves as an inert in the combustion process. The diluents studied in the present work are N_2 or CO_2. The oxidant is air considered to be formed by 3.76 mol of N_2 per 1 mol of O_2. Which is a simplified composition of the atmospheric air when other species as argon or carbon dioxide are not considered, leaving 79% of N_2 and 21% of O_2.

Three different mixtures are defined before further development:

a) **Combustible–air mixtures:** These are mixtures containing only the combustible and air without the presence of any diluent. Furthermore, in Sections 3 and 4 the FL of these mixtures are considered known quantities. Its lower flammability limit is denoted by LFL_A and its upper flammability limit by UFL_A.
b) **Combustible–diluent mixtures:** These are mixtures formed by the

combustible and the diluent without the presence of air. It is considered that the combustible is mixed with the diluent before the addition of air. The mole fractions of combustible and diluent in this mixture are denoted by y_F and y_d, respectively, being $y_F + y_d = 1$.

c) **Combustible–diluent–air mixtures:** These are mixtures formed by the combustible, the diluent and the air. The FL are the leanest or richest combustible concentrations on these mixtures which can sustain flame propagation for a fixed diluent concentration. Thus, it is evident that the FL depend on at least another concentration, which can be the diluent concentration or the air concentration.

When the FL of a combustible–diluent–air mixture is determined experimentally a common procedure would be to make vacuum in the combustion chamber (vessel), then add the combustible on the first place, the diluent on the second place and the air on the last place. In this sense, the composition of the combustible–diluent mixture is important for the determination of the flammability limits of the combustible–diluent–air mixture.

According to the previous definitions, it is considered that once the combustible–diluent mixture has been formed, then 1 mol of it mixes with air to form a combustible–diluent–air mixture. The motivation for this consideration is that it makes easier to develop and to apply the methods presented in the next sections. That is because it is possible to start the analysis from a well-established combustible–diluent mixture and evaluate the variations of the FL of combustible–diluent–air mixtures. Hence, the diluent concentration is varied through its mole fraction y_d in the combustible–diluent mixture.

The experimental data of the FL of combustible–diluent–air mixtures are generally presented in graphs similar to Fig. 1. In such graphs, the combustible concentration (FL) is given in the ordinate, the diluent concentration (P_d) is given in the axis, and, the air concentration is given as the difference, $P_{air} = 100\% - FL - P_d$. The combustible concentration has been denoted as the FL for simplicity. However, the composition of a combustible–diluent–air mixture at the FL is defined by at least two independent concentrations.

The envelope shown in Fig. 1 is formed by two curves which correspond to the LFL and UFL, respectively. The intercepts with the ordinate are denoted by LFL_A and UFL_A, at these points the diluent concentration is zero. Therefore, these intercepts represent the FL of the combustible–air mixture.

The combustible–diluent–air mixtures inside the envelope, shown in Fig. 1, are flammable and those outside of it are non-flammable. As the diluent concentration is increased the LFL slightly increases and the UFL decreases. Therefore, a combustible–diluent–air mixture is less flammable than a combustible–air mixture.

It is now important to establish the mathematical relations between the combustible–diluent–air mixture components (characterized by FL, P_d and P_{air}) and 1 mol of the aforementioned combustible–diluent mixture (characterized by y_F and y_d).

In one mole of the combustible–diluent mixture there are y_F moles of combustible. Thus, the number of moles of combustible in the combustible–diluent–air mixture is equal to the combustible mole fraction in the combustible–diluent mixture. In the rest of this article y_F and y_d are simply called the combustible mole fraction and the diluent mole fraction.

The number of moles of air (n_{air}) in the combustible–diluent–air mixture is determined by using the number of moles of oxygen in that mixture ($\nu_{air,d}^{FL}$), being $n_{air} = 4.76\nu_{air,d}^{FL}$. Therefore, the FL is determined as the number of moles of combustible divided by the number of moles of mixture and multiplied by 100%, as shown in Eq. (1). Notice that in the denominator of Eq. (1) the unity corresponds to the sum $y_F + y_d = 1$.

$$FL = \frac{y_F}{1 + 4.76\nu_{air,d}^{FL}} 100\% \tag{1}$$

In the case of a combustible–air mixture Eq. (1) is applied by taking $y_F = 1$. Then, the number of moles of oxygen would be represented by $\nu_{air,A}^{FL}$ and the FL by LFL_A or UFL_A.

The number of moles of combustible, y_F, are related to the combustible and diluent concentrations, FL and P_d, by Eq. (2).

$$y_F = \frac{FL}{FL + P_d} \tag{2}$$

It is possible to write a similar expression for the diluent mole fraction, $y_d = P_d/(FL + P_d)$. Making reference again to Fig. 1, it is interesting to observe that the experimental data on the FL of combustible–diluent–air mixtures can also be presented by using y_d in the axis and FL in the ordinate as was done by Kondo et al. [25,26]. The results of the methods developed in the present article will be presented in that way on Section 6.

Substitution of Eq. (2) into Eq. (1) and some rearrangements yield Eq. (3) which relates $\nu_{air,d}^{FL}$ to FL and P_d.

$$\nu_{air,d}^{FL} = \frac{1}{4.76}\left(\frac{100}{FL + P_d} - 1\right) \tag{3}$$

It is also necessary to consider the number of moles of oxygen at the stoichiometric composition (ν_{air}^{s}) when y_F moles of combustible are considered. Eq. (4) gives this number of moles,

$$\nu_{air}^{s} = y_F\left(x_C + \frac{x_H}{4} - \frac{x_O}{2}\right) \tag{4}$$

where, x_C, x_H and x_O are the number of moles of carbon, monoatomic hydrogen and monoatomic oxygen in the combustible molecule, respectively.

At some composition of the combustible–diluent–air mixture the LFL and the UFL are equal as it is shown by the intersection of both curves in Fig. 1. Kondo et al. [25,26] called this intersection the Fuel Inertization Point (FIP), while Britton et al. [27] called it the Limiting Oxygen Concentration (LOC). In the present work, the term FIP is adopted.

In general, for a fixed diluent concentration in the combustible–diluent–air mixture, there are two different FL, the mixture will be flammable when the combustible concentration is between the FL. On the other hand, at the FIP there is only one value of the FL for a fixed diluent concentration. Therefore, at the FIP there is only one composition for which the combustible–diluent–air mixture is flammable.

If the diluent concentration is increased beyond its value at the FIP the combustible–diluent–air mixture becomes non-flammable. The FIP can also be identified in terms of the diluent mole fraction y_d^{FIP} as shown in Eq. (5).

$$y_d^{FIP} = \frac{P_d^{FIP}}{FL_{FIP} + P_d^{FIP}} = 1 - y_F^{FIP} \tag{5}$$

In a recent study Zhang et al. [28] evaluated the effect of ozone addition to syngas–diluent–air mixtures. As expected, the ozone

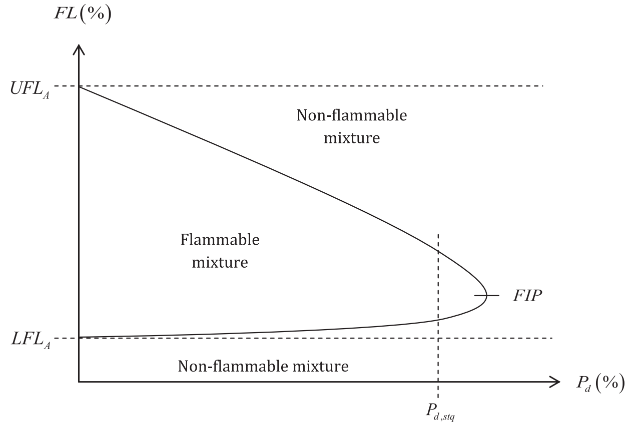


Fig. 1. General behavior of the FLs of a combustible–diluent–air mixture.

addition increases the UFL and decreases the LFL. Therefore, the effect of the diluent species can be reverted when more oxidant is added.

2.2. Quantification of the diluent's effect at the FL

The diluent's effect can be measured in terms of the number of moles of oxygen at the FL of a combustible–diluent–air mixture and the number of moles of oxygen at the FL of a combustible–air mixture, these are introduced as $\nu^{FL}_{air,d}$ and $\nu^{FL}_{air,A}$, respectively. In the following development, the subscripts A and d make reference to the combustion processes of the combustible–air and the combustible–diluent–air mixtures, respectively.

An expression relating $\nu^{FL}_{air,A}$ and $\nu^{FL}_{air,d}$ can be written in terms of the mole fractions of the combustible–diluent mixture and a factor called k_{FL}, as shown in Eq. (6).

$$\nu^{FL}_{air,d} = y_F \nu^{FL}_{air,A} + k_{FL} \tag{6}$$

The first term on the right-hand side of Eq. (6), namely $y_F \nu^{FL}_{air,A}$, represents the number of moles of oxygen at the FL of a combustible–air mixture containing y_F moles of combustible (instead of 1 mol). The second term on the right-hand side quantifies the effect of adding y_d moles of diluent to the mixture. Therefore, the factor k_{FL} is a measure of the diluent's effect on the FL.

Furthermore, if the experimental values of $\nu^{FL}_{air,A}$ and $\nu^{FL}_{air,d}$ are known, then, the experimental value of k_{FL} can be obtained from Eq. (6). The results of such calculations performed with experimental data of the FL of propane–CO_2–air mixtures are shown in Table 1. The experimental data presented on Table 1 was taken from Zabetakis' work [2]. The average value of k_{FL} at the lower flammability limit (k^{av}_{LFL}) and at the upper flammability limit (k^{av}_{UFL}) are also presented in Table 1 together with the sample standard deviations (S).

The results of estimating the FL are also presented in Table 1, where the Absolute Relative Errors (ARE) have values lower than 5% in all cases except for the LFL of the propane–CO_2–air mixture with 25% of CO_2.

Since the FIP point was found to belong to the rich side, the estimation of the FL for 27.93% of CO_2 concentration was performed by using k^{av}_{UFL}. Also because the FIP is found for a rich mixture, the value of the k_{LFL} at the FIP was not used to determine the k^{av}_{LFL} presented in Table 1. The good results obtained for the propane–CO_2–air mixture suggest that a method based on the approximation of k^{av}_{FL} can be useful to estimate the FL of combustible–diluent–air mixtures. The development of such method is presented in Section 3 and validated with more experimental data on Section 6.

It should be noticed that each combustible–diluent pair will present a different value of k^{av}_{LFL} and k^{av}_{UFL}, as shown in Tables 2 and 3. Therefore, it is necessary to perform a validation procedure showing that the average values k^{av}_{LFL} and k^{av}_{UFL} can be used to estimate the FL of combustible–diluent–air mixtures at different y_d. The validation procedure is described on Section 6, it was applied to all the available experimental data and the results are shown in Section 6.1. The conclusion was that the average values k^{av}_{LFL} and k^{av}_{UFL} can be used to determine the FL of combustible–diluent–air mixtures.

To this point the factor k_{FL} was obtained from Eq. (6) by using the experimental values of $\nu^{FL}_{air,A}$ and $\nu^{FL}_{air,d}$. However, another expression for this factor can be obtained by writing the energy conservation equations to the reactions shown in Eqs. (7) and (8) and using them on Eq. (6).

