



Full Length Article

Determination of upper flammability limits of C–H–O compounds in air at reference temperature and atmospheric pressure

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HIGHLIGHTS

- Method for determination of UFL in air of C–H–O compound.
- The method uses basic combustion theory.
- The method is simple and can be easily implemented.
- The 95% confidence intervals for each compound were determined.
- The method showed good accuracy in comparison with experimental data.

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ABSTRACT

The objective of the present article was to develop and validate a method for the determination of the upper flammability limits (UFLs) in air, at atmospheric pressure and reference temperature, of flammable compounds containing carbon, hydrogen and oxygen in their molecules, called C–H–O compounds for simplicity.

The developed method applies basic combustion theory and chemical equilibrium. The upper flammability limits are determined by correlating a parameter named θ , which is the ratio of the adiabatic flame temperature at the stoichiometric composition to the adiabatic flame temperature at the UFL composition.

A total set of 208 C–H–O compounds was considered, it was divided into a correlation set of 136 compounds and a prediction set of 72 compounds. The method's accuracy was tested in terms of the average of the absolute values of the relative errors (AARE) and in terms of the squared correlation coefficient (R^2). Also, the 95% confidence interval was determined. For the correlation, prediction and total sets the AAREs were 9.66%, 7.63% and 8.95%, respectively. The R^2 was 0.9382 for the correlation set, 0.9188 for the prediction set, and 0.9346 for the total set.

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1. Introduction

A gaseous mixture of a flammable compound with air (or other oxidant) is either flammable or non-flammable. For given pressure and temperature conditions the flammability limits are the concentration limits above or below which the flame propagation is not possible.

The lower flammability limit (LFL) of a flammable compound is its minimum volumetric concentration, in a gaseous mixture with air at determined temperature and pressure conditions, for which a flame is able to propagate. If the flammable compound concentration is decreased, the flame is unable to propagate.

The upper flammability limit (UFL) of a flammable compound is its maximum volumetric concentration, in a gaseous mixture with air at determined temperature and pressure conditions, for which a flame is able to propagate. If the flammable compound concentration is increased, the flame is unable to propagate.

In a previous work the experimental determination of the flammability limits have been addressed; they were determined experimentally by applying standardized test methods [1]. In another work, the flammability limits of ethanol were determined at different initial temperatures and pressures [2]. Earlier works by Zabetakis [3] and by Coward and Jones [4] describe a different apparatus used before the standardized tests were established. Experimental determination of the flammability limits of several compounds is being carried out since the first half of the 20th century.

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Nomenclature

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

\bar{c}_p	average heat capacity at constant pressure, kJ/mol-K
g^0	specific Gibbs free energy at the standard-state pressure, kJ/mol
ΔG_T^0	standard-state Gibbs function change, kJ/mol
$\bar{h}_{f,i}^0$	formation enthalpy at standard conditions in molar base, kJ/mol
h_i	specific absolute enthalpy in molar base, kJ/mol
h_{ar}	enthalpy of 4.76 mol of air, kJ
H_C	heat liberated at the stoichiometric combustion process, kJ
H_{UFL}	heat liberated in the combustion process at the UFL, kJ
K_{sc}	equilibrium constant for the water – gas homogeneous reaction
K_{cc}	equilibrium constant for the water – gas heterogeneous reaction
M_i	molecular weight, g/mol
n_i	number of moles, mol
p	pressure, kPa or atm
R	universal ideal gas constant, kJ/mol-K

R^2	squared correlation coefficient
s	specific entropy, kJ/mol-K
T	temperature, K or °C
T_{UFL}	adiabatic flame temperature at the UFL composition, K
T_r	reference temperature, K
T_{stq}	adiabatic flame temperature at the stoichiometric composition, K
ν_{ar}^s	number of moles of oxygen at the stoichiometric composition, mol
ν_{ar}^{UFL}	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
θ	ratio T_{stq}/T_{Lsi}

Subscripts

calc	calculated value of a variable or parameter for a data set
exp	experimental value of a variable or parameter for a data set
min	minimum value of a variable or parameter for a data set
max	maximum value of a variable or parameter for a data set
mean	mean value of a variable or parameter for a data set

The UFL is more sensitive to the flammability criterion than the LFL. It is also sensible to the direction of flame propagation [4]. This sensibility is an additional difficulty for the development of accurate methods for the determination of the UFLs of flammable compounds.

