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Flammability limits temperature dependence of pure compounds in air at atmospheric pressure

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ABSTRACT

The objective of the present work is to study the temperature dependence of the flammability limits for pure compounds, and to develop a methodology to determine these limits in air at atmospheric pressure and at different initial temperatures of the mixture.

A method to determine the lower flammability limits in those conditions was developed and compared with other methods available in the literature. The developed method shows an average absolute relative error of 3.25% and a squared correlation coefficient of 0.9928. Particularly, in the case of compounds with more than 5 carbon atoms, the method presents better accuracy than other available methods.

Likewise, a method to determine the upper flammability limits was developed and compared with other widely accepted method. In this case, the developed methodology shows an average absolute relative error of 3.60% and a squared correlation coefficient of 0.9957, showing better accuracy than the available method.

1. Introduction

A flammable gas forming a mixture with air can be flammable or non-flammable in the presence of an ignition source. In a flammable mixture a flame can propagate through it while in a non-flammable mixture a flame cannot propagate. Given certain conditions of temperature and pressure, the key parameter that defines the flammability condition of a mixture is its composition.

A stoichiometric mixture of a flammable compound and air is always flammable. By slightly increasing the air to flammable gas ratio above the stoichiometric condition, a flammable lean mixture is obtained; this process can be repeated until the mixture becomes non-flammable. At this condition the mixture would be too lean as to sustain flame propagation. The leaner composition of the mixture which can sustain flame propagation is known as the lower flammability limit (LFL) and it is characterized by the mole percentage of the flammable gas in that mixture.

On the other hand, by slightly decreasing the air to flammable gas ratio below the stoichiometric condition, a flammable rich mixture is obtained; this process can be repeated until the mixture becomes non-flammable. At this point the mixture is too rich to sustain flame propagation. The richest composition of the mixture which can sustain flame propagation is known as the upper flammability limit (UFL) and it is also characterized by the mole percentage of the flammable gas in that mixture.

Other parameters that affect the flammability limits are the temperature and pressure conditions at which the process occurs. If one of these parameters is held constant and the other is varied, the values of the LFL and UFL will change.

The importance of determining the flammability limits (FL) of a flammable gas relies on the safety operation of several industrial processes; the knowledge of the FL is used to adopt safety measures. Experimental data on the FL for several compounds is available on the literature, mainly at atmospheric pressure and reference temperature conditions. However, there are a large number of flammable compounds for which experimental data of the FL are not known. Furthermore, the FL depends on the pressure and temperature conditions, in which cases fewer experimental data is available.

In the present work the temperature dependence of the flammability limits is studied considering atmospheric pressure. The aim of the study is to develop an accurate methodology to determine the LFL and UFL in air at atmospheric pressure and at different initial mixture temperatures. There are several methods for the

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Abbreviations

FL	Flammability limit
LFL	Lower flammability limit
UFL	Upper flammability limit
ARE	Absolute value of the relative error
AARE	Average of the absolute values of the relative errors

Symbols

c_p	Heat capacity at constant pressure, kJ/mol-K
$\overline{c}_p$	Average heat capacity at constant pressure, kJ/mol-K
$\overline{h}^0_{f,i}$	Formation enthalpy at standard conditions in molar base, kJ/mol
h_i	Absolute enthalpy in molar base, kJ/mol
$\Delta\overline{h}_i$	Specific sensible enthalpy, kJ/mol
H_C	Heat of combustion, kJ
$H_{FL,0}$	Heat released at the flammability limit at the temperature T_0, kJ
$H_{FL,T}$	Heat released at the flammability limit at the temperature T, kJ
I	Parameter defined in section 6
L_T	Heat losses in the combustion process for the initial temperature T, kJ
k_{UFL}	Slope of a straight line representing $\theta_{UFL,T}/\theta_{UFL,0}$
M_i	Molecular weight, g/mol
m	Slope of a straight line
n_i	Number of moles of species i, mol
R^2	Squared correlation coefficient
T	Temperature, K or °C
T_0	Temperature considered as reference, K or °C
$T_{UFL,T}$	Adiabatic flame temperature at the UFL for an initial temperature T, K
$T_{stq,T}$	Adiabatic flame temperature at the stoichiometric composition for an initial temperature T, K
ν_{ar}	Number of moles of oxygen at the FL composition, mol
ν^s_{ar}	Number of moles of oxygen at the stoichiometric composition, mol
ν^{UFL}_{ar}	Number of moles of oxygen at the UFL composition, mol
x_C	Number of moles of carbon in the molecule of the flammable compound, mol
x_H	Number of moles of hydrogen in the molecule of the flammable compound, mol
x_O	Number of moles of oxygen in the molecule of the flammable compound, mol
ϕ	Equivalence ratio
$\theta_{UFL,T}$	Ratio $T_{stq,T}/T_{UFL,T}$
$\theta_{UFL,0}$	Ratio $T_{stq,0}/T_{UFL,0}$

Subscripts

0	Variable taken at a temperature considered as reference
ar	Variable related to air
calc	Calculated value of a variable or parameter
exp	Experimental value of a variable or parameter
F	Variable related to the flammable compound
P	Products
R	Reactants
T	Variable taken at some temperature T

determination of the LFL available in the specialized literature, those with wider application were implemented and compared with the method developed in the present work. On the other hand, fewer methods are available to determine the UFL and only one is widely accepted; this method was implemented and compared with the method developed in the present work. In order to develop and test the methods proposed in the present study, a set of experimental data of the FL at atmospheric pressure and different initial temperature was obtained from the literature.

2. The behavior of the flammability limits with different initial temperatures

Consider n_F moles of a flammable gas forming a mixture with n_{ar} moles of air. If the mixture corresponds to one of the FL, such limit would be determined by Eq. (1).

$$FL = \frac{n_F}{n_F + n_{ar}} = \frac{1}{1 + (n_{ar}/n_F)} = \frac{1}{1 + 4.76\nu_{ar}} \tag{1}$$

Therefore, the number of moles of air per mole of flammable gas ($4.76\nu_{ar}$), defines the value of the FL. The number of moles of oxygen in the air is given by ν_{ar}. The values of the FL depend on the pressure and temperature conditions.

When the initial pressure of the mixture is held constant the FL of a flammable gas will vary with the initial mixture temperature. From the experimental data, the following behavior is observed:

i) The lower flammability limit (LFL) decreases with the increase of the initial mixture temperature. That is, the ratio n_{ar}/n_F increases in value.

ii) The upper flammability limit (UFL) increases with the increase of the initial mixture temperature. In other words, the ratio n_{ar}/n_F decreases in value.

iii) The flammability limits vary linearly with the increase of the mixture initial temperature. The slope of the function is negative for the LFL and positive for the UFL. Eq. (2) represents this behavior:

$$\frac{FL}{FL_0} = 1 + m(T - T_0) \tag{2}$$

3. The modified Burgess − Wheeler Law

The energy conservation equation for the combustion process at constant pressure of 1 mol of flammable gas in air and at an initial temperature T is shown in Eq. (3).

$$\overline{h}^0_{f,F} + \Delta\overline{h}_{F,T} + n_{ar}\Delta\overline{h}_{ar,T} = \sum_T n_i\overline{h}^0_{f,i} + \sum_T n_i\Delta\overline{h}_i + L_T \tag{3}$$

Dividing by the total number of moles of the reactants $(1 + n_{ar})$ and rearranging:

$$FL_T\cdot\Delta\overline{h}_{F,T} + (1 - FL_T)\Delta\overline{h}_{ar,T} + FL_T\cdot H_{FL,T} = FL_T\left(\sum_T n_i\Delta\overline{h}_i + L_T\right) \tag{4}$$

where $H_{FL,T}$ is the heat released at the FL, given by Eq. (5), and L_T represents the heat losses at the initial temperature.

$$H_{FL,T} = \overline{h}^{0}_{f,F} - \sum_{T} n_i \overline{h}^{0}_{f,i} \tag{5}$$

It can be observed in Eq. (4) that the sum of the sensible enthalpies of the reactants and the heat liberated in the combustion process is used to increase the sensible enthalpies of the products and overcome the heat losses.