The reaction shown in Eq. (7) represents the combustion of 1 mol of the combustible at its FL in air (free of diluent). While, the reaction shown in Eq. (8) represents the combustion of 1 mol of the combustible–diluent mixture at its FL in air.

$$C_{x_C}H_{x_H}O_{x_O} + \nu^{FL}_{air,a}(O_2 + 3.76N_2) \rightarrow n_{O_2,A}O_2 + 3.76\nu^{FL}_{air,A}N_2 + (products)_A \tag{7}$$

$$\begin{aligned} &y_F C_{x_C}H_{x_H}O_{x_O} + y_d M_d + \nu^{FL}_{air,d}(O_2 + 3.76N_2) \\ &\rightarrow n_{O_2,d}O_2 + 3.76\nu^{FL}_{air,d}N_2 + y_d M_d + (products)_d \end{aligned} \tag{8}$$

Notice that on the right-hand side of Eqs. (7) and (8) the species on the products are oxygen (O_2), nitrogen (N_2), diluent (M_d) and other species as CO_2, CO, H_2, H_2O, etc. At this point it is not important to specify all the product species in the reaction, it is enough to understand that there can be several species in the product gases. Thus, the following assumptions are applied before writing the energy conservation equation:

i. The process is adiabatic and at constant pressure
ii. The nitrogen in the air behaves as an inert
iii. The diluent behaves as an inert
iv. At the LFL the excess oxygen behaves as an inert
v. At the UFL the oxygen reacts completely
vi. The combustion products are at chemical equilibrium.

The assumption (i) establishes that the process is adiabatic and at constant pressure, this has already been explained in a previous work [29]. Nevertheless, it is important to point out that in order to obtain a reliable experimental measurement of the FL the heat losses to the vessel and to the exterior must be minimized. Also, it is expected that at the FL the flame would freely propagate, as would happen under constant pressure conditions.

The assumptions (ii)–(v) are commonly adopted to reduce the number of species in the products. They simplify the solution process by reducing the number of unknowns without introducing significant errors regarding the calculations of the adiabatic flame temperatures and the concentrations of the major species on the products.

The assumption (vi) is necessary to close the system of equations at the UFL. This is due to the appearance of species of incomplete combustion that introduce more unknowns to the problem. This assumption has also been applied in previous works [29,30].

The product species formed on the combustion reaction are represented by n_j, these species include CO_2, H_2O, O_2 and N_2 in the case

Table 1
Determination of the values of k_{LFL} and k_{UFL} for propane–CO_2–air mixtures at the flammability limits. Experimental data by Zabetakis [2].

CO_2 (%)	Lower Flammability Limit					Upper Flammability Limit				
	LFL_{exp} (%)	y_d	k_{LFL}	LFL_{calc} (%)	ARE (%)	UFL_{exp} (%)	y_d	k_{UFL}	UFL_{calc} (%)	ARE (%)
0.00	2.11	0.000	–	–	–	9.50	0.000	–	–	–
5.00	2.29	0.686	−0.566	2.32	1.42	8.39	0.373	0.280	8.45	0.62
10.00	2.50	0.800	−0.602	2.53	1.11	7.31	0.578	0.275	7.38	1.02
15.00	2.71	0.847	−0.614	2.74	0.80	6.29	0.705	0.264	6.33	0.73
20.00	2.99	0.870	−0.648	2.92	2.17	5.39	0.788	0.244	5.34	0.90
25.00	3.32	0.883	−0.694	3.07	7.64	4.61	0.844	0.223	4.44	3.55
27.93	3.86	0.879	–	–	–	3.86	0.879	0.237	3.77	2.20
			$k^{av}_{LFL} = -0.624$ ($S = 0.04$)					$k^{av}_{UFL} = 0.254$ ($S = 0.02$)		

FL_{calc} was determined with k^{av}_{FL}.

Table 2

Relevant parameters for combustible–N_2–air mixtures.

Combustible	Formula	LFL_A (%)	UFL_A (%)	N_2 (%) FIP	FL (%) FIP	ϕ_{FIP}	LHV (kJ/g)	k_{LFL}^{av}	k_{UFL}^{av}	Refs.
Methane	CH_4	5.00	15.00	36.73	6.64	1.116	50.14	−0.2866	0.0960	[2]
Methane	CH_4	4.90	15.80	39.24	5.25	0.900	50.14	−0.3191	0.1956	[25]
Methane	CH_4	5.30	15.50	37.71	5.60	0.940	50.14	−0.2117	0.1654	[43]
Methane	CH_4	5.00	15.70	41.57	5.07	0.905	50.14	−0.1781	0.1401	[45][a]
Methane	CH_4	5.10	15.60	39.75	5.23	0.905	50.14	−0.1790	0.1486	[45][b]
Methane	CH_4	5.30	14.85	36.04	5.30	0.860	50.14	−0.2025	0.1477	[45][c]
Methane	CH_4	5.46	14.35	33.12	5.43	0.841	50.14	−0.2023	0.1464	[45][d]
Ethane	C_2H_6	3.00	12.48	43.04	3.67	1.146	47.62	−0.2270	0.1607	[2]
Ethane	C_2H_6	3.00	13.60	50.65	3.40	1.233	47.62	−0.2118	0.1327	[43]
Propane	C_3H_8	2.11	9.50	41.72	3.00	1.292	46.43	−0.2788	0.1607	[2]
Propane	C_3H_8	2.03	10.00	45.60	2.40	1.098	46.43	−0.3427	0.1794	[25]
Propane	C_3H_8	2.11	10.00	47.86	2.56	1.227	46.43	−0.2118	0.1561	[43]
Butane	C_4H_{10}	1.79	8.38	39.31	2.62	1.396	45.82	−0.3104	0.1250	[2]
Butane	C_4H_{10}	1.74	8.38	43.83	2.26	1.298	45.82	−0.2134	0.1478	[43]
isoButane	i-C_4H_{10}	1.68	7.80	41.77	1.95	1.082	45.67	−0.2791	0.2107	[44]
Pentane	C_5H_{12}	1.27	7.62	42.23	2.17	1.488	45.44	−0.4116	0.1218	[2]
Hexane	C_6H_{14}	1.18	7.45	41.43	1.82	1.451	45.19	−0.2807	0.1558	[2]
Ethylene	C_2H_4	2.60	35.80	48.85	3.60	1.081	47.26	−0.2997	0.2436	[2]
Ethylene	C_2H_4	2.74	31.50	55.78	3.18	1.106	47.26	−0.2043	0.2528	[25]
Ethylene	C_2H_4	3.00	30.67	54.58	3.33	1.131	47.26	−0.2124	0.1966	[43]
Propylene	C_3H_6	2.40	10.16	42.00	3.00	1.168	45.87	−0.2145	0.1144	[2]
Propylene	C_3H_6	2.16	11.00	45.55	2.60	1.074	45.87	−0.2262	0.2726	[25]
Propylene	C_3H_6	2.33	10.28	45.00	3.00	1.236	45.87	−0.2181	0.1120	[43]
isoButylene	C_4H_8	1.81	9.00	39.44	2.69	1.329	45.06	−0.2837	0.1515	[2]
1-Butene	C_4H_8	1.60	9.76	43.60	2.56	1.358	45.75	−0.3724	0.1461	[2]
3-Methyl-1-Butene	C_5H_{10}	1.52	9.22	43.70	1.85	1.214	45.02	−0.2577	0.1511	[2]
Butadiene	C_4H_6	2.00	11.62	47.69	2.58	1.357	44.61	−0.2501	0.1747	[2]
Cyclopropane	C_3H_6	2.36	10.48	40.60	3.20	1.220	46.32	−0.2637	0.1591	[2]
Benzene	C_6H_6	1.40	7.12	42.60	2.00	1.289	40.63	−0.2184	0.0538	[2]
Hydrogen	H_2	4.00	75.00	71.33	4.67	0.463	120.91	−0.2101	0.0883	[46]
Methane + propane	$0.2CH_4 + 0.8C_3H_8$	2.35	10.82	45.00	2.82	1.133	46.74	−0.2134	0.1657	[43]
Methane + propane	$0.4CH_4 + 0.6C_3H_8$	2.71	11.65	43.79	3.18	1.083	47.16	−0.2129	0.1633	[43]
Methane + propane	$0.6CH_4 + 0.4C_3H_8$	3.29	12.86	42.50	3.71	1.052	47.74	−0.2129	0.1894	[43]
Methane + propane	$0.8CH_4 + 0.2C_3H_8$	4.00	14.00	40.69	4.59	1.039	48.63	−0.2133	0.1783	[43]
Ethane + propane	$0.2C_2H_6 + 0.8C_3H_8$	2.25	11.62	46.54	2.63	1.155	46.61	−0.2146	0.1753	[43]
Ethane + propane	$0.4C_2H_6 + 0.6C_3H_8$	2.29	11.24	47.00	2.82	1.179	46.80	−0.2156	0.1447	[43]
Ethane + propane	$0.6C_2H_6 + 0.4C_3H_8$	2.50	12.08	47.76	3.06	1.212	47.03	−0.2191	0.0785	[43]
Ethane + propane	$0.8C_2H_6 + 0.2C_3H_8$	2.50	12.76	49.63	3.03	1.156	47.30	−0.2142	0.1448	[43]
Methane + ethylene	$0.2CH_4 + 0.8C_2H_4$	3.13	28.28	52.62	3.75	1.146	47.62	−0.2101	0.2479	[43]
Methane + ethylene	$0.4CH_4 + 0.6C_2H_4$	3.64	22.95	50.00	4.09	1.103	48.05	−0.2101	0.2408	[43]
Methane + ethylene	$0.6CH_4 + 0.4C_2H_4$	3.88	18.78	47.08	4.39	1.033	48.59	−0.2373	0.1884	[43]
Methane + ethylene	$0.8CH_4 + 0.2C_2H_4$	4.44	17.04	42.92	5.00	1.005	49.26	−0.2128	0.1901	[43]
Ethylene + propylene	$0.2C_2H_4 + 0.8C_3H_6$	2.38	10.88	46.67	2.75	1.087	46.07	−0.2135	0.1812	[43]
Ethylene + propylene	$0.4C_2H_4 + 0.6C_3H_6$	2.54	13.23	48.70	3.08	1.184	46.29	−0.2121	0.1877	[43]
Ethylene + propylene	$0.6C_2H_4 + 0.4C_3H_6$	2.59	17.31	51.25	3.15	1.183	46.56	−0.2101	0.1816	[43]
Ethylene + propylene	$0.8C2H_4 + 0.2C_3H_6$	2.62	23.10	52.92	3.10	1.105	46.88	−0.2406	0.1656	[43]
Aviation gasoline	Gasoline 100-130	1.33	7.10	40.77	2.05	–	44.16	−0.3204	0.1557	[46]
Jet propellant	JP-4	1.28	8.16	42.80	2.00	–	43.49	−0.2434	0.1786	[46]
Liquefied petroleum gas	LPG	1.81	8.86	35.00	3.42	1.439	46.21	−0.3106	0.0711	[47]
Liquefied petroleum gas	LPG	1.87	7.69	35.00	3.58	1.514	46.21	−0.3599	0.0300	[47]
Natural gas	NG[e]	5.00	15.50	–	–	–	49.96	−0.3142	−0.0072	[48]
Methanol	CH_4O	6.56	36.35	45.83	8.13	1.260	21.01	−0.2668	0.1582	[2]
Ethanol	C_2H_6O	3.40	18.70	44.00	4.90	1.369	27.79	−0.3031	0.1793	[2]
Dimethyl ether	C_2H_6O	3.39	26.07	46.48	4.11	1.187	28.88	−0.2434	0.3357	[2]
Dimethyl ether	C_2H_6O	3.30	26.20	51.00	3.78	1.194	28.88	−0.2341	0.5245	[25]
Diethyl ether	$C_4H_{10}O$	1.86	36.30	48.65	2.96	1.749	34.20	−0.2449	0.3001	[2]
Methyl formate	$C_2H_4O_2$	5.80	21.70	44.81	6.79	1.335	15.56	−0.2242	0.1271	[2]
Methyl formate	$C_2H_4O_2$	5.25	22.60	48.25	5.60	1.155	15.56	−0.2260	0.1292	[25]
Methyl acetate	$C_3H_6O_2$	3.08	15.87	43.33	4.52	1.444	20.22	−0.3523	0.1228	[2]
Acetone	C_3H_6O	2.48	13.04	41.15	3.76	1.300	29.14	−0.3879	0.1710	[2]
Methyl ethyl ketone	C_4H_8O	2.00	11.27	44.62	2.77	1.378	31.98	−0.3198	0.1592	[2]
Carbon monoxide	CO	12.30	73.08	56.67	15.38	1.310	10.11	−0.2307	0.0829	[46]

Note: The flammability limits correspond to 25 °C and 1 atm. except for the following: a) 1 atm and 300 K; b)1 atm and 250 K; c) 1 atm and 200 K; d) 1 atm and 150 K; e) 0.96% of CH_4 and 0.04% of C_2H_6.

of the LFL, and, CO_2, CO, H_2, H_2O and N_2 in the case of the UFL. It is necessary to point out that the present formulation is valid even if more species were to be considered. The method developed in Section 4 will consider only the aforementioned species.