The flammability criteria are given by standardized procedures like that described by the American Standard ASTM E681, applied by Coronado et al. [2]: a mixture is considered flammable if the flame propagates upwards and outwards from the ignition point, located at the center of a spherical reaction vessel, forming an arc of at least 90° on the vessel's wall.

In other experimental configuration, described by Coward and Jones [4], the flame propagation is observed inside a cylindrical tube. The ignition source is located at one end of the cylindrical tube, and the flammability criterion establishes that a mixture is flammable if the flame propagates a certain distance towards the opposite end of the tube. This criterion can be applied for upward, downward or horizontal flame propagation. The flammability limits will present different values depending on the direction of flame propagation.

Another flammability criterion is given by the European Norm BS-EN 1839, adopted by Cui et al. [5]: a mixture is flammable if the pressure inside the reaction vessel presents an increase of 5% relative to its initial value.

A comparison of the flammability limits of some compounds determined by applying different standardized procedures has been provided by Schröder and Molnarne [6].

Several researchers have devoted their efforts to develop methods to calculate the flammability limits in air using known properties of the flammable compound and relying on existing data. The objective of the present work is to develop such a method to determine the UFL of C–H–O compounds, i.e. compounds which have carbon, hydrogen and oxygen in their molecular structure, by using

basic combustion theory, chemical equilibrium and known properties of the flammable compounds.

2. Brief review of methods for the determination of the UFL

There are some published methods for the determination of the UFL of flammable compounds in air at reference temperature and atmospheric pressure. In this section these methods are briefly described. They will be compared with the method developed in the present work in the Results and discussions section.

High and Danner [7] developed one of the earliest group contribution methods for the calculation of the UFL. A number of 24 molecular groups were considered and the 95% confidence intervals were obtained. The set of experimental values comprised 117 compounds.

Seaton [8] presented a second order group contribution method, where the input parameters are 38 molecular groups. A total of 139 flammable compounds were considered for development and validation. The result was a correlation which relies on the knowledge of the molecular structure of the flammable compound in order to be applied.

Lazzús [9] developed a neural network to determine the flammability limits. The input parameters are 42 molecular groups; 328 flammable compounds were considered for training and 90 for validation. The result was a neural network which is trained to predict the flammability limits in air of organic compounds.

Kondo et al. [10] developed a method to determine a parameter named F-number from which the flammability limits can be estimated. The result was a correlation which uses molecular structure information and 17 empirical coefficients. A total set of 238 flammable compounds was considered.

Albahri [11] presented a structural molecular group contribution method which resulted in a correlation that uses 20 structural groups for the calculation of the UFL. The number of flammable compounds considered was 477.

Gharagheizi [12] used quantitative molecular properties in order to obtain a correlation which determines the UFL. The correlation uses 5 quantitative molecular properties that are determined by a separate procedure on Dragon Software. The total set consisted on 865 flammable compounds.

Pan et al. [13] obtained a correlation for the prediction of the UFL. The correlation uses 4 quantitative molecular properties. The total set had 588 compounds, from which 114 compounds were used in the test set. In order to determine the quantitative molecular properties, the Dragon Software must be used.

Mendiburu et al. [14] developed a semi-empirical method based on adiabatic flame temperature and chemical equilibrium. The method determines the UFL of C–H compounds in air at atmospheric pressure and reference temperature. The total set had 115 flammable compounds, from which 53 compounds were considered in the prediction set.

Frutiger et al. [15] presented a group contribution method and the uncertainty analysis for the determination of flammability-related properties, including the UFL. For the determination of the UFL, a set of 351 compounds was considered. The group contribution parameters must be identified for each flammable compound by applying Simplified Molecular Input Line Entry Specification (SMILES).