The modified Burgess – Wheeler Law, proposed by Zabetakis et al. [1] for the LFL, can de stated as follows:

“For a flammable gas the sum of the heat liberated at the LFL and the sensible enthalpies of the reactants is a constant”. This statement is represented by Eq. (6).

$$FL_T\left[\left(\Delta\overline{h}_{F,T} - \Delta\overline{h}_{ar,T}\right) + H_{FL,T}\right] + \Delta\overline{h}_{ar,T} = FL_T\left(\sum_{T} n_i \Delta\overline{h}_i + L_T\right) = K \tag{6}$$

The term between brackets on the left hand side of Eq. (6) is dominated by the heat liberated, $H_{FL,T}$. The maximum amount of heat which can be released corresponds to the complete combustion of the flammable gas.

As the mixture initial temperature increases, the heat liberated at the LFL will also increase because there is less fuel which, being at a higher initial temperature, can react more efficiently towards complete combustion.

As the mixture initial temperature increases, the heat released at the UFL will decrease, since there is more fuel in excess and the product distribution contains more species of incomplete combustion.

The flammability limit FL_0 at some temperature T_0 is considered as a known variable. The temperature T_0 can be selected as the reference temperature without losing generality. In consequence, the enthalpies of formation are determined at T_0. Therefore, Eq. (6) becomes:

$$FL_0 H_{FL,0} = FL_0\left(\sum_{T_0} n_i \Delta\overline{h}_i + L_{T_0}\right) = K \tag{7}$$

For simplicity in the formulation, the sensible enthalpies will be represented by using the average heat capacities at constant pressure, as shown in Eqs. (8) And (9). Also the temperature difference is expressed as$\Delta T = T - T_0$.

$$\overline{c}_{p,ar,T} = \frac{1}{T - T_0}\int_{T_0}^{T} c_{p,ar}\,\mathrm{d}T \tag{8}$$

$$\overline{c}_{p,R,T} = \frac{1}{T - T_0}\int_{T_0}^{T} \left(c_{p,F} - c_{p,ar}\right)\mathrm{d}T \tag{9}$$

Dividing the left hand side of Eq. (6) by that of Eq. (7), using Eqs. (8) and (9), and rearranging, the expression shown in Eq. (10) is obtained.

$$\frac{FL_T}{FL_0} = \frac{H_{FL,0}}{H_{FL,T} + \overline{c}_{p,R,T}\Delta T}\left(1 - \frac{\overline{c}_{p,ar,T}}{FL_0 H_{FL,0}}\Delta T\right) = 1 + m\Delta T \tag{10}$$

Solving Eq. (10) to find the slope yields Eq. (11).

$$m = \frac{H_{FL,0}}{H_{FL,T} + \overline{c}_{p,R,T}\Delta T}\left(\frac{1}{\Delta T} - \frac{1}{\Delta T}\,\frac{H_{FL,T} + \overline{c}_{p,R,T}\Delta T}{H_{FL,0}} - \frac{\overline{c}_{p,ar,T}}{FL_0 H_{FL,0}}\right) \tag{11}$$

Therefore, for the determination of m, it would be necessary to know the heat liberated at different initial temperatures of the flammable mixture. Some assumptions must be made in order to express Eq. (11) in simpler terms:

- The heat liberated at the LFL is constant at different initial temperatures of the mixture. Furthermore, it is equal to the heat of combustion as shown below:

$$H_C = \overline{h}^{0}_{f,F} - x_C \overline{h}^{0}_{f,CO_2} - \frac{x_H}{2}\overline{h}^{0}_{f,H_2O} \tag{12}$$

- The average heat capacities at constant pressure of the reactants can be represented by the heat capacity of air. Therefore, $\overline{c}_{p,R,T} = 0$.
- The slope of the function at the UFL and at the LFL presents the same value, but with different sign.

Considering these assumptions in Eq. (11) and replacing the results in Eq. (10):

$$\frac{LFL_T}{LFL_0} = 1 - \frac{\overline{c}_{p,ar,T}}{FL_0 H_C}(T - T_0) \tag{13}$$

$$\frac{UFL_T}{UFL_0} = 1 + \frac{\overline{c}_{p,ar,T}}{FL_0 H_C}(T - T_0) \tag{14}$$

According to Zabetakis [2], the slope of Eqs. (13) and (14) can be obtained by considering that the heat capacity at constant pressure of air is constant and equal to 0.0075 kcal/mol-K, and that the product $LFL_0 H_C$ is constant and equal to 10.4 kcal/mol, then:

$$\frac{LFL_T}{LFL_0} = 1 - 0.000721(T - T_0) \tag{15}$$

$$\frac{UFL_T}{UFL_0} = 1 + 0.000721(T - T_0) \tag{16}$$

In the present work, Zabetakis' equations will be validated with experimental data and compared with two developed methods.

4. Methods to determine the FL at different initial temperatures

Most of the methods available in the literature were developed to determine the LFLs, such as the works of Catoire and Nauder [3], Rowley et al. [4], Britton [5], Britton and Frurip [6], Mendiburu et al. [7], Zlochower [8], Mendiburu et al. [9] and Liaw and Chen [10]. Fewer studies are devoted to determine the UFLs at different initial temperatures, among them the works of Mendiburu et al. [11] and Liaw and Chen [10].

Some of these works ([7] [8], and [10]), are based on the assumption that the adiabatic flame temperature at the LFL is constant with respect to the initial mixture temperature. Such consideration gives good results for the case of hydrocarbons; however, the theoretical results deviate from the experimental data for CHO compounds. The method developed by Liaw and Chen [10] was applied to predict both FL by considering heat losses in the processes. The authors [10] concluded that the differences in the LFLs prediction were negligible with respect to the heat losses; also, the predicted UFLs based on adiabatic conditions were more accurate than those predicted by considering heat losses.

Some of the above cited works [2–4,6] are considered for comparison with the results obtained by using Eqs. (15) and (16) and with the methods developed in the present study.

5. Empirical equations for FLs at different initial temperatures

There are several studies which have developed empirical equations to represent experimental data. A list of such works is presented in Table 1, along with other relevant information.