The energy conservation equation for the combustible–air mixture is presented in Eq. (9). The terms on the right-hand side of Eq. (9) represent the absolute enthalpies of the species formed by the reaction, the nitrogen in the air and the excess oxygen (if any), respectively. All these enthalpies are taken at the adiabatic flame temperature. The terms on the left-hand side of Eq. (9) represent the absolute enthalpies of the combustible and the air, respectively, these enthalpies are taken at the reactant's temperature.

Table 3
Relevant parameters for combustible–CO2–air mixtures.

Combustible	Formula	LFL_A (%)	UFL_A (%)	CO_2 (%) FIP	FL (%) FIP	ϕ_{FIP}	LHV (kJ/g)	k^{av}_{LFL}	k^{av}_{UFL}	Refs.
Methane	CH_4	5.00	15.00	23.27	7.32	1.004	50.14	−0.4696	0.2376	[2]
Methane	CH_4	4.90	15.80	24.94	6.47	0.898	50.14	−0.5366	0.3436	[26]
Ethane	C_2H_6	3.00	12.48	30.93	4.37	1.125	47.62	−0.4164	0.2699	[2]
Propane	C_3H_8	2.11	9.50	27.93	3.86	1.346	46.43	−0.6248	0.2536	[2]
Propane	C_3H_8	2.03	10.00	31.22	2.90	1.048	46.43	−0.2306	0.4013	[26]
Butane	C_4H_{10}	1.79	8.38	27.34	3.21	1.429	45.82	−0.4880	0.2389	[2]
isoButane	i-C_4H_{10}	1.68	7.80	27.23	2.30	1.011	45.67	−0.2932	0.3160	[44]
Pentane	C_5H_{12}	1.27	7.62	28.27	2.85	1.573	45.44	−0.7001	0.2286	[2]
Hexane	C_6H_{14}	1.18	7.45	29.11	2.25	1.482	45.19	−0.5254	0.2791	[2]
Ethylene	C_2H_4	2.60	35.80	39.04	4.80	1.220	47.26	−0.3311	0.3990	[2]
Ethylene	C_2H_4	2.74	31.50	41.98	4.00	1.057	47.26	−0.3289	0.4392	[26]
Propylene	C_3H_6	2.40	10.16	27.80	3.80	1.190	45.87	−0.3585	0.2284	[2]
Propylene	C_3H_6	2.16	11.00	34.11	3.25	1.111	45.87	−0.4101	0.4542	[26]
isoButylene	C_4H_8	1.81	9.00	25.96	3.15	1.271	45.06	−0.4678	0.2914	[2]
1-Butene	C_4H_8	1.60	9.76	31.60	3.00	1.310	45.75	−0.6615	0.2712	[2]
3-Methyl-1-Butene	C_5H_{10}	1.52	9.22	30.74	2.56	1.368	45.02	−0.3918	0.2994	[2]
Butadiene	C_4H_6	2.00	11.62	34.42	3.23	1.357	44.61	−0.3425	0.3210	[2]
Cyclopropane	C_3H_6	2.63	10.48	29.23	3.92	1.256	46.32	−0.4518	0.2464	[2]
Benzene	C_6H_6	1.40	7.12	28.20	2.72	1.406	40.63	−0.3978	0.1389	[2]
Hydrogen	H_2	4.00	75.00	55.33	7.33	0.468	120.91	−0.2533	0.2494	[46]
Jet propellant	JP-4	1.28	8.16	29.00	2.52	–	43.49	−0.5935	0.2899	[46]
Natural gas	NG	5.00	15.50	–	–	–	49.96	−0.4323	0.1367	[48][a]
Methanol	CH_4O	6.56	36.35	32.08	10.00	1.233	21.01	−0.4735	0.2822	[2]
Ethanol	C_2H_6O	3.40	18.70	31.00	6.00	1.360	27.79	−0.5716	0.3410	[2]
Dimethyl ether	C_2H_6O	3.39	26.07	32.59	5.36	1.233	28.88	−0.4447	0.5762	[2]
Dimethyl ether	C_2H_6O	3.30	26.20	34.98	4.68	1.108	28.88	−0.3798	0.6816	[26]
Diethyl ether	$C_4H_{10}O$	1.85	36.30	33.85	4.07	1.874	34.20	−0.2708	0.3765	[2]
Methyl formate	$C_2H_4O_2$	5.80	21.70	31.85	8.21	1.305	15.56	−0.4038	0.1956	[2]
Methyl formate	$C_2H_4O_2$	5.25	22.60	35.41	7.10	1.176	15.56	−0.3388	0.2245	[26]
Methyl acetate	$C_3H_6O_2$	3.08	15.87	28.70	5.96	1.520	20.22	−0.7200	0.2746	[2]
Acetone	C_3H_6O	2.48	13.04	27.50	4.48	1.254	29.14	−0.7188	0.3264	[2]
Methyl ethyl ketone	C_4H_8O	2.00	11.27	32.50	3.35	1.366	31.98	−0.5104	0.2413	[2]
Carbon monoxide	CO	12.30	73.08	40.77	21.54	1.360	10.11	−0.4617	0.1521	[46]

Note: The flammability limits correspond to 25 °C and 1 atm. a) 0.96% of CH_4 and 0.04% of C_2H_6.

$$\bar{h}_A + v^{FL}_{ar,A}(\bar{h}_{O_2} + 3.76\bar{h}_{N_2}) = \sum_A n_j\bar{h}_j + 3.76v^{FL}_{ar,A}\bar{h}_{N_2,A} + n_{O_2,A}\bar{h}_{O_2,A} \tag{9}$$

The reference temperature is generally assumed as 25 °C; however, another value can be assumed, and the enthalpies would be related to that reference temperature. Considering that the reactants are at the reference temperature in Eq. (9) and rearranging, Eq. (10) is obtained. The heat released at the combustion process of the combustible–air mixture ($H_{C,A}$) is determined by Eq. (11).

$$v^{FL}_{air,A} = \frac{H_{C,A} - \sum_A n_j\Delta\bar{h}_j - n_{O_2,A}\bar{h}_{O_2,A}}{3.76\bar{h}_{N_2,A}} \tag{10}$$

$$H_{C,A} = \bar{h}^0_{f,A} - \sum_A n_j\bar{h}^0_{f,j} \tag{11}$$

Analogously, the energy conservation equation for the combustible–diluent–air mixture is presented in Eq. (12). The terms on the right-hand side of Eq. (12) represent the absolute enthalpies of the species formed in the reaction, the nitrogen in the air, the excess oxygen (if any) and the diluent, respectively. All these enthalpies are taken at the adiabatic flame temperature. The terms on the left-hand side of Eq. (12) represent the absolute enthalpies of the combustible, the diluent and the air, respectively. All these enthalpies are taken at the reactants' temperature.

$$y_F\bar{h}_A + y_d\bar{h}_{d,R} + v^{FL}_{air,d}(\bar{h}_{O_2} + 3.76\bar{h}_{N_2}) = \sum_d n_j\bar{h}_j + 3.76v^{FL}_{air,d}\bar{h}_{N_2,d} + n_{O_2,d}\bar{h}_{O_2,d} + y_d\bar{h}_{d,P} \tag{12}$$

Considering the reactants at the reference temperature in Eq. (12) and rearranging, Eq. (13) is obtained. The heat released at the combustion process of the combustible–diluent–air mixture ($H_{C,d}$) is given in Eq. (14).

$$v^{FL}_{air,d} = \frac{H_{C,d} - \sum_d n_j\Delta\bar{h}_j - n_{O_2,d}\bar{h}_{O_2,d} - y_d\Delta\bar{h}_{d,P}}{3.76\bar{h}_{N_2,d}} \tag{13}$$

$$H_{C,d} = y_F\bar{h}^0_{f,A} - \sum_d n_j\bar{h}^0_{f,j} \tag{14}$$

Notice that the heat release terms, given in Eqs. (11) and (14), can represent processes of complete or incomplete combustion depending on which species are expected in the products. Hence, another form to obtain k_{FL} is to substitute Eqs. (10) and (13) into Eq. (6) and rearrange to obtain the expression shown below:

$$k_{FL} = \frac{1}{3.76}\left[\left(\frac{1}{y_d}\frac{H_{C,d}}{\bar{h}_{N_2,d}} - \frac{y_F}{y_d}\frac{H_{C,A}}{\bar{h}_{N_2,A}}\right) - \left(\frac{1}{y_d}\frac{\sum_d n_j\Delta\bar{h}_j}{\bar{h}_{N_2,d}} - \frac{y_F}{y_d}\frac{\sum_A n_j\Delta\bar{h}_j}{\bar{h}_{N_2,A}}\right) - \left(n_{O_2,d}\frac{1}{y_d}\frac{\bar{h}_{O_2,d}}{\bar{h}_{N_2,d}} - n_{O_2,A}\frac{y_F}{y_d}\frac{\bar{h}_{O_2,A}}{\bar{h}_{N_2,A}}\right)\right] - \frac{1}{3.76}\frac{\Delta\bar{h}_{d,P}}{\bar{h}_{N_2,d}} \tag{15}$$

In order to calculate k_{FL} by using Eq. (15) it is necessary to know the products composition and the adiabatic flame temperature. As aforementioned, when the reaction is representing the LFL, then, complete combustion can be assumed and the products include CO_2, H_2O, O_2, N_2 and M_d [31,32]. On the other hand, if the reaction is representing the UFL, then, incomplete combustion is expected and the products may include CO_2, CO, H_2O, H_2, N_2 and M_d, and, even C (carbon graphite) in some cases [30,29].

Although through different approaches several authors have developed methods for estimation of the FL of combustible–diluent–air mixtures by assuming that the adiabatic flame temperatures are constant and equal to that at the FL without diluent [33–42]. However, this assumption is a source of error when the FL are calculated. To prove this, the adiabatic flame temperatures at the experimental FL of propane–CO_2–air mixtures were determined, and the results are presented in Fig. 2. There is a significant difference between the adiabatic flame temperatures determined at the FL without diluent and those with diluent. Thus, a constant adiabatic flame temperature is not assumed in the present work, the method developed in the next section relies in a correlation to determine k_{FL}^{av}.