3. Development of the proposed method

As observed in Section 2, most of the published articles deal with the problem of determining the UFL by directly applying an approximation method to this quantity. The combustion process taking place at the UFL is generally not analyzed. This constitutes the first motivation of the present work: to include basic combustion theory in the method for the determination of the UFL. If basic combustion theory is applied the UFL is not directly determined, it is instead calculated by using an approximate value of the adiabatic flame temperature at this limit.

The same concept has been applied by Mendiburu et al. [16] for the determination of the LFL of C–H–O compounds. In the case of the LFL, it was assumed that complete combustion is achieved. Therefore, the method developed for the LFL is simpler than the method developed for the UFL, mainly because combustion is incomplete at the UFL.

Since basic combustion theory is used in the development of the present method it is better to analyze compounds of similar characteristics, for example, compounds containing C, H and O atoms in their molecules. This observation is related to the values of the adiabatic flame temperatures and to the global combustion reactions assumed to represent the process at the UFL. It will be shown later that this approach allows the determination of the UFL by using simple and widely known properties of the flammable compounds.

The method developed in the present work is based on the following idea: by knowing an approximate value of the adiabatic flame temperature at the UFL (T_{UFL}) it is possible to determine the number of moles of oxygen per mole of the flammable compound (ν_{ar}^{UFL}).

Adopting a simple air molecule where for one mole of oxygen there are 3.76 mol of nitrogen, the number of moles of air at the UFL will be $4.76\nu_{ar}^{UFL}$. Therefore, the UFL can be calculated by Eq. (1).

$$UFL = \frac{100\%}{1 + 4.76\nu_{ar}^{UFL}} \quad (1)$$

In this sense, the method is similar to those based on the calculated adiabatic flame temperature that were developed for the determination of the LFL [17,18]. Also among these works, those by Rowley et al. [19] and Mendiburu et al. [20,16] can be considered.

In the method developed in the present work, the value of T_{UFL} is determined by a parameter called θ_{UFL} . That parameter is defined as the ratio of the adiabatic flame temperature at the stoichiometric composition (T_{stq}) to the value of T_{UFL} . This concept is the same adopted for the case of the LFL in previous work by Mendiburu et al. [16].

$$\theta_{UFL} = \frac{T_{stq}}{T_{UFL}} \quad (2)$$

The motivation for the use of θ_{UFL} came from the observation of its values for several compounds. It was noticed that θ_{UFL} did not present high variation from one compound to another, which is not the case for UFL or T_{UFL} .

Evidence of the above observation is shown in Table 1, where the total set consists of 208 C–H–O compounds, the correlation set consists of 136 C–H–O compounds and the prediction set consists of 72 C–H–O compounds. In Table 1 the minimum ($\theta_{UFL,min}$), maximum ($\theta_{UFL,max}$), mean ($\theta_{UFL,mean}$) and the standard deviation (σ_θ) are shown for the θ_{UFL} of the considered compounds. Also in Table 1 the minimum (UFL_{min}), maximum (UFL_{max}), mean (UFL_{mean}) and standard deviation (σ_{UFL}) are shown for the UFLs of the considered compounds. It can be observed that the standard deviation σ_θ represents between 7.3 and 7.9% of the mean value $\theta_{UFL,mean}$. On the other hand, the standard deviation σ_{UFL} represents between 33.3 and 50.2% of the mean value UFL_{mean} . Therefore, the information of Table 1 confirms the observation regarding the small variation of θ_{UFL} from one compound to another.

The correlation procedure was performed for θ_{UFL} and not for either the UFL or the T_{UFL} . Furthermore, it will be shown that θ_{UFL} can be correlated by a combination of five simple parameters: the number of moles of carbon (x_C), hydrogen (x_H) and oxygen (x_O), the molecular weight (M) and the formation enthalpy ($\bar{h}_{f,F}^0$) of the flammable compound.

The determination of the adiabatic flame temperature at the stoichiometric composition is widely known and can be found in classic combustion literature [21,22].