The slope of Eq. (2) can be determined for each compound of the experimental data set compiled for the development of the present work. The slopes determined by directly adjusting the straight lines to the experimental data are represented by $m_{LFL,\mathrm{exp}}$ and $m_{UFL,\mathrm{exp}}$, for the LFL and UFL, respectively. The resulting values for $m_{LFL,\mathrm{exp}}$ and $m_{UFL,\mathrm{exp}}$ are presented in Tables 2 and 3, respectively. Other parameters are also shown in Tables 2 and 3, these will be introduced later.

The use of the experimentally determined slopes allows the estimation of the FL at different initial temperatures for the compounds presented in Tables 2 and 3

6. Method for estimating the LFL at different initial temperatures

The method for the determination of the LFL's at different mixture initial temperatures is based on a procedure that adjusts a correlation function to approximate the value of the slope determined with the experimental data. Therefore, a calculated slope for the LFLs is obtained, $m_{LFL,calc}$.

In the method proposed by Zabetakis [2], there are no means to differentiate among flammable gases because the slope is the same for all compounds. In order to differentiate among flammable gases the parameter I is introduced.

In the works of Kondo et al. [17] and Rowley et al. [28], a spherical vessel of 12 L volume was used in the experiments. Assuming that the mixture behaves as an ideal gas, at atmospheric pressure, with a 12 L volume, and knowing the initial temperature, the number of moles of the mixture can be determined (n_T). The value of n_T will change with the initial temperature; however, for the determination of parameter I, the value of n_T corresponds to the initial mixture temperature T_0. Also, since at the initial temperature T_0, the lower flammability limit LFL_0 is known, the number of moles of the flammable gas (n_F) can be easily determined. Taking into account these considerations, the value of the parameter I can be determined by Eq. (17).

$$I = \frac{M_F}{n_F H_C} \tag{17}$$

The parameter I is the combination of the molecular weight of the flammable gas(M_F), its heat of combustion (H_C), given by Eq. (12), and the number of moles of the flammable gas (n_F), when the mixture is at T_0, atmospheric pressure and occupies a volume of 12 L.

By applying a multiple linear regression, the following correlation was obtained for the calculated slope:

$$m_{LFL,calc} = \frac{8.3959}{10^4} + \frac{9.6643}{10^5} I + \frac{2.6402}{10^6} I^2 + \frac{8.3413}{10^{10}} H_C \cdot I \tag{18}$$

The values of the parameters I, H_C and $m_{LFL,calc}$ for the studied compounds are presented in the last three columns of Table 2. The validation of the proposed method is presented in Section 8 of Results and Discussions.

7. Method for estimating the UFL at different initial temperatures

The method to determine the UFL's at different initial temperatures of the mixture is based on the calculated adiabatic flame temperature. Additionally, some considerations are assumed to determine this temperature:

i) A fraction of the flammable gas undergoes complete combustion,
ii) The unreacted flammable gas is treated as an inert and its sensible enthalpy is represented by the sensible enthalpy of an equal mass of air,
iii) The sensible enthalpies of the flammable gases are determined by considering average heat capacities at constant pressure.

The global combustion reaction is, then, given by Eq. (19).

$$C_{x_C}H_{x_H}O_{x_O} + \nu_{ar}^{UFL}(O_2 + 3,76N_2) \rightarrow \phi^{-1}\left(x_C CO_2 + \frac{x_H}{2} H_2O\right) + 3,76\nu_{ar}^{UFL} N_2 + \left(1 - \phi^{-1}\right) C_{x_C}H_{x_H}O_{x_O} \tag{19}$$

where ν_{ar}^{UFL} is the number of moles of oxygen at the UFL composition and ϕ is the equivalence ratio given by Eq. (20).

Table 1
Works which present experimental data accompanied by empirical correlations.

Reference	Studied compounds	Flammability limits	Temperature range (°C)	Pressure range (kPa)
Goethals et al. [12]	Toluene	LFL, UFL	60–225	100–500
Liu and Zhang [13]	Hydrogen	LFL, UFL	21–90	100–400
Vanderstraeten et al. [14]	Methane	UFL	20–200	100–5500
Van den Schoor [15]	Ethane	UFL	20–250	100–3000
	Propane	UFL	20–250	100–1000
	n-Butane	UFL	20–250	100–300
	Ethylene	UFL	20–260[a]	100–3000
	Propylene	UFL	20–250[b]	100–1000
Hustad and Sonju [16]	Methane	LFL	25–450	101.325
	Commercial Butane	LFL	25–450	101.325
	Hydrogen	LFL	25–450	101.325
	Carbon Monoxide	LFL	25–450	101.325

[a] The temperature range was 20–230 from 1500 to 2500 kPa and it was 20–200 for 3000 kPa.
[b] The temperature range was 20–200 for 1000 kPa.

Table 2
Values of parameters for the determination of the LFL at different initial temperatures of the mixture.