Another important simplification applied by other authors is related to the UFL. Since the mass conservation equations are not enough to establish the composition of the products, some authors specify a certain reaction order for the oxygen in the reactants [37,38,41]. Those authors considered that the O_2 reacts to form CO in the first place, H_2O in the second place and if any more O_2 is available it reacts to form CO_2 in the third place. In the present work, it was assumed that the products are at chemical equilibrium instead of establishing a reaction order for the oxygen in the reactants.

3. Empirical method to determine the FL of combustible–diluent–air mixtures

The present section is concerned with the development and application procedure of a method to estimate the FL of combustible–diluent–air mixtures. To achieve this objective two sub-sections are presented. The first one deals with the development of the method and the experimental data used for correlation and validation. The second sub-section deals exclusively with the procedure for the application of the method.

3.1. Development of the empirical method to determine the FL of combustible–diluent–air mixtures

In this section the k_{FL}^{av} will be correlated by using some of the available experimental data. Since there is one k_{FL}^{av} for each combustible–diluent–air system, there are 60 values of k_{LFL}^{av} and k_{UFL}^{av} for combustible–N_2–air mixtures. On the other hand, there are 31 of these values for combustible–CO_2–air mixtures. The behavior shown by hydrogen and carbon monoxide was different from that shown by other compounds. Therefore, these two compounds were not considered in the correlations to be shown on this section. In the case of H_2 and CO it is recommended to use the values of k_{FL}^{av} presented on Tables 2 and 3.

The criteria to form the correlation sets was that at least 25% of the combustible–diluent–air systems would be left for the prediction sets. Therefore, 45 data of k_{FL}^{av} for dilution with N_2 and 23 data for dilution with CO_2 were considered for the correlation sets. Random numbers were generated for each combustible–diluent–air system using Microsoft Excel, and these were ordered from greater to lesser values. Then, the first 45 systems were selected for the correlation set of dilution with N_2 and the first 23 for the correlation set of dilution with CO_2. The procedure was repeated for the data of LFL and UFL separately.

The experimental data for combustible–diluent–air mixtures were obtained from works by Zabetakis [2], Zhao [43], Kondo et al. [25], Kondo et al. [26], Kondo et al. [44], Li et al. [45], Kuchta [46], Mishra and Rahman [47] and Liao et al. [48]. The data correspond to 60 combustible–N_2–air systems and 31 combustible–CO_2–air systems, as aforementioned.

For the combustible–N_2–air mixtures the total set of experimental data was formed by 455 data of LFLs (without considering the FIP values), and, 514 data of UFLs. The FL at the FIP were considered on the UFL case because, as shown in Tables 2 and 3, most of the mixtures present $\phi_{FIP} > 1$, exceptions to this rule are hydrogen and some experimental data for methane.

The data set of LFLs was divided into a correlation set and a prediction set with 340 and 115 experimental data, respectively. On the other hand, the data set of UFLs was divided into a correlation set and a prediction set with 380 and 134 experimental data, respectively. In both cases the correlation set included data of 45 combustible–N_2–air systems and the prediction set included data of 15 combustible–N_2–air systems.

For the combustible–CO_2–air mixtures the total set of experimental data was formed by 166 data of LFLs (without considering the FIP values), and, 197 data of UFL. The data set of LFLs was divided into a correlation set and a prediction set with 125 and 41 experimental data, respectively. On the other hand, the data set of UFLs was divided into a correlation set and a prediction set with 146 and 51 experimental data, respectively. In both cases the correlation set included data of 23 combustible–CO_2–air systems and the prediction set included data of 8 combustible–CO_2–air systems.

As has been shown in Section 2, the experimental data can be used to determine the k_{FL} by applying Eq. (6). Then, the values of k_{FL}^{av} can be obtained. These calculations were performed for the available combustible–diluent–air mixtures and the results are presented in Tables 2 and 3. In those tables are also presented the standard deviations ($S_{FL,i}$) for each combustible, their lower heating values (LHV), the value of the FL at the FIP, the diluent concentration at the FIP, the equivalence ratio at the FIP (ϕ_{FIP}) and the FL of the combustible–air mixture (FL_A).

The empirical method approximates the value of k_{FL}^{av} by a correlation. As aforementioned, the combustible–diluent mixture is represented by the mole fractions y_F or y_d. In this method the LFL_A and UFL_A of the combustible–air mixture, corresponding to $y_d = 0$, are considered as known quantities.

Examination of Eqs. (6) and (15) shows that the k_{FL}^{av} depend on the values of the LHV and of the flammability limits without dilution, LFL_A and UFL_A. Therefore, the LHV and the FL presented in Tables 2 and 3, and their combinations, were used as independent variables. It was found that, to keep the variance inflation factors (VIF) low, the independent variables had to be standardized.

Another reason to use LHV, LFL_A and UFL_A for correlation is that, it will be easier to apply the method to combustibles which present more complex compositions. For instance, the Law of Le Chatelier and the Law of Burgess–Wheeler have been applied by Algunaibet et al. [49] to complex combustibles as diesel and gasoline because these rules are simple and rely on well-known independent variables.

A multiple linear regression procedure was applied in Minitab Software, considering the standardized variables shown in Eqs. (16) and (17). It was assumed that k_{FL}^{av} was a function of z_1, z_2 and their combinations, as shown in Eq. (18).

$$z_1 = \frac{LHV_i - LHV_{avg}}{S_{LHV}} \tag{16}$$

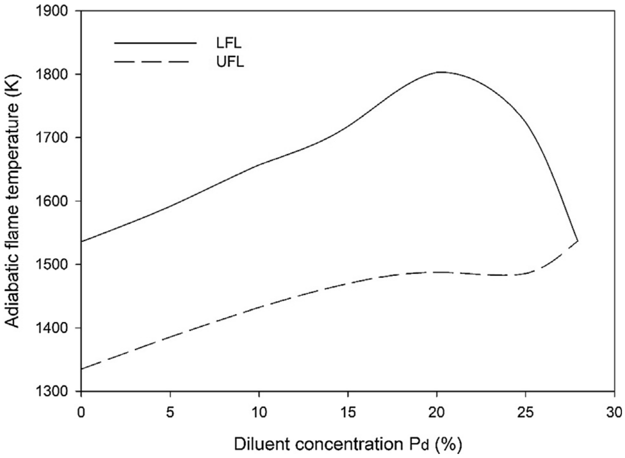


Fig. 2. Adiabatic flame temperatures at the flammability limits of propane–CO_2–air mixtures. Experimental data taken from Zabetakis [2].

$$z_2 = \frac{FL_{A,i} - FL_{A,avg}}{S_{FL}} \tag{17}$$

$$k_{FL}^{av} = f\{z_1, z_2, (z_1 z_2), z_1^2, z_2^2, (z_1 z_2)^2\} \tag{18}$$

A backward elimination method, with a significance level $\alpha = 0{,}1$, provided the correlations for the LFL and UFL of dilution with N_2 and the UFL of dilution with CO_2. On the other hand, a forward selection method with a significance level $\alpha = 0{,}25$ provided the correlation for the LFL of dilution with CO_2. The general form of the obtained correlations is shown in Eq. (19), in which L might be k_{LFL}^{av} or k_{UFL}^{av}.

$$L = a_0 + a_1 z_1 + a_2 z_2 + a_3 (z_1 z_2) + a_4 z_1^2 + a_5 z_2^2 + a_6 (z_1 z_2)^2 \tag{19}$$

The coefficients (a_i), p-values, variance inflation factors (VIF) and squared correlation coefficients (R^2) are presented in Table 4. It is important to notice that although the R^2 are not too high, the correlations represent adequately the variability of the k_{FL}^{av} as shown by the low p-values and VIFs.

In Section 6 the k_{FL}^{av} calculated by using Eq. (19) and the information of Table 4 will be applied to determine the FL of combustible–diluent–air mixtures.

3.2. Procedure for application of the empirical method to determine the FL of combustible–diluent–air mixtures

The method for estimating the FL of combustible–diluent–air mixtures can be applied by following the procedure shown below:

i. The values of LFL_A and/or UFL_A of the combustible–air mixture must be known in order to determine the value of $v_{air,A}^{FL}$ by using Eq. (1) with $y_F = 1$.
ii. The value of the mole fraction of the diluent, y_d, on the combustible–diluent mixture is also a known parameter.
iii. The value of k_{LFL}^{av} and/or k_{UFL}^{av} are determined from the correlation presented in Eq. (19) together with the information given in Table 4. The standardized independent variables must be determined by Eqs. (16) and (17).
iv. The number of moles of oxygen at the FL of the combustible–diluent–air mixture, $v_{air,d}^{FL}$, is determined by applying Eq. (6) taking into account that $y_F = 1 - y_d$.
v. Finally, the value of the LFL and/or UFL of the combustible–diluent–air mixture is obtained by applying Eq. (1) with the value of $y_F = 1 - y_d$.

As can be seen the procedure for application of the developed method is simple and can be easily implemented in any spreadsheet software or as a routine in MATLAB. A sample calculation can be found in the Supplementary Material.

4. Method to determine the diluent mole fraction at the FIP

The objective of this section is to develop a method for the determination of the diluent mole fraction at the FIP (y_d^{FIP}). The section is divided into three sub-sections: The first one is concerned with the development of the method in terms of a combustion process of a rich mixture assuming chemical equilibrium, it is also concerned with establishing the parameters that must be known in order to estimate y_d^{FIP} and providing correlations to approximate these parameters. The second one is concerned with the determination of the adiabatic flame temperature at the LFL_A ($T_{LFL,A}$) of the combustible–air mixture that must be known in order to apply the method developed in 4.1. Finally, the third sub-section is an outline of the application procedure of the developed method.

4.1. Development of the method to determine the diluent mole fraction at the FIP

The mole fractions of the combustible–diluent mixture at the FIP establish the limit for a flammable combustible–diluent–air mixture. If the mole fraction of the diluent is increased, beyond its value at the FIP (y_d^{FIP}), the mixture would be non-flammable under the considered

Table 4
Information used in Eq. (19) for the flammability limits (FL) calculation.

	Flammability Limits for dilution with N_2					
	LFL ($R^2 = 0.219$)			UFL ($R^2 = 0.538$)		
	Coefficient	VIF	p-values	Coefficient	VIF	p-values
a_0	-2.3808×10^{-1}	–	0.000	1.9958×10^{-1}	–	0.000
a_1	0.0	–	–	-6.1268×10^{-2}	4.96	0.004
a_2	3.3183×10^{-2}	1.75	0.001	5.6992×10^{-2}	1.43	0.000
a_3	0.0	–	–	-4.2119×10^{-2}	6.99	0.020
a_4	0.0	–	–	-2.7750×10^{-2}	5.01	0.003
a_5	-1.8869×10^{-2}	1.75	0.016	0.0	–	–
a_6	0.0	–	–	-8.2907×10^{-3}	5.83	0.003
	$FL_{A,avg} = 2.904$		$S_{FL} = 1.392$	$LHV_{avg} = 43.711$		$S_{LHV} = 7.818$
				$FL_{A,avg} = 15.144$		$S_{FL} = 8.394$
	Flammability limits for dilution with CO_2					
	LFL ($R^2 = 0.078$)			UFL ($R^2 = 0.426$)		
	Coefficient	VIF	p-values	Coefficient	VIF	p-values
a_0	-4.6388×10^{-1}	–	0.188	4.0034×10^{-1}	–	0.013
a_1	0.0	–	–	-6.2961×10^{-2}	2.47	0.086
a_2	0.0	–	–	4.7020×10^{-2}	1.35	0.083
a_3	0.0	–	–	0.0	–	–
a_4	1.4387×10^{-3}	1.00	0.0188	-9.4863×10^{-2}	2.04	0.007
a_5	0.0	–	–	0.0	–	–
a_6	0.0	–	–	0.0	–	–
	$LHV_{avg} = 39.569$		$S_{LHV} = 10.062$	$LHV_{avg} = 37.539$		$S_{LHV} = 11.502$
				$FL_{A,avg} = 16.144$		$S_{FL} = 10.319$

The LHV are in MJ/kg.