The values of the flammability limits depend on the initial temperature and pressure conditions of the mixture. In the present work, the UFL is determined at the reference temperature of 25 °C and at atmospheric pressure. Experimental observation has shown that for a constant initial pressure, the UFL presents higher values for higher initial temperatures. This behavior can be observed in Fig. 1, where experimental data by Kondo et al. [23] are depicted. The LFL presents lower values when the initial temperature is higher and the initial pressure is held constant. This behavior can also be observed in Fig. 1. However, the dependence

Table 1
Comparison of the standard deviation of θ_{UFL} and of the UFL.

Parameter	Correlation set	Prediction set	Total set
$\theta_{UFL,min}$	1.87	1.94	1.87
$\theta_{UFL,mean}$	2.41	2.35	2.39
$\theta_{UFL,max}$	2.67	2.57	2.67
σ_θ	0.18 (7.3%)	0.19 (7.9%)	0.18 (7.7%)
UFL_{min}	2.30	5.10	2.30
UFL_{mean}	9.01	8.97	9.00
UFL_{max}	36.50	19.00	36.50
σ_{UFL}	4.53 (50.2%)	2.99 (33.3%)	4.06 (45.1%)

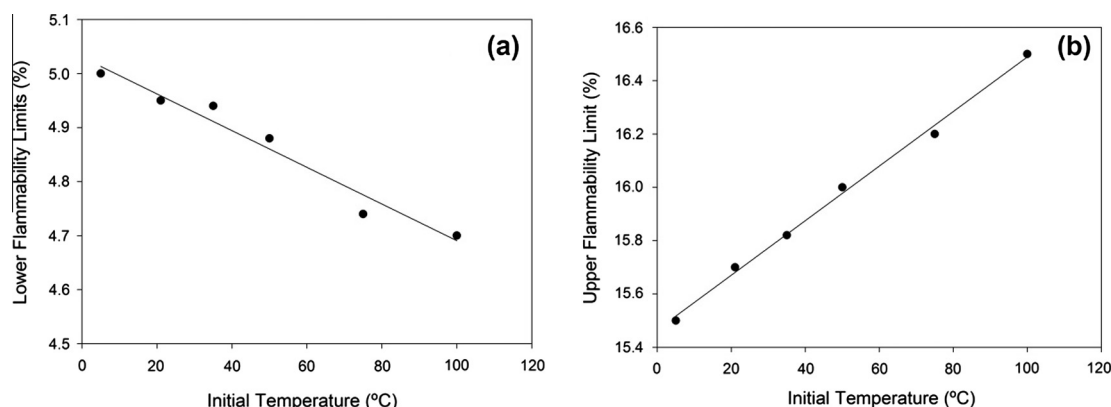


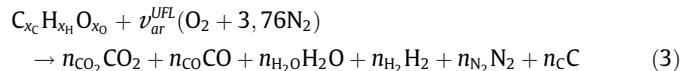
Fig. 1. Temperature dependence of the flammability limits of methane at atmospheric pressure: (a) lower flammability limit and (b) upper flammability limit. Experimental data by Kondo et al. [23].

of the flammability limits on the mixture's initial temperature will be addressed in future work.

3.1. Adiabatic flame temperature at the UFL

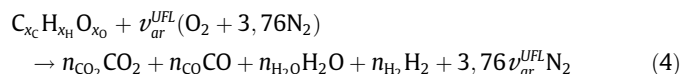
The adiabatic flame temperatures at the UFL of a correlation set must be determined in order to obtain a correlation for θ_{UFL} . Therefore, in this sub-section the UFL is considered a known value.