References	Compounds	Formula	CAS#	$m_{LFL,\text{exp}}$ $(1/{}^\circ C)$	H_C (kJ)	I $(g/mol.kJ)$	$m_{LFL,calc}(1/{}^\circ C)$
Kondo et al. [17]	Dimethyl ether	C_2H_6O	115-10-6	0.000957	1328.42	2.0745	0.001054
Kondo et al. [17]	Methyl formate	$C_2H_4O_2$	107-31-3	0.000825	933.80	2.4318	0.001092
Kondo et al. [17]	Methane	CH_4	74-82-8	0.000658	802.30	0.8121	0.000920
Wierzba and Wang [18]	Methane	CH_4	74-82-8	0.000850	802.30	0.8315	0.000922
Li et al. [19]	Methane	CH_4	74-82-8	0.000609	802.30	0.8200	0.000921
White [20]	Methane	CH_4	74-82-8	0.000658	802.30	0.6359	0.000903
Kondo et al. [17]	Propane	C_3H_8	74-98-6	0.000810	2043.17	2.1098	0.001059
Kondo et al. [17]	iso-Butane	C_4H_{10}	75-28-5	0.000915	2649.02	2.6170	0.001116
Kondo et al. [17]	Propylene	C_3H_6	115-07-1	0.000915	1926.45	2.0078	0.001048
Kondo et al. [17]	Ethylene	C_2H_4	74-85-1	0.000823	1323.17	1.5453	0.000997
Craven and Foster [21]	Ethylene	C_2H_4	74-85-1	0.000836	1323.17	1.6344	0.001006
White [20]	Ethylene	C_2H_4	74-85-1	0.000745	1323.17	1.2317	0.000964
White [20]	Acetylene	C_2H_2	74-86-2	0.000913	1255.60	1.4325	0.000985
Kondo et al. [17]	Carbon Monoxide	CO	630-08-0	0.000791	282.99	1.6125	0.001003
Wierzba and Wang [18]	Carbon Monoxide	CO	630-08-0	0.000882	282.99	1.4832	0.000989
Karim et al. [22]	Carbon Monoxide	CO	630-08-0	0.000801	282.99	1.4663	0.000987
White et al. [20]	Carbon Monoxide	CO	630-08-0	0.000844	282.99	1.2168	0.000961
Kondo et al. [17]	Ammonia	NH_3	7664-41-7	0.000575	316.80	0.6950	0.000908
White [23] (downward)	Ammonia	NH_3	7664-41-7	0.000970	316.80	0.5706	0.000896
White [23] (horizontal)	Ammonia	NH_3	7664-41-7	0.000582	316.80	0.5878	0.000897
White [23] (upward)	Ammonia	NH_3	7664-41-7	0.000559	316.80	0.6645	0.000905
Ciccarelli et al. [24]	Ammonia	NH_3	7664-41-7	0.000861	316.80	0.6528	0.000904
Chang et al. [25]	Methanol	CH_4O	67-56-1	0.001500	672.17	2.2808	0.001075
Coronado et al. [26]	Ethanol	C_2H_6O	64-17-5	0.001213	1278.52	1.9264	0.001038
Goethals [12]	Toluene	C_7H_8	108-88-3	0.001327	3772.06	4.7745	0.001376
White et al. [20]	n-Pentane	C_5H_{12}	109-66-0	0.000696	3271.77	2.8878	0.001149
Chang et al. [25]	Benzene	C_6H_6	71-43-2	0.000909	3169.51	5.7145	0.001493
Wierzba and Wang [18]	Hydrogen	H_2	1333-74-0	0.001460	241.83	0.4343	0.000882
Ciccarelli et al. [24]	Hydrogen	H_2	1333-74-0	0.000848	241.83	0.3701	0.000876
Karim et al. [22]	Hydrogen	H_2	1333-74-0	0.003358	241.83	0.4100	0.000880
White et al. [20]	Hydrogen	H_2	1333-74-0	0.000872	241.83	0.1772	0.000857
Wierzba et al. [27]	Hydrogen	H_2	1333-74-0	0.001034	241.83	0.3454	0.000873
Rowley et al. [28]	Methanol	CH_4O	67-56-1	0.001149	672.17	1.3951	0.000980
Rowley et al. [28]	1-hexine	C_6H_{10}	693-02-7	0.001603	3692.56	5.2554	0.001437
Rowley et al. [28]	Butanol	$C_4H_{10}O$	71-36-3	0.001310	2506.22	3.9705	0.001273
Rowley et al. [28]	Methyl benzoate	$C_8H_8O_2$	93-58-3	0.002212	3846.18	8.7010	0.001908
Rowley et al. [28]	1-Octanol	$C_8H_{18}O$	111-87-5	0.001820	4968.61	8.1929	0.001843
Rowley et al. [28]	Phenetole	$C_8H_{10}O$	103-73-1	0.002015	4255.71	7.3406	0.001717
Rowley et al. [28]	4-Methyl-2-pentanol	$C_6H_{14}O$	108-11-2	0.001584	3709.81	5.7482	0.001500
Rowley et al. [28]	Dibutyl amine	$C_8H_{19}N$	111-92-2	0.002210	3882.81	9.6620	0.002051
Rowley et al. [28]	2-penteno	$C_{10}H_{16}$	80-56-8	0.001979	5853.43	8.2118	0.001851
Rowley et al. [28]	2-methyl-1,3-propanediol	$C_4H_{10}O_2$	2163-42-0	0.001750	2277.32	6.9605	0.001653
Rowley et al. [28]	Hexyl Formate	$C_7H_{14}O_2$	629-33-4	0.001763	3928.95	7.7408	0.001771
Rowley et al. [28]	Octyl formate	$C_9H_{18}O_2$	112-32-3	0.002056	5151.68	10.1597	0.002138
Rowley et al. [28]	Di iso butyl phthalate	$C_{16}H_{22}O_4$	84-69-5	0.004312	7869.14	22.0334	0.004395
Rowley et al. [28]	Ethyl Lactate	$C_5H_{10}O_3$	97-64-3	0.001754	2481.66	6.9838	0.001658

$$\phi = \frac{\nu_{ar}^{s}}{\nu_{ar}^{UFL}} \tag{20}$$

The number of moles of oxygen at the stoichiometric composition (ν_{ar}^{s}) is determined as follows:

$$\nu_{ar}^{s} = x_C + \frac{x_H}{4} - \frac{x_O}{2} \tag{21}$$

Since the mass of air is equal to that of the unreacted flammable gas, the equivalent number of moles of air is determined using the following relation:

$$n_{ar}^{eq} = \left(1-\phi^{-1}\right)\frac{M_F}{M_{ar}} \tag{22}$$

The molecular weight of air (M_{ar}) was considered as 28.96 g/mol. The energy conservation law is given by Eq. (23).

$$\begin{aligned}\phi^{-1}h_F + \left[\nu_{ar}^{UFL} + \left(1-\phi^{-1}\right)M_m\right]h_{ar,R} \\ = \phi^{-1}\left(x_C h_{CO_2} + \frac{x_H}{2}h_{H_2O}\right) + 3,76\nu_{ar}^{UFL}h_{N_2} + \left(1-\phi^{-1}\right)M_m h_{ar,P}\end{aligned} \tag{23}$$

where M_m represents the ratio $M_m = M_F/M_{ar}$, the subscripts R and P refer to reactants and products, respectively. Isolating the number of moles of oxygen at the UFL Eq. (24) is obtained.

$$\nu_{ar}^{UFL} = \frac{\nu_{ar}^{s}M_m\left(h_{ar,P}-h_{ar,R}\right)}{h_F - x_C h_{CO_2} - \frac{x_H}{2}h_{H_2O} + M_m\left(h_{ar,P}-h_{ar,R}\right) + \nu_{ar}^{s}\left(h_{ar,R} - 3,76h_{N_2}\right)} \tag{24}$$

Table 3
Values of parameters for the determination of the UFL at different initial temperatures of the mixture.

References	Composto	Fórmula	$m_{UFL,\mathrm{exp}}$ $(1/°C)$	$\overline{h}^0_{f,F}$ (kJ/mol)	I $(g/mol.kJ)$
Kondo et al. [17]	Methane	CH_4	0.000633	−74.9	0.2560
Wierzba and Wang [18]	Methane	CH_4	0.000719	−74.9	0.2910
Li et al. [19]	Methane	CH_4	0.000532	−74.9	0.2611
Van Den Schoor [15]	Methane	CH_4	0.000941	−74.9	0.2504
Vanderstraeten et al. [14]	Methane	CH_4	0.000854	−74.9	0.2552
White [20]	Methane	CH_4	0.000740	−74.9	0.3106
Kondo et al. [17]	Propane	C_3H_8	0.000314	−104.7	0.4413
Van Den Schoor [15]	Propane	C_3H_8	0.001470	−104.7	0.4240
Kondo et al. [17]	iso-Butane	C_4H_{10}	0.000025[a]	−134.2	0.5565
Kondo et al. [17]	Propylene	C_3H_6	0.000469	20.4	0.4250
Van Den Schoor [15]	Propylene	C_3H_6	0.001413	20.4	0.3502
Kondo et al. [17]	Ethylene	C_2H_4	0.001284	52.5	0.1393
White [20]	Ethylene	C_2H_4	0.000808	52.5	0.3102
Van Den Schoor [15]	Ethylene	C_2H_4	0.001522	52.5	0.1218
Kondo et al. [17]	Ammonia	NH_3	0.000695	−45.9	0.3645
Ciccarelli et al. [24]	Ammonia	NH_3	0.000770	−45.9	0.3714
White [23] (downward)	Ammonia	NH_3	0.001038	−45.9	0.5412
White [23] (horizontal)	Ammonia	NH_3	0.000680	−45.9	0.4196
White [23] (upward)	Ammonia	NH_3	0.00633	−45.9	0.4022
Goethals [12]	Toluene	C_7H_8	0.000506	50.1	0.6829
Wierzba and Wang [18]	Hydrogen	H_2	0.000397	0.0	0.0227
Ciccarelli et al. [24]	Hydrogen	H_2	0.000379	0.0	0.0222
White [20]	Hydrogen	H_2	0.000367	0.0	0.0233
Wierzba et al. [27]	Hydrogen	H_2	0.000339	0.0	0.0213
Chang et al. [25]	Benzene	C_6H_6	0.001667	82.9	1.0477
Van Den Schoor [15]	Ethane	C_2H_6	0.000694	−84.0	0.2556
Van Den Schoor [15]	n-Butane	C_4H_{10}	0.001165	−125.6	0.4613
White [20]	n-pentane	C_5H_{12}	0.000678	−146.8	0.9819
White [20]	Acetylene	C_2H_2	0.002551	226.7	0.0755
Kondo et al. [17]	Dimethyl ether	C_2H_6O	0.002928	−184.1	0.2758
Kondo et al. [17]	Methyl formate	$C_2H_4O_2$	0.000928	−336.9	0.5754
Chang et al. [25]	Methanol	CH_4O	0.002584	−205.0	0.3142
Coronado et al. [26]	Ethanol	C_2H_6O	0.004661	−234.0	0.4139
Kondo et al. [17]	Carbon Monoxide	CO	0.000390	−110.5	0.2728
Wierzba and Wang [18]	Carbon Monoxide	CO	0.000569	−110.5	0.3033
White [20]	Carbon Monoxide	CO	0.000268	−110.5	0.2833