Table 5
Information used in Eq. (19) for the Fuel Inertization Point (FIP) calculation.

	Fuel Inertization Point for dilution with N_2					
	$LHV_{avg} = 42.057$; $S_{LHV} = 10.159$; $LFL_{A,avg} = 3.149$; $S_{LFL} = 1.889$					
	θ_d ($R^2 = 0.410$)			ϕ ($R^2 = 0.638$)		
	Coefficient	VIF	p-values	Coefficient	VIF	p-values
a_0	9.8694×10^{-1}	–	0.000	1.1825	–	0.000
a_1	5.4050×10^{-2}	1.39	0.000	-1.0775×10^{-1}	1.47	0.000
a_2	3.6254×10^{-2}	1.39	0.001	-1.6605×10^{-1}	3.05	0.000
a_3	0.0	–	–	0.0	–	–
a_4	0.0	–	–	0.0	–	–
a_5	0.0	–	–	2.4997×10^{-2}	3.15	0.006
a_6	0.0	–	–	0.0	–	–
	Fuel inertization point for dilution with CO_2					
	$LHV_{avg} = 37.292$; $S_{LHV} = 11.768$; $LFL_{A,avg} = 2.990$; $S_{LFL} = 2.372$					
	θ_d ($R^2 = 0.306$)			ϕ ($R^2 = 0.456$)		
	Coefficient	VIF	p-values	Coefficient	VIF	p-values
a_0	9.8435×10^{-1}	–	0.026	1.2354	–	0.008
a_1	6.1818×10^{-2}	2.26	0.008	-1.5933×10^{-1}	2.68	0.004
a_2	5.3154×10^{-2}	2.26	0.021	-3.6088×10^{-1}	9.55	0.001
a_3	0.0	–	–	0.0	–	–
a_4	0.0	–	–	0.0	–	–
a_5	0.0	–	–	7.7318×10^{-2}	6.10	0.004
a_6	0.0	–	–	0.0	–	–

The LHV are in MJ/kg.

temperature and pressure conditions. Therefore, it is useful to be able to estimate the value of y_d^{FIP}.

As stated in Section 3 the FIP is generally found for rich mixtures, with the exception of hydrogen and some data for methane. In order to find the value of y_d^{FIP}, two parameters must be known. These parameters can be:

a) The equivalence ratio, and,
b) The adiabatic flame temperature.

Some authors have presented approaches to the determination of the FIP. For instance, Razus et al. [50] developed a method to determine the FIP of combustible–N_2–air mixtures by a linear correlation which approximates the adiabatic flame temperature at that point (T_{FIP}). In a later work, Razus et al. [51] extended the aforementioned method to combustible–diluent–air mixtures with N_2, CO_2 or H_2O as the added diluents. In both works an average value of the equivalence ratio at the FIP (ϕ_{FIP}) had to be known or assumed. Shebeko et al. [52] postulated that a combustible–diluent–air mixture at the FIP reacts completely to form CO and H_2O, in other words, they stated that at the FIP the mixtures were stoichiometric with respect to the combustion to form CO and H_2O in the products. However, the authors performed the calculations and found that this is not an accurate approximation for most of the considered combustible–diluent–air mixtures. Therefore, the method to be developed in this section will approximate the value of ϕ_{FIP} by means of a correlation and also provide the means to estimate the value of the adiabatic flame temperature at the FIP (T_{FIP}).

The equivalence ratio at the FIP, ϕ_{FIP}, can be related to the number of moles of oxygen at the FIP, v_{air}^{FIP}, and to the combustible mole fraction at the FIP, y_F^{FIP}, as shown in Eq. (20).

$$v_{air}^{FIP} = \frac{y_F^{FIP}}{\phi_{FIP}}\left(x_C + \frac{x_H}{4} - \frac{x_O}{2}\right) = \frac{y_F^{FIP}}{\phi_{FIP}} v_{air,1}^{s} \tag{20}$$

where $v_{air,1}^{s}$ represents the number of moles of oxygen for the stoichiometric combustion of 1 mol of combustible.

Table 6
Results obtained by using k_{FL}^{av} calculated directly from experimental data.

Diluent	N	AARE (%)	R^2	ARE ≤10%	ARE 10 – 20%	ARE > 20%	ARE_{max} (%)
			Lower flammability limit				
N_2	467	1.42	0.9973	461	6	0	17.89[a]
CO_2	175	3.07	0.9894	164	8	3	23.86[b]
			Upper flammability limit				
N_2	528	3.35	0.9973	491	26	11	48.12[c]
CO_2	208	4.19	0.9959	184	16	8	39.88[c]

a) JP–4, b) Diethyl ether, c) Dimethyl ether.

At the FIP there is enough oxygen as to form CO, CO_2 and H_2O. Therefore, the combustion reaction shown in Eq. (21) can be adopted.

$$y_F^{FIP} C_{xC}H_{xH}O_{xO} + y_d^{FIP} M_d + v_{air}^{FIP}(O_2 + 3{,}76N_2) \rightarrow \begin{matrix} n_{CO_2}CO_2 + n_{CO}CO + n_{H_2O}H_2O \\ + n_{H_2}H_2 + 3.76 v_{air}^{FIP} N_2 + y_d^{FIP} M_d \end{matrix} \tag{21}$$

A more detailed discussion on the assumption of this global reaction can be found in previous works by Mendiburu et al. [29,30]. The assumptions presented in Section 2 are also adopted in the following development.

The mass conservation law yields Eqs. (22)(24), and, the energy conservation law yields Eq. (25).

$$y_F^{FIP} x_C = n_{CO} + n_{CO_2} \tag{22}$$

$$y_F^{FIP} \frac{x_H}{2} = n_{H_2O} + n_{H_2} \tag{23}$$

$$y_F^{FIP} x_O = n_{CO} + 2n_{CO_2} + n_{H_2O} - 2v_{air}^{FIP} \tag{24}$$

$$y_F^{FIP} h_F + y_d^{FIP} h_{d,R} + v_{air}^{FIP}(h_{O_2,R} + 3.76 h_{N_2,R}) = \begin{matrix} n_{CO_2}h_{CO_2} + n_{CO}h_{CO} + n_{H_2O}h_{H_2O} \\ + n_{H_2}h_{H_2} + 3.76 v_{air}^{FIP} h_{N_2} + y_d^{FIP} h_{d,P} \end{matrix} \tag{25}$$

where the subscripts R and P refer to reactants and products, respectively. In accordance with assumption vi (see Section 2) an equilibrium reaction must be adopted. The water–gas homogeneous reaction shown in Eq. (26) is adopted and the equilibrium equation obtained from it is given in Eq. (27).

$$H_2O + CO \leftrightarrow CO_2 + H_2 \tag{26}$$

$$n_{CO_2} n_{H_2} = K_{eq} n_{H_2O} n_{CO} \tag{27}$$

where, K_{eq} is the equilibrium constant calculated at the adiabatic flame temperature. The procedures applied to determine K_{eq} and the other thermodynamic properties will be presented in Section 5.

Using Eqs. (22) to (24), the number of moles of CO_2, H_2O and H_2 are expressed as functions of the number of moles of CO and the combustible mole fraction y_F^{FIP}. The obtained expressions are presented in Eqs. (S.1) to (S.3) of the Supplementary Material.

Then, substitution of those expressions and of Eq. (20) into Eq. (25), and some rearrangements, yield n_{CO} in terms of y_F^{FIP} as shown in Eq. (28).

$$n_{CO} = y_F^{FIP} m + n \tag{28}$$

where

$$m = \frac{\left(\begin{matrix} h_F + \frac{v_{air,1}^{s}}{\phi_{FIP}}(h_{ar,R} - 3.76h_{N_2} + 2h_{H_2} - 2h_{H_2O}) - \frac{x_H}{2}h_{H_2} \\ + x_C(2h_{H_2O} - 2h_{H_2} - h_{CO_2}) + x_O(h_{H_2} - h_{H_2O}) + (h_{d,P} - h_{d,R}) \end{matrix}\right)}{h_{CO} - h_{CO_2} + h_{H_2O} - h_{H_2}} \tag{29}$$

$$n = \frac{h_{d,R} - h_{d,P}}{h_{CO} - h_{CO_2} + h_{H_2O} - h_{H_2}} \tag{30}$$

Table 7
Results obtained with the empirical method developed in Section 3.

Diluent	Set	N	AARE (%)	R^2	ARE $\leq 10\%$	ARE 10–20%	ARE $> 20\%$	ARE_{max} (%)
				Lower flammability limit				
N_2	Corr.	340	3.89	0.9877	317	22	1	22.64
	Pred.	115	4.40	0.9583	106	6	3	23.73
	Total	455	4.02	0.9833	423	28	4	23.73
CO_2	Corr.	125	7.34	0.9712	93	22	10	39.72
	Pred.	41	6.02	0.9250	32	8	1	24.77
	Total	166	7.01	0.9660	125	30	11	39.72
				Upper flammability limit				
N_2	Corr.	380	4.14	0.9914	344	27	9	32.91
	Pred.	134	3.26	0.9945	127	5	2	20.26
	Total	514	3.91	0.9920	471	32	11	32.91
CO_2	Corr.	146	5.85	0.9782	111	30	5	23.92
	Pred.	51	4.75	0.9809	46	5	0	21.76
	Total	197	5.57	0.9792	157	35	5	23.92

In the previous steps, Eqs. (22) to (24), were rearranged to express the number of moles of CO_2, H_2O and H_2 in terms of the number of moles of CO and the combustible mole fraction. Afterwards, the number of moles n_{CO_2}, n_{H_2O} and n_{H_2} are expressed as functions of y_F^{FIP} alone by employing Eq. (28). Finally, substitution of these expressions into Eq. (27), and some rearrangements, yield the expression shown in Eq. (31).

$$a_v(y_F^{FIP})^2 + b_v y_F^{FIP} + c_v = 0 \tag{31}$$

where

$$a = 1-K_{eq} \tag{32}$$

$$a_v = am^2 + 2\frac{v_{ar,1}^s}{\phi_{FIP}}(am-x_C) + x_C[2x_C-(2a+1)m] + x_O(am-x_C) + \frac{x_H}{2}(x_C-m) \tag{33}$$

$$b_v = 2amn + 2an\frac{v_{ar,1}^s}{\phi_{FIP}} - (2a+1)nx_C + anx_O - n\frac{x_H}{2} \tag{34}$$

$$c_v = an^2 \tag{35}$$

In order to obtain a solution for Eq. (31) it is necessary to know an approximate value of ϕ_{FIP} and also of the adiabatic flame temperature at FIP, T_{FIP}. Therefore, the value of T_{FIP} is related to that of the adiabatic flame temperature at the LFL of the combustible–air mixture ($T_{LFL,A}$) by a parameter called θ_d defined in Eq. (36).

$$\theta_d = \frac{T_{FIP}}{T_{LFL,A}} \tag{36}$$

In this section the values of θ_d and ϕ will be correlated by using some of the available experimental data. There are 52 experimental data for combustible–N_2–air mixtures at the FIP for which the values of θ_d and ϕ can be determined. On the other hand, there are 30 of these values for combustible–CO_2–air mixtures. The behavior shown by hydrogen was different from that shown by other compounds. Therefore, it was not considered in the correlations to be shown on this section. In the case of H_2 the FIP is presented in Tables 2 and 3.