At the UFL composition the mixture is fuel rich and incomplete combustion is expected. Species of incomplete combustion such as CO, C and H₂ appear on the products. A one-step global reaction representing the combustion process would be:

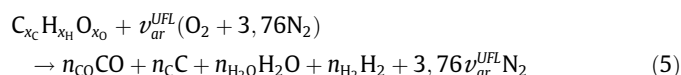


where n_i represents the number of moles of the i th compound in the products. The objective is to obtain a one-step global reaction as simple as possible; the reaction presented in Eq. (3) can be simplified. Considering the UFLs of methane and ethylene given as 15% and 36% [3], respectively, and assuming that all the carbon reacts to form CO, the required number of moles of oxygen would be 0.50 for methane and 1.00 for ethylene. On the other hand, at the UFL, the available number of moles of oxygen is 1.19 and 0.38 mol, respectively. Therefore, it is reasonable to assume that methane would react to form CO₂, CO, H₂O, H₂ and N₂ without significant concentration of C in the products; and, it is also reasonable to assume that ethylene would react to form CO, C, H₂O, H₂ and N₂ without significant concentration of CO₂. The aforementioned considerations imply that two one-step global reactions can be adopted:

Global reaction without condensate



Global reaction with condensate



The assumption of these two reactions with less product species, instead of one with more product species, will simplify the process for the determination of the number of moles of oxygen in the next sub-section.

In order to determine the adiabatic flame temperature the following considerations are adopted:

- (i) The combustion process is incomplete and can be represented by at least one of the one-step global reactions given in Eqs. (4) and (5).
- (ii) The nitrogen does not react.
- (iii) The combustion process takes place at constant pressure.
- (iv) There is no work crossing the system's boundaries.
- (v) The process is adiabatic.
- (vi) The initial temperature of the reactants is known.
- (vii) The gases are considered ideal gases.
- (viii) The combustion products are in chemical equilibrium.

Some of the above assumptions are of key importance and shall be further explained in what follows:

Coward and Jones [4] stated that the flammability limits should be determined at constant pressure and such configuration has been applied by Mishra and Rahman [24] in their experiments. A constant pressure combustion process has been assumed in other works related to the determination of flammability limits [17,16,18,25] and this consideration is consistent with the experimental determination. As a first argument, the American Norm ASTM E681 [26] is considered. In this configuration, a borosilicate flask is used as the combustion chamber and, in order to facilitate venting, a rubber cover rests on top of the flask's neck. Therefore, the experimental determination of flammability limits with ASTM E681 is not a constant volume process because the rubber cover comes out with the pressure increase. As a second argument, the European Norm BS-EN 1839 adopted by Cui et al. [5] is considered. In this configuration, a closed vessel is used and a mixture is considered flammable if the pressure rise after the ignition is higher than 5%. This means that, according to BS-EN 1839, the flammability limits would be found in mixtures which present a pressure rise of just about 5%. Thus, the consideration of a constant pressure combustion process is justified. Furthermore, the experimental flammability limits are not restricted to confined flammable mixtures; on the contrary, they are intended to represent unconfined flammable mixtures where a flame could propagate at constant pressure.

It is known that the flammability limits are influenced by the quenching effect of the test vessel walls. The size of the vessel must be sufficient to minimize the walls quenching effect on the flammability limits. This has been stated by Coward and Jones [4] and also in the American Norm ASTM E681 [26]. In a recent work by Liaw and Chen [25] the initial temperature effect on the flammability limits was studied by applying adiabatic and a non-adiabatic models. It was shown that the adiabatic model performed better than the non-adiabatic one. Therefore, the assumption of an adiabatic combustion process is also justified.

For most compounds at the UFL composition, only one of the reactions shown in Eqs. (4) and (5) will produce realistic values once chemical equilibrium is assumed. However, there are few cases where both reactions could produce realistic values. Under such circumstances, the reaction which produces the higher adiabatic flame temperature is preferred because it would represent a combustion process where more fuel has reacted to form combustion products.

3.1.1. Adiabatic flame temperature at the UFL for the reaction without condensate

Applying the mass conservation law to the reaction without condensate, the following equations are obtained:

$$x_C = n_{CO} + n_{CO_2} \quad (6)$$

$$\frac{x_H}{2} = n_{H_2O} + n_{H_2} \quad (7)$$

$$x_O = n_{CO} + 2n_{CO_2} + n_{H_2O} - 2\nu_{ar}^{UFL} \quad (8)$$

Since the