[a] The UFL variation for this compound was small.

The adiabatic flame temperature for the UFL at any initial temperature T was determined by solving Eq. (23); this temperature is denoted by $T_{UFL,T}$. Also, the adiabatic flame temperature at the stoichiometric composition and at any initial temperature T was determined and denoted by $T_{stq,T}$.

The value of the upper flammability limit at T_0 was used to determine the adiabatic flame temperature denoted by $T_{UFL,0}$, the adiabatic flame temperature at the stoichiometric composition and at T_0 was determined and is denoted by $T_{stq,0}$.

The ratio of the adiabatic flame temperature at the stoichiometric composition to that at the UFL composition is represented by $\theta_{UFL,T}$. At the initial temperature T_0 the value of this ratio is denoted by $\theta_{UFL,0}$. The following equation shows that the quotient $\theta_{UFL,T}/\theta_{UFL,0}$ increases its value linearly as the initial temperature difference increases.

$$\frac{\theta_{UFL,T}}{\theta_{UFL,0}} = \frac{T_{stq,T}/T_{UFL,T}}{T_{stq,0}/T_{UFL,0}} = 1 + k_{UFL}(T_T - T_0) \tag{25}$$

In order to approximate the value of $T_{UFL,T}$, it is necessary to determine the factor k_{UFL}. In the method here proposed, this is done by means of a correlation. Once the value of the adiabatic flame temperature has been approximated, the number of moles of oxygen can be determined using Eq. (24). In the present work, a total of 18 flammable compounds were studied, obtaining two correlation functions:

For C–H compounds, hydrogen and ammonia.

$$k_{UFL} = \frac{3.7611}{10^4} - \frac{3.0500}{10^4} I + \frac{2.5988}{10^6} \overline{h}^0_{f,F} + \frac{2.0798}{10^8} \left(\overline{h}^0_{f,F}\right)^2 \tag{26}$$

For C–H–O compounds and carbon monoxide

$$k_{UFL} = -\frac{5.8362}{10^{-3}} - \frac{3.8838}{10^4} I - \frac{6.7817}{10^5} \overline{h}^0_{f,F} - \frac{1.4430}{10^7} \left(\overline{h}^0_{f,F}\right)^2 \tag{27}$$

The value of the parameter I is calculated with Eq. (17), and the number of moles of the flammable gas is determined by considering UFL_0. The other parameter used was the enthalpy of formation of the flammable gas $(\overline{h}^0_{f,F})$. Once the ratio $\theta_{UFL,T}/\theta_{UFL,0}$ has been approximated, Eq. (28) is employed to determine the desired adiabatic flame temperature:

$$T_{UFL,T} = \frac{T_{stq,T}}{\theta_{UFL,0}} \left(\frac{\theta_{UFL,T}}{\theta_{UFL,0}}\right)^{-1} \tag{28}$$

To perform the calculations, the flammable compounds' heat capacities at constant pressure were obtained from the NIST Chemistry Web Book [29]. The data were then adjusted to two degree polynomials as a function of temperature ranging from 100 to 1500 K. An analogous expression to that shown in Eq. (8) was used setting the integration interval from T_0 to T. The other species' absolute enthalpies were determined by using the NASA–Glenn coefficients given by McBride et al. [30]. The values of the necessary parameters are presented in Table 3.

Table 4
Results and comparison of the method for determining the LFL at different initial temperatures of the mixture.

Method	N	AARE (%)	R^2
Britton and Frurip [6]	161	4.44	0.9946
Catoire and Naudet [3]	140	14.64	0.9003
Rowley et al. [4]	109	5.95	0.9857
Zabetakis [2]	180	4.82	0.9948
This work	180	3.25	0.9928

Table 5
Further comparison of the method for the LFL at different initial temperatures.

Set	N	Zabetakis [2]		Britton and Frurip [6]		This work	
		AARE (%)	R^2	AARE (%)	R^2	AARE (%)	R^2
$x_C \leq 5$	110	2.36	0.9978	2.75	0.9955	2.73	0.9972
$x_C > 5$	30	11.74	0.6844	10.33	0.7553	2.01	0.9851
NH_3	21	4.70	0.8593	4.88	0.8499	5.76	0.7649
H_2	19	8.28	0.9439	–	–	5.47	0.9639