The criteria to form the correlation sets was that around 20% of the combustible–diluent–air mixtures at the FIP would be left for the prediction sets. Therefore, 42 data for dilution with N_2 and 23 data for dilution with CO_2 were considered for the correlation sets. Random numbers were generated using Microsoft Excel for each combustible–diluent–air mixture at the FIP, and these were ordered from greater to lesser values. Then, the first 42 were selected for the correlation set of dilution with N_2 and the first 23 for the correlation set of dilution with CO_2.

The obtained correlations have the same form presented in Eq. (19), where L might be θ_d or ϕ. A backward elimination method, with a significance level $\alpha = 0{,}1$, was applied in Minitab Software to obtain the coefficients (a_i), p-values, variance inflation factors (VIF) and squared correlation coefficients (R^2) presented in Table 5. It is important to notice that although the R^2 are not too high, the correlations represent adequately the variability of θ_d and ϕ as shown by the low p-values and VIFs.

The correlation shown in Eq. (19) is also applied to the case of carbon monoxide. However, on this case there is no H_2 or H_2O in the products, and, because of this, the water-gas homogeneous reaction is not applicable for equilibrium considerations. In the case of CO, it is assumed that all the oxygen reacts with part of the CO to form CO_2 and the remaining CO appears unreacted on the products. Thus, on the case of carbon monoxide the energy conservation equation is given by Eq. (37) and the value of y_F^{FIP} is determined by solving Eq. (38).

In order to obtain Eq. (38) from Eq. (37), it is necessary to substitute Eq. (20) into Eq. (37), to use the fact that $y_d^{FIP} = 1-y_F^{FIP}$, and to perform some rearrangements.

$$y_F^{FIP}h_F + y_d^{FIP}h_{d,R} + v_{air}^{FIP}h_{ar,R} = 2v_{air}^{FIP}h_{CO_2} + (y_F-2v_{air}^{FIP})h_{CO} + 3.76v_{air}^{FIP}h_{N_2} + y_d^{FIP}h_{d,P} \tag{37}$$

$$y_{F,CO}^{FIP} = \frac{h_{d,P}-h_{d,R}}{h_F + \frac{v_{ar,1}^s}{\phi_{FIP}}(h_{ar,R} + 2h_{CO}-2h_{CO_2}-3{,}76h_{N_2})-h_{CO} + h_{d,P}-h_{d,R}} \tag{38}$$

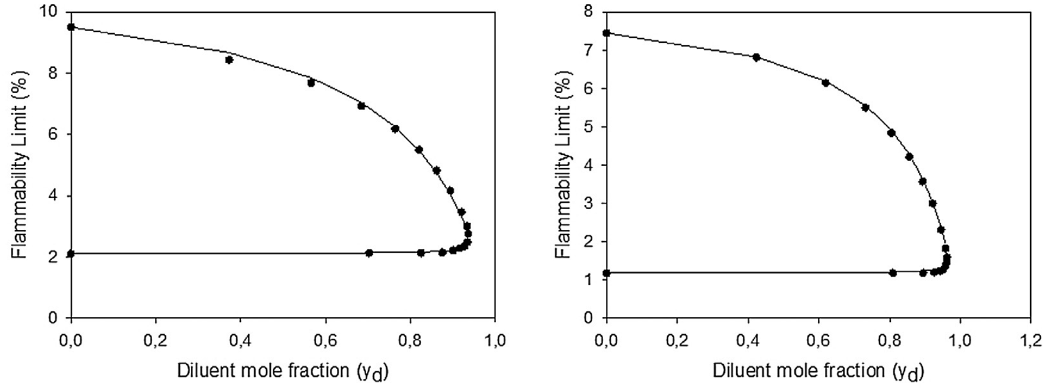
4.2. Determination of the adiabatic flame temperature at the LFL

In order to obtain the value of T_{FIP} it is necessary to determine the values of θ_d and $T_{LFL,A}$. The value of θ_d is determined by Eq. (19) together with the parameters given in Table 5. On the other hand, the value of the $T_{LFL,A}$ is obtained by considering the combustion process of the combustible–air mixture at the LFL_A, for which the complete combustion reaction shown in Eq. (39) is adopted.

$$C_{x_C}H_{x_H}O_{x_O} + v_{air,A}^{LFL}(O_2 + 3{,}76N_2) \rightarrow x_C CO_2 + \frac{x_H}{2}H_2O + (v_{air,A}^{LFL}-v_{air}^s)O_2 + 3.76v_{air,A}^{LFL}N_2 \tag{39}$$

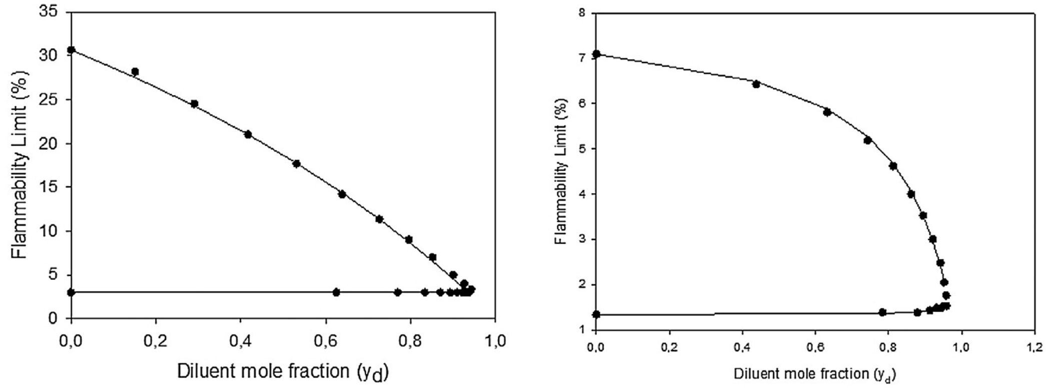
The energy conservation equation for this reaction is shown in Eq. (40). In the case of O_2 and N_2 the subscripts R and P are used to differentiate between the enthalpies of these species in the reactants and in the products, respectively.

$$h_F + v_{air,A}^{LFL}(h_{O_2,R} + 3.76h_{N_2,R}) = x_C h_{CO_2} + \frac{x_H}{2}h_{H_2O} + (v_{air,A}^{LFL}-v_{air}^s)h_{O_2,P} + 3.76v_{air,A}^{LFL}h_{N_2,P} \tag{40}$$



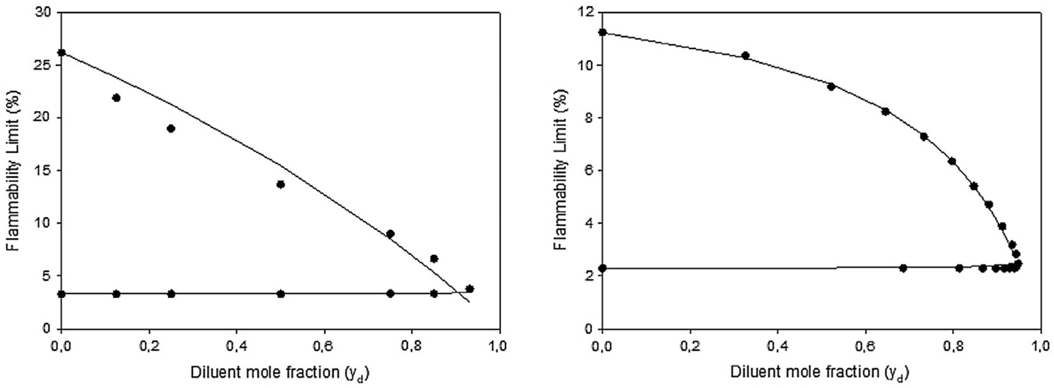
Propane [2]

Hexane [2]



Ethylene [43]

Gasoline 100/130 [46]



Dimethyl ether [25]

0.4 Ethane and 0.6 Propane [43]

● Experimental Flammability limits
—— Calculated Flammability limits

Fig. 3. Comparison of experimental and calculated flammability limits for combustible–N_2–air mixtures at 25 °C and 1 atm.

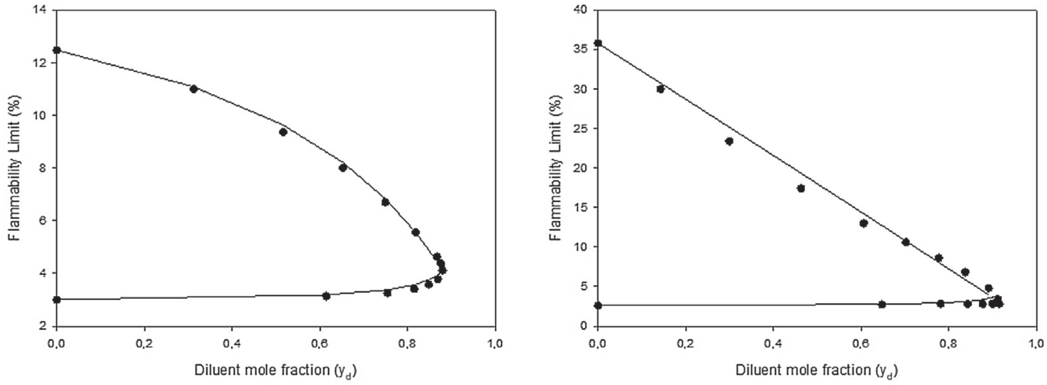
The adiabatic flame temperature at the LFL_A ($T_{LFL,A}$) is obtained by solving Eq. (40). In order to do so it is possible to apply the Newton–Raphson method described in textbooks on numerical methods [53,54].

In the present work a routine was written in MATLAB in order to obtain the values of $T_{LFL,A}$. The obtained adiabatic flame temperatures are provided in Tables 9 and 10 (to be introduced later).