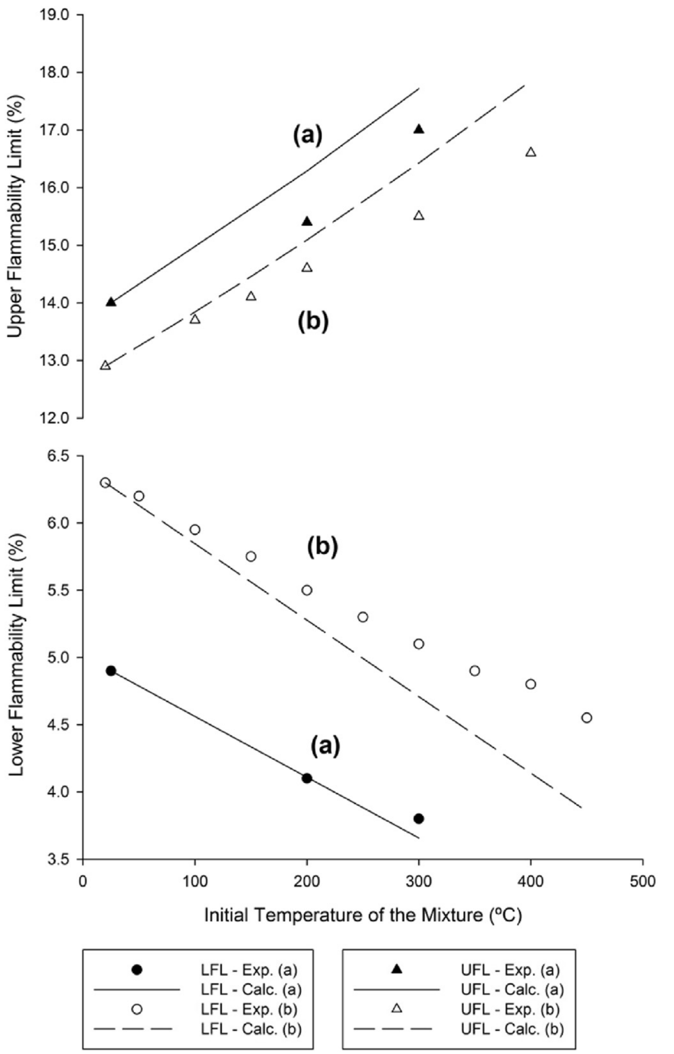

Fig. 1. Calculated and experimental flammability limits of methane (CH_4) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by: (a) Wierzba and Wang [18] and (b) White [20].

8. Results and discussions

The method proposed in the present study was implemented along with the methods available in the literature. The results are compared in terms of the absolute relative error (ARE), for an individual flammable gas; in terms of the average absolute relative error (AARE), for a set of flammable gases; and in terms of the squared correlation coefficient (R^2), also for a set of flammable gases. The subscripts "exp" and "calc" refer to experimental and calculated data, respectively.

The absolute relative error, ARE, is determined using Eq. (29). The average absolute relative error, AARE, is determined using Eq. (30), where N is the number of experimental data.

$$ARE = \frac{|LI_{\text{exp}} - LI_{calc}|}{LI_{\text{exp}}} 100\% \tag{29}$$

$$AARE = \frac{1}{N}\sum_{i=1}^{N} ARE_i \tag{30}$$

According to Montgomery [31], the squared correlation

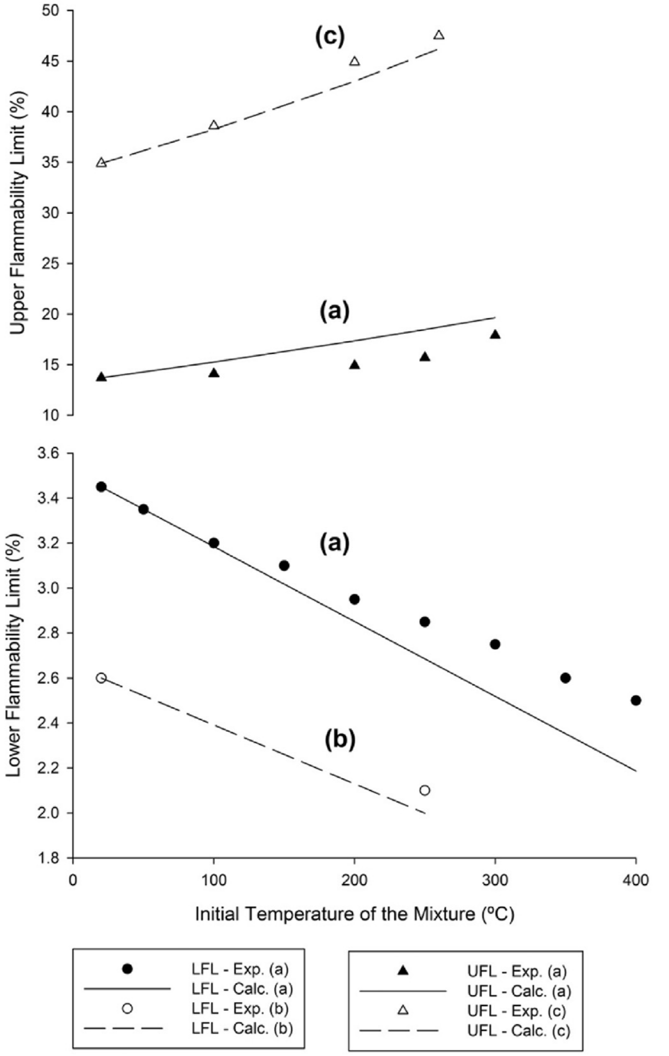

Fig. 2. Calculated and experimental flammability limits of ethylene (C_2H_4) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by: (a) White [20], (b) Craven and Foster [21] and (c) Van Den Schoor [15].

coefficient, R^2, is calculated with Eq. (31).

$$R^2 = 1 - \frac{SSE}{SST} \tag{31}$$

where the sum of squares of the errors (SSE) and the total sum of squares (SST) are calculated using Eq. (32) and Eq. (33), respectively.

$$SSE = \sum_{i=1}^{N} \left(LI_{\exp} - LI_{calc}\right)^2 \tag{32}$$

$$SST = \sum_{i=1}^{N} \left(LI_{\exp}\right)^2 - \frac{\sum_{i=1}^{N} LI_{\exp}}{N} \tag{33}$$

8.1. *Results of the method for LFL at different initial temperatures*

The results obtained by applying the methods for estimating the LFL at different initial temperatures and at atmospheric pressure are presented in this section. In total, 180 experimental points were assessed, aside from the reference points. For the sake of comparison, Table 4 presents the results derived from the methods proposed by Britton and Frurip [6], Catoire and Naudet [3], Rowley et al. [4], and Zabetakis [2], along with the method proposed in this study.

The method developed in the present work presents better results in terms of AARE. Whereas in terms of correlation coefficient R^2, the method presents better results than those by Catoire and Naudet [3] and by Rowley et al. [4]; and a slightly lower value of R^2 with respect to the methods of Zabetakis [2] and Britton and Frurip [6].

Further comparison with the methods of Zabetakis [2] and Britton and Frurip [6] is presented in Table 5. Here, the data is classified into flammable gases with up to 5 carbon atoms ($x_C \le 5$), flammable gases with more than 5 carbon atoms ($x_C > 5$), ammonia (NH_3) and hydrogen (H_2).

When determining the LFLs of flammable gases with up to 5 carbon atoms, all the methods present similar values of R^2. The method proposed by Zabetakis [2] is slightly more accurate.

The method developed in the present work presents a higher value of R^2 (0.9851) when applied to determine the LFLs of

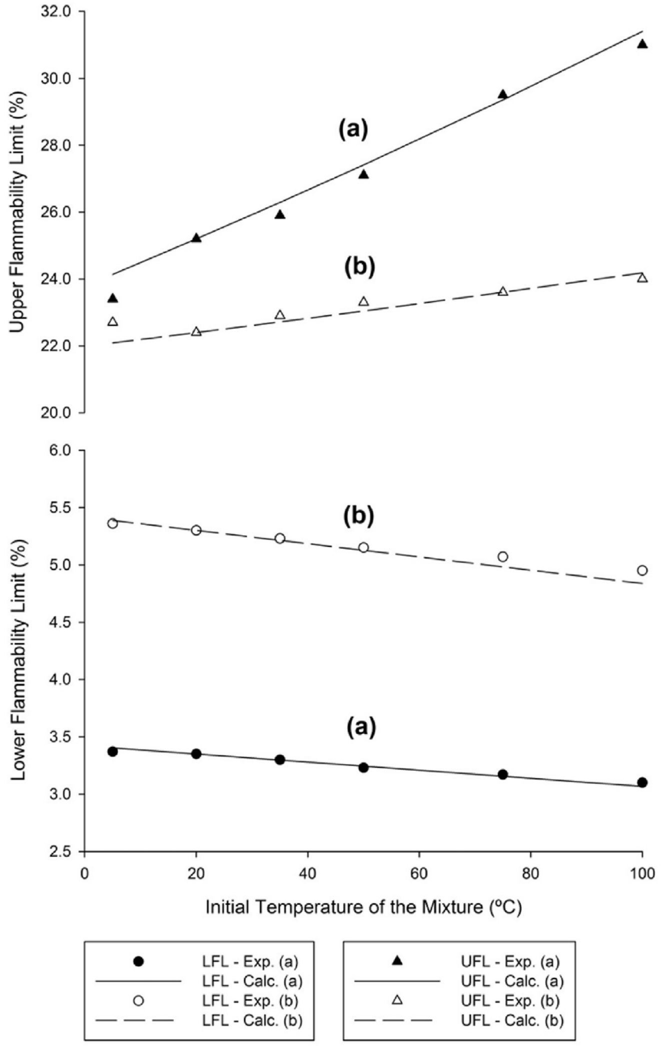

Fig. 3. Calculated and experimental flammability limits of (a) dimethyl ether (C_2H_6O) and (b) methyl formate ($C_2H_4O_2$) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by Kondo et al. [17].

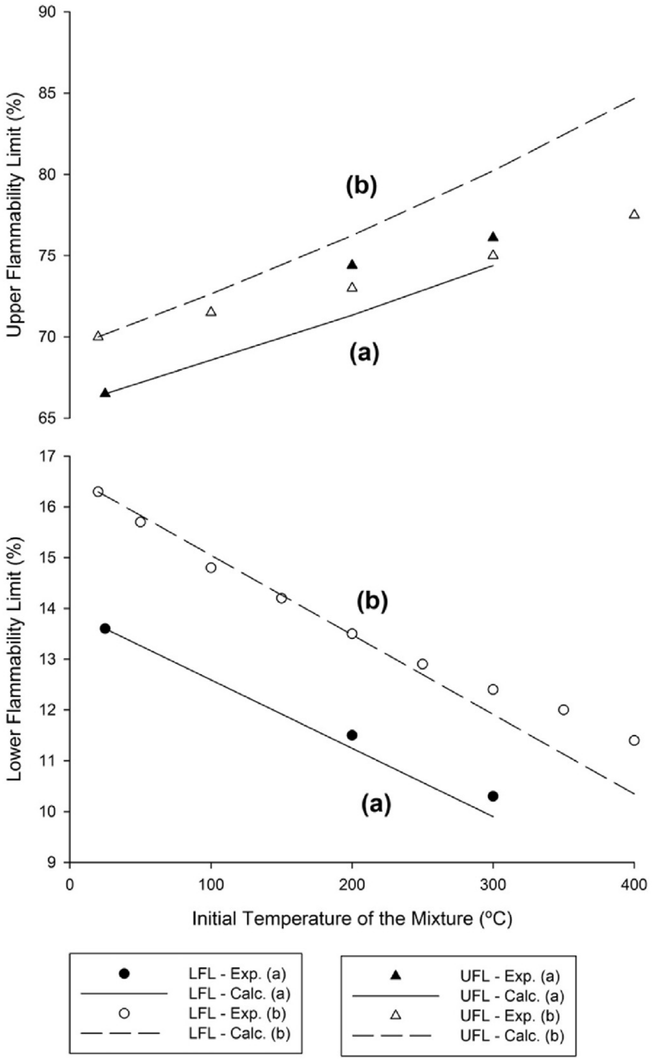

Fig. 4. Calculated and experimental flammability limits of carbon monoxide (CO) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by: (a) Wierzba and Wang [18] and (b) White [20].

flammable gases with more than 5 carbon atoms. Therefore, the present method is more accurate for flammable gases with higher molecular weights.

In the case of ammonia, the three methods present unsatisfactory values of R^2; the method of Zabetakis [2] presents the highest R^2 (0.8593). From these results, it is recommended to use the experimental values of $m_{LFL,\exp}$ for ammonia, as reported in Table 2, instead of any of the empirical methods tested here.

In the case of hydrogen, the method developed in this work presents the higher accuracy, with R^2 of 0.9639, which is considered satisfactory.

The analysis of the results reveals that the proposed method should be used for estimating the LFL at different initial temperatures of heavier flammable gases($x_C > 5$). On the other hand, for lighter flammable gases ($x_C \leq 5$), the method proposed by Zabetakis [2] is recommended due to its higher accuracy and simplicity of implementation.

The LFLs calculated for some flammable gases using the method proposed here are presented in Figs. 1–8; the experimental data from the different sources are also presented in the figures. A good agreement between the experimental data and the estimated values using the method proposed in the present study is observed.

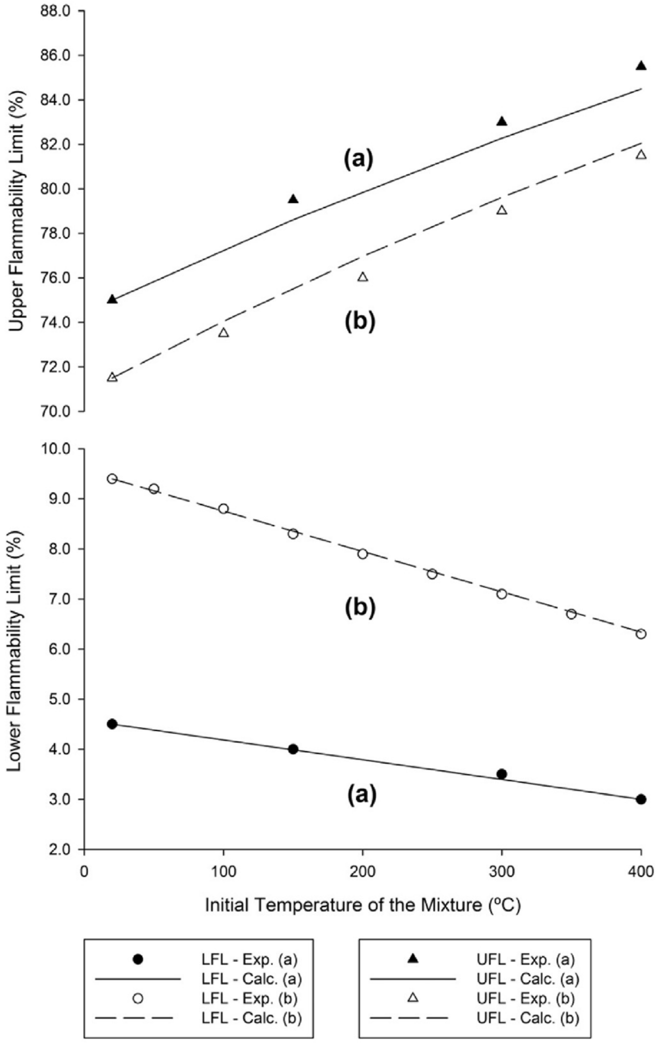

Fig. 5. Calculated and experimental flammability limits of hydrogen (H_2) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by: (a) Ciccarelli et al. [24]. and White [20].