4.3. Procedure for the application of the method to determine the diluent mole fraction at the FIP

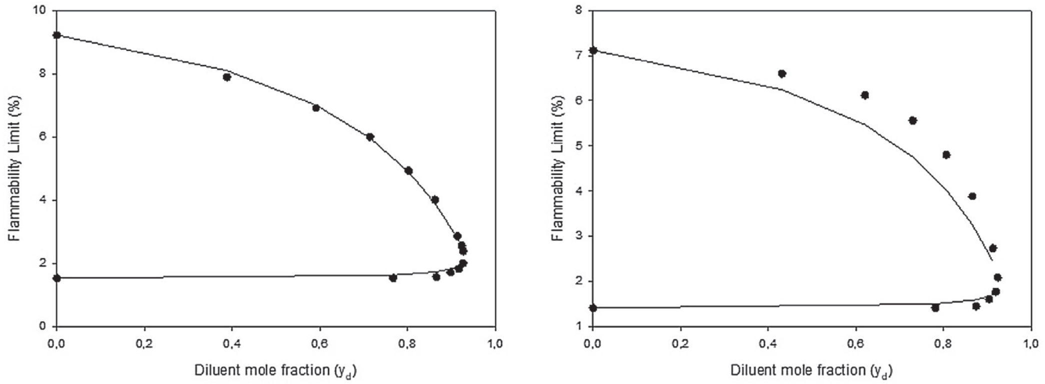
The method aims to determine the value of y_d^{FIP}, this parameter can be estimated by applying the following procedure:

i. The value of $T_{LFL,A}$ is obtained by solving Eq. (40).
ii. The approximated values of θ_d and ϕ_{FIP} are obtained by applying the correlation shown in Eq. (19) together with the parameters provided in Table 5.
iii. The approximated value of T_{FIP} is obtained from Eq. (36) by using



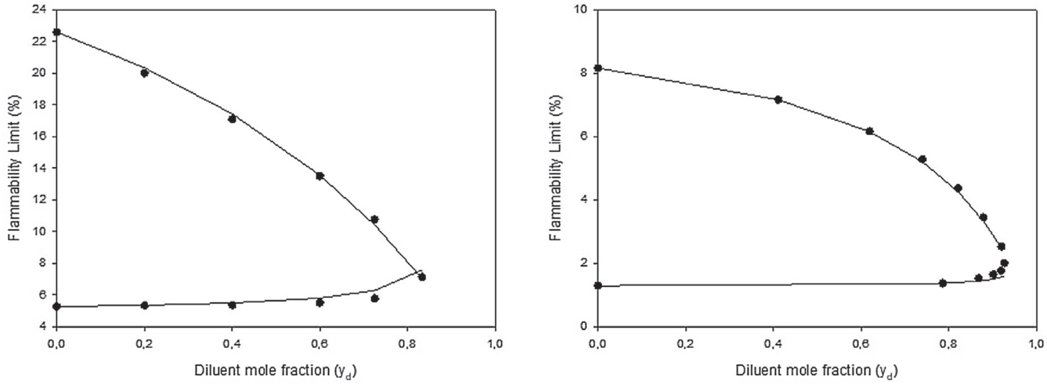
Ethane [2]

Ethylene [2]



3-Methyl-1-butene [2]

Benzene [2]



Methyl formate [26]

JP-4 [46]

● Experimental Flammability limits
— Calculated Flammability limits

Fig. 4. Comparison of experimental and calculated flammability limits for combustible–CO_2–air mixtures at 25 °C and 1 atm.

the values of $T_{LFL,A}$ and θ_d, obtained in the previous steps.

iv. The equilibrium constant and enthalpies are determined by applying the procedures explained in Section 5, using the value of T_{FIP} for the products and 298.15 K for the reactants.

v. The parameters m and n are obtained from Eqs. (29) and (30). Then, the parameters a, a_v, b_v and c_v are determined by Eqs. (32) to (35).

vi. The value of y_F^{FIP} is obtained from Eq. (31). Then, the value of y_d^{FIP} is obtained by the relation: $y_d^{FIP} = 1 - y_F^{FIP}$. Since Eq. (31) is a quadratic equation, the correct value of y_F^{FIP} is that for which the number of moles of CO_2, H_2O and H_2 are all positive.

vii. In the case of CO, the steps iv and vi are omitted and the value of y_F^{FIP} is directly obtained from Eq. (38). Then, the value of y_d^{FIP} is obtained by the relation: $y_d^{FIP} = 1 - y_F^{FIP}$.

The procedure for application of this method is also simple and can be implemented in any spreadsheet software or as a routine in MATLAB. A sample calculation can be found in the Supplementary Material.

5. Thermodynamic properties

In the present study all the thermodynamic properties were determined by using the NASA–Glenn coefficients given by McBride et al. [55]. The absolute enthalpies and entropies in mole basis are determined by Eqs. (41) and (42), respectively. On the other hand, the

Table 8
Comparison of the overall accuracy of the developed empirical method with other available methods.

Reference	Lower Flammability Limit						Upper Flammability Limit					
	N	*AARE* (%)	R^2	*ARE* ≤10%	*ARE* 10 – 20%	*ARE* > 20%	N	*AARE* (%)	R^2	*ARE* ≤10%	*ARE* 10 – 20%	*ARE* > 20%
						Combustible–N_2–air mixtures						
This work	455	4.02	0.9833	423	28	4	514	3.91	0.9920	471	32	11
Kondo et al. [25]	455	4.44	0.9795	415	35	5	514	9.87	0.9302	350	93	71
Wang et al. [57]	–	–	–	–	–	–	514	4.39	0.9729	456	42	16
						Combustible–CO_2–air mixtures						
This work	166	7.01	0.9660	125	30	11	197	5.57	0.9792	157	35	5
Kondo et al. [26]	166	6.92	0.9651	128	23	15	197	14.41	0.8600	99	56	42
Wang et al. [57]	–	–	–	–	–	–	197	5.65	0.9557	167	19	11

Gibbs free energies in mole basis at the standard–state pressure, are determined by Eq. (43).

$$\frac{h(T)}{RT} = -\frac{a_1}{T^2} + a_2\frac{\ln T}{T} + a_3 + a_4\frac{T}{2} + a_5\frac{T^2}{3} + a_6\frac{T^3}{4} + a_7\frac{T^4}{5} + \frac{b_1}{T} \tag{41}$$

$$\frac{s(T)}{R} = -a_1\frac{T^{-2}}{2} - a_2T^{-1} + a_3\ln T + a_4T + a_5\frac{T^2}{2} + a_6\frac{T^3}{3} + a_7\frac{T^4}{4} + b_2 \tag{42}$$

$$\frac{g^0(T)}{RT} = \frac{h(T)}{RT} - \frac{s(T)}{R} \tag{43}$$

where, R is the universal gas constant. The equilibrium constant for the water–gas homogeneous reaction is determined by Eq. (44).

$$K_{eq} = \exp(-\Delta G_T^0/RT) = \exp(-[g^0_{T,CO_2} - g^0_{T,CO} - g^0_{T,H_2O}]/RT) \tag{44}$$

where ΔG_T^0 is the standard–state Gibbs function change.

6. Results and discussions

The validation of the developed methods will be provided in terms of the absolute value of the relative errors (ARE), the average of the relative errors (AARE) and the correlation coefficients (R^2), presented in Eqs. (45) to (47).

$$ARE = \frac{|FL_{calc} - FL_{\exp}|}{FL_{\exp}}100\% \tag{45}$$

$$AARE = \frac{1}{N}\sum_{i=1}^{N} ARE_i \tag{46}$$

$$R^2 = 1 - \frac{SSE}{SST} \tag{47}$$

where SSE is the sum of squares of the errors and SST is the total sum of squares as defined by Montgomery [56]:

$$SEE = \sum_{i=1}^{N}(FL_{calc,i} - FL_{\exp,i})^2 \tag{48}$$

$$SST = \sum_{i=1}^{N}(FL_{\exp,i})^2 - \frac{\left(\sum_{i=1}^{N} FL_{\exp,i}\right)^2}{N} \tag{49}$$

Three validations are necessary:

a) Validation to show that k_{FL}^{av} can be used to determine the FL (as stated in Section 2),
b) Validation of the empirical method to determine the FL (developed in Section 3),
c) Validation of the method to determine y_d^{FIP} (developed in Section 4).

6.1. Validation to show that k_{FL}^{av} can be used to determine the FL

The experimental data considered 642 data at the LFL and 736 data at the UFL. These data include dilution with N_2 and CO_2. The FLs of the combustible–diluent–air mixtures were estimated by using the k_{FL}^{av} which were determined from the experimental data and were presented in Tables 2 and 3. The obtained results are shown in Table 6.

The AAREs are lower than 4.2% and the R^2 are higher than 0.989 in all cases. Only 3 mixtures presented AREs above 20% at the LFL while 19 did at the UFL. A total of 14 mixtures presented AREs between 10 and 20% at the LFL while 37 did at the UFL. A number of 625 mixtures presented AREs below 10% at the LFL while 675 did at the UFL.

At the LFL the maximum ARE of 23.86% corresponds to a diethyl ether–CO_2–air mixture [2], being the experimental and calculated values of 2.59% and 1.97%, respectively. At the UFL the maximum ARE of 48.12% corresponds to a dimethyl ether–N_2–air mixture [25], being the experimental and calculated values of 3.78% and 1.96%, respectively. As aforementioned only a few compounds presented AREs above 20%.

From the information regarding the AARE, AREs and R^2 it is concluded that the values of k_{FL}^{av} can be used to determine the FL of combustible–diluent–air mixtures.

6.2. Validation of the empirical method to determine the FL of combustible–diluent–air mixtures

The results obtained with the empirical method developed in Section 3 are presented in Table 7. Some results obtained for combustible–diluent–air mixtures are depicted in Figs. 3 and 4 to show the accuracy of the method. Also, the results obtained for all the combustible–diluent–air mixtures, considered in this study, are depicted in Figs. S.1 to S.17 of the Supplementary material.

As can be observed on Figs. 3 and 4 the developed method follows the trend presented by the experimental data, i.e., the LFL is slightly increased and the UFL is decreased with the increase of the diluent mole fraction on the combustible–diluent mixture. The higher deviations on these figures are for dimethyl ether diluted with N_2 and for benzene diluted with CO_2. In both cases the deviations appear at the UFL and the AREs are lower than 20%. Also, on Figs. 3 and 4 it is shown that the flammability limits of hydrocarbon mixtures and more complex fuels as 0.4 ethane with 0.6 propane, gasoline 100/130 and JP-4 are correctly determined by the developed method. The same conclusion can be drawn by inspection of the Figures provided on the Supplementary Material.

The combustible–N_2–air mixtures present AAREs of 3.89%, 4.40% and 4.02% for the correlation, prediction and total sets, respectively, at the LFL. On the other hand, present AAREs of 4.14%, 3.26% and 3.91% for the correlation, prediction and total sets, respectively, at the UFL. The values of R^2 range between 0.9583 and 0.9945.

The combustible–CO_2–air mixtures present AAREs of 7.34%, 6.02% and 7.01% for the correlation, prediction and total sets, respectively, at the LFL. On the other hand, present AAREs of 5.85%, 4.75% and 5.57%

Table 9
Results obtained with the method developed in Section 4 for combustible–N_2–air mixtures.