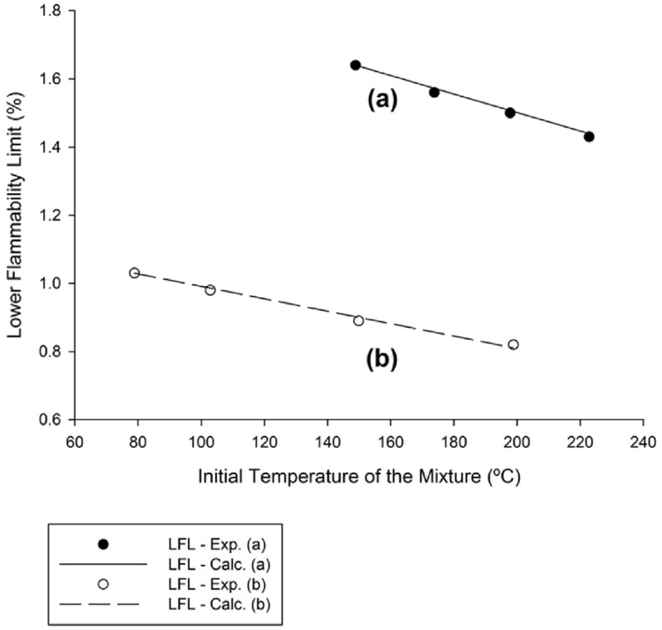

Fig. 6. Calculated and experimental flammability limits of (a) 2-methyl-1,3-propanediol ($C_4H_{10}O_2$) and (b) hexyl formate ($C_7H_{14}O_2$) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by Rowley et al. [28].

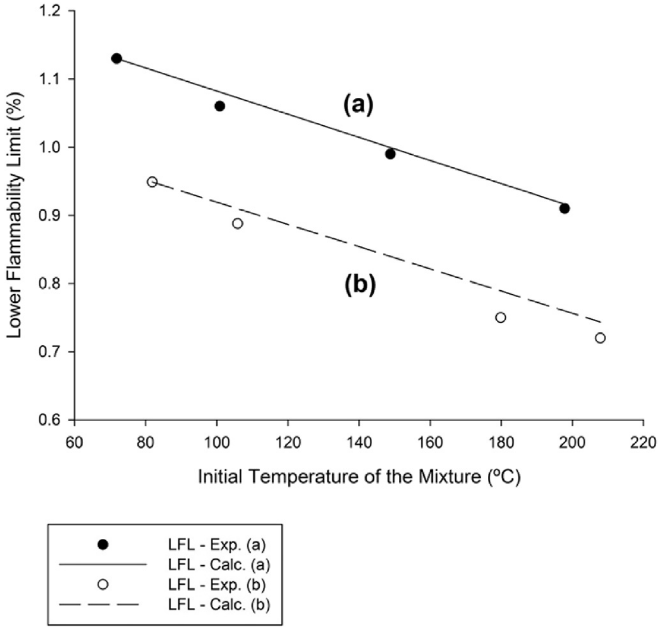

Fig. 7. Calculated and experimental flammability limits of (a) 4-methyl-2-pentanol ($C_6H_{14}O$) and (b) phenetole ($C_8H_{10}O$) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by Rowley et al. [28].

The results for all the considered compounds are presented in Table S1 of the supplementary material.

8.2. Results of the method for the UFL at different initial temperatures

The results obtained with the methods to determine the UFLs in air at different initial temperatures and at atmospheric pressure are

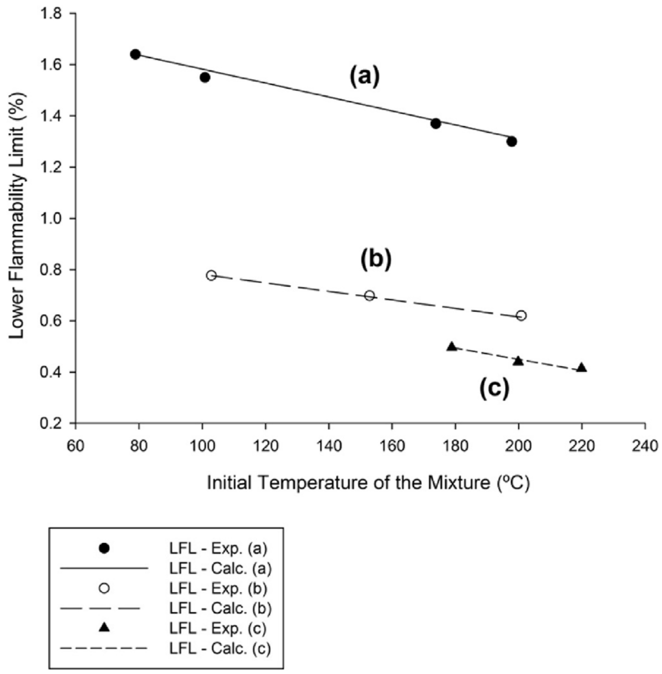

Fig. 8. Calculated and experimental flammability limits of (a) ethyl lactate ($C_5H_{10}O_3$), (b) octyl formate ($C_9H_{18}O_2$) and (c) di iso butyl phthalate ($C_{16}H_{22}O_4$) at different initial temperatures of the mixture and atmospheric pressure. Experimental data by Rowley et al. [28].

Table 6
Results and comparison of the method for determining the UFL at different initial temperatures of the mixture.

Reference	N	AAER (%)	R^2
Zabetakis [2]	129	5.01	0.9748
This work	129	3.60	0.9957

presented in Table 6. Without considering the reference points, a total of 129 experimental points were assessed.

The method developed in the present work was compared with the method proposed by Zabetakis [2], resulting in AARE values of 3.60% and 5.01%, respectively. The coefficients of determination, R^2, resulted 0.9957 for the method developed in the present work and 0.9748 for the method of Zabetakis [2]. This result implies a better accuracy of the here proposed method.

The UFLs for some flammable gases calculated with the developed method are presented in Fig. 1 through 5, along with the experimental data. The results suggest a good agreement between the experimental data and the calculated values of UFLs at different initial temperatures of mixture. The results for all the considered compounds are presented in Table S2 of the supplementary material.

9. Conclusions

In the present work, a method to determine the lower flammability limits (LFL) and upper flammability limits (UFL) of pure compounds in air at atmospheric pressure and at different initial temperatures was developed.

The method to determine the LFL was compared with other available methods by Zabetakis [2], Catoire and Naudet [3], Rowley et al. [4] and Britton and Frurip [6]. The method by Zabetakis [2] shows slightly better accuracy when predicting the LFL of compounds with 5 or less carbon atoms; whereas the method proposed here presents better accuracy when predicting the LFL of compounds with more than 5 carbon atoms. For the method proposed here, the average absolute relative error (AARE) is 3.25% and the squared correlation coefficient (R^2) results equal to 0.9928.

With respect to method proposed here to determine the UFL, it was compared with the method presented by Zabetakis [2]. In this case, the method developed here shows better accuracy, presenting an AARE of 3.60% and a R^2 of 0.9957.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.energy.2016.12.036.

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