Compound	Formula	$T_{LFL,A}$ (K)	y_d Exp.	y_d Calc.	*ARE* (%)	Refs.
Correlation Set						
Methane	CH_4	1482.4	0.8469	0.8856	4.57	[2]
Methane	CH_4	1543.4	0.8707	0.8680	0.31	[43]
Ethane	C_2H_6	1536.1	0.9215	0.9208	0.07	[2]
Ethane	C_2H_6	1536.1	0.9371	0.9208	1.74	[43]
Propane	C_3H_8	1535.8	0.9329	0.9378	0.53	[2]
Propane	C_3H_8	1535.8	0.9493	0.9379	1.21	[43]
Butane	C_4H_{10}	1638.2	0.9375	0.9363	0.13	[2]
Butane	C_4H_{10}	1606.9	0.9510	0.9404	1.11	[43]
Pentane	C_5H_{12}	1492.4	0.9511	0.9602	0.96	[2]
Ethylene	C_2H4	1336.1	0.9314	0.9474	1.72	[2]
Ethylene	C_2H_4	1474.5	0.9424	0.9344	0.86	[43]
isoButylene	C_4H_8	1603.1	0.9361	0.9437	0.81	[2]
3-Methyl-1-Butene	C_5H_{10}	1651.9	0.9593	0.9472	1.26	[2]
Butadiene	C_4H_6	1675.3	0.9487	0.9402	0.90	[2]
Benzene	C_6H_6	1581.9	0.9552	0.9563	0.12	[2]
Methane + propane	$0.4CH_4 + 0.6C_3H_8$	1511.2	0.9324	0.9277	0.50	[43]
Methane + propane	$0.6CH_4 + 0.4C_3H_8$	1534.6	0.9196	0.9152	0.48	[43]
Methane + propane	$0.8CH_4 + 0.2C_3H_8$	1522.4	0.8986	0.9051	0.73	[43]
Ethane + propane	$0.2C_2H_6 + 0.8C_3H_8$	1539.0	0.9466	0.9347	1.26	[43]
Ethane + propane	$0.4C_2H_6 + 0.6C_3H_8$	1490.1	0.9433	0.9377	0.60	[43]
Ethane + propane	$0.6C_2H_6 + 0.4C_3H_8$	1508.5	0.9399	0.9323	0.81	[43]
Methane + ethylene	$0.2CH_4 + 0.8C_2H_4$	1434.3	0.9335	0.9335	0.00	[43]
Methane + ethylene	$0.4CH_4 + 0.6C_2H_4$	1496.4	0.9244	0.9202	0.45	[43]
Methane + ethylene	$0.6CH_4 + 0.4C_2H_4$	1460.8	0.9148	0.9176	0.31	[43]
Methane + ethylene	$0.8CH_4 + 0.2C_2H_4$	1486.7	0.8957	0.9053	1.08	[43]
Ethylene + propylene	$0.2C_2H_4 + 0.8C_3H_6$	1546.7	0.9444	0.9383	0.64	[43]
Ethylene + propylene	$0.4C_2H_4 + 0.6C_3H_6$	1544.6	0.9406	0.9360	0.49	[43]
Ethylene + propylene	$0.6C_2H_4 + 0.4C_3H_6$	1489.6	0.9421	0.9390	0.33	[43]
Ethylene + propylene	$0.8C_2H_4 + 0.2C_3H_6$	1423.2	0.9447	0.9426	0.22	[43]
Methanol	CH_4O	1535.5	0.8494	0.8646	1.79	[2]
Ethanol	C_2H_6O	1524.3	0.8998	0.9169	1.90	[2]
Dimethyl Ether	C_2H_6O	1564.5	0.9188	0.9196	0.08	[2]
Diethyl Ether	$C_4H_{10}O$	1605.3	0.9426	0.9416	0.11	[2]
Methyl Formate	$C_2H_4O_2$	1728.3	0.8685	0.8611	0.85	[2]
Methyl Acetate	$C_3H_6O_2$	1565.6	0.9056	0.9184	1.42	[2]
Acetone	C_3H_6O	1494.7	0.9163	0.9359	2.14	[2]
Methyl Ethyl Ketone	C_4H_8O	1593.0	0.9416	0.9380	0.37	[2]
Carbon Monoxide	CO	1378.1	0.7865	0.7783	1.03	[46]
Methane	CH_4	1461.9	0.8820	0.8908	1.00	[25]
Ethylene	C_2H_4	1385.0	0.9461	0.9431	0.31	[25]
Propylene	C_3H_6	1510.8	0.9460	0.9443	0.18	[25]
iso-Butane	C_4H_{10}	1565.4	0.9550	0.9449	1.06	[44]
Prediction Set						
Propane	C_3H_8	1496.0	0.9500	0.9425	0.79	[25]
Hexane	C_6H_{14}	1594.0	0.9579	0.9567	0.12	[2]
Cyclopropane	C_3H_6	1617.6	0.9269	0.9344	0.80	[2]
Propylene	C_3H_6	1624.7	0.9333	0.9317	0.18	[2]
Propylene	C_3H_6	1591.8	0.9375	0.9357	0.20	[43]
1-Butene	C_4H_8	1480.7	0.9445	0.9564	1.25	[2]
Methane + propane	$0.2CH_4 + 0.8C_3H_8$	1515.1	0.9410	0.9344	0.69	[43]
Ethane + propane	$0.8C_2H_6 + 0.2C_3H_8$	1433.6	0.9425	0.9378	0.50	[43]
Dimethyl Ether	C_2H_6O	1536.6	0.9310	0.9234	0.82	[25]
Methyl Formate	$C_2H_4O_2$	1620.4	0.8960	0.8863	1.08	[25]
Correlation Set	**AARE (%)**	**0.87**				
Prediction Set	**AARE (%)**	**0.64**				
Total Set	**AARE (%)**	**0.82**				

for the correlation, prediction and total sets, respectively, at the UFL. The values of R^2 range between 0.9250 and 0.9809.

At the LFL, the 88.24% of the calculated FLs present AREs below 10% and just 2.41% present AREs above 20%. On the other hand, at the UFL, the 88.32% of the calculated FLs present AREs below 10% and just 2.26% present AREs above 20%.

In Table 8 the developed method is compared with the methods developed by Wang et al. [57], to estimate the UFL, and by Kondo et al. [25,26], to estimate both the LFL and UFL. These two methods were selected for comparison because they are also based on empirical equations and can be applied straightforwardly to the available data. The comparison of the performance in terms of the R^2 and AARE at the LFL shows that the developed method has a better performance than the method by Kondo et al. [25,26]. Also, at the UFL the developed method shows a better performance than the methods by Wang et al. [57] and by Kondo et al. [25,26]. Although, the methods of Kondo et al. [25,26] showed good accuracy at the LFL and that of Wang et al. [57] showed good accuracy at the UFL.

Therefore, the method developed in Section 3 shows good accuracy and can be applied to determine the FLs of combustible–diluent–air mixtures when dilution with N_2 and CO_2 is being considered. Also, this method can be extended to other diluents when experimental data are available.

Table 10
Results obtained with the method developed in Section 4 for combustible–CO_2–air mixtures.

Compound	Formula	$T_{LFL,A}$ (K)	y_d Exp.	y_d Calc.	*ARE* (%)	Refs.
Correlation Set						
Ethane	C_2H_6	1536.1	0.8762	0.8780	0.21	[2]
Propane	C_3H_8	1496.0	0.9150	0.8995	1.69	[26]
Propane	C_3H_8	1535.8	0.8787	0.8921	1.52	[2]
Butane	C_4H_{10}	1638.2	0.8950	0.8816	1.50	[2]
Hexane	C_6H_{14}	1594.0	0.9282	0.9107	1.89	[2]
Ethylene	C_2H_4	1336.1	0.8905	0.9154	2.80	[2]
Ethylene	C_2H_4	1385.0	0.9130	0.9095	0.39	[26]
Propylene	C_3H_6	1624.7	0.8797	0.8854	0.65	[2]
isoButylene	C_4H_8	1603.1	0.8917	0.8974	0.65	[2]
1-Butene	C_4H_8	1480.7	0.9133	0.9200	0.73	[2]
3-Methyl-1-Butene	C_5H_{10}	1651.9	0.9232	0.8983	2.70	[2]
Butadiene	C_4H_6	1675.3	0.9142	0.8942	2.19	[2]
Cyclopropane	C_3H_6	1617.6	0.8818	0.8898	0.91	[2]
Benzene	C_6H_6	1581.9	0.9120	0.9145	0.27	[2]
Methanol	CH_4O	1535.5	0.7624	0.8043	5.49	[2]
Ethanol	C_2H_6O	1524.3	0.8378	0.8630	3.01	[2]
Diethyl Ether	$C_4H_{10}O$	1605.3	0.8926	0.8875	0.56	[2]
Methyl Acetate	$C_3H_6O_2$	1565.6	0.8280	0.8553	3.30	[2]
Acetone	C_3H_6O	1494.7	0.8599	0.8853	2.96	[2]
Methyl Ethyl Ketone	C_4H_8O	1593.0	0.9067	0.8819	2.73	[2]
Dimethyl Ether	C_2H_6O	1536.6	0.8820	0.8733	0.99	[26]
Methyl Formate	$C_2H_4O_2$	1620.4	0.8330	0.8220	1.31	[26]
Carbon Monoxide	CO	1378.1	0.6543	0.6354	2.89	[46]
Prediction Set						
Methane	CH_4	1482.4	0.7607	0.8124	6.79	[2]
Methane	CH_4	1461.9	0.7940	0.8210	3.40	[26]
iso-Butane	C_4H_{10}	1565.4	0.9220	0.8969	2.72	[26]
Pentane	C_5H_{12}	1492.4	0.9085	0.9216	1.44	[2]
Propylene	C_3H_6	1510.8	0.9130	0.9047	0.91	[26]
Dimethyl Ether	C_2H_6O	1564.5	0.8588	0.8678	1.05	[2]
Methyl Formate	$C_2H_4O_2$	1728.3	0.7950	0.7876	0.93	[2]
Correlation Set	**AARE (%)**	**1.80**				
Prediction Set	**AARE (%)**	**2.46**				
Total Set	**AARE (%)**	**1.95**				

Table 11
Comparison of the method developed in Section 4 to determine y_d^{FIP} with other available methods.

Method	N	AARE
Combustible–N_2–air mixtures		
This work	52	0.82
Bade et al. [37]	7	2.30
Liaw et al. [39]	6	1.28
Hansen and Crowl[a,c] [36]	11	15.30
Hansen and Crowl[b,c] [36]	38	12.82
Combustible–CO_2–air mixtures		
This work	30	1.95
Bade et al. [37]	7	6.83
Liaw et al. [39]	6	3.25

[a] Thermodynamic method.

[b] Empirical method.

[c] The method actually determines the limiting oxygen concentration.

6.3. Validation of the method to determine y_d^{FIP}

The values of the diluent mole fractions at the FIP were determined by using the method described in Section 4. The results for dilution with N_2 and CO_2 are presented in Tables 9 and 10, respectively. In those tables, the AAREs for dilution with N_2 and CO_2 were 0.82% and 1.95%, respectively. As aforementioned, the knowledge of y_d^{FIP} allows to establish the FIP of combustible–diluent–air mixtures.

In all but two cases, the AREs were below 5% which means that the method is very accurate. On the case of the combustible–N_2–air mixtures 50 compounds presented AREs of less than 2% and only 2 presented an ARE between 2% and 5%. On the other hand, on the case of the combustible–CO_2–air mixtures 18 compounds presented ARES of less than 2% and 12 compounds presented AREs between 2% and 7%. All this information can be observed in Tables 9 and 10. The values of $T_{LFL,A}$ are also provided in those tables.

The developed method is also compared with other available methods in Table 11. It is observed that the developed method considered a larger number of data and also presents the lower AAREs for dilution with N_2 and CO_2.

Therefore, the developed method can be applied to determine the diluent mole fraction at the FIP of combustible–diluent–air mixtures when the diluents are N_2 or CO_2. This method is simple and relies on basic combustion theory and empirical correlations. Also, the method can be easily extended to other diluents.

7. Conclusions

It was demonstrated that a factor called k_{FL}^{av} can represent the variation of the FLs of combustible–diluent–air mixtures. The diluent species considered on this study were N_2 and CO_2.

An empirical method to determine the FLs of combustible–diluent–air mixtures, at 25 °C and 1 atm, was developed. This method showed good accuracy and can be applied by knowing the LHV of the combustible and the FL of the combustible–air mixture (without diluent).

An empirical method to determine the diluent mole fraction at the Fuel Inertization Point (FIP), at 25 °C and 1 atm, was developed. This method also showed good accuracy when applied to combustible–N_2–air mixtures and combustible–CO_2–air mixtures.

The developed methods are simple and can be easily implemented in spreadsheet software or any other platform.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2018.03.18.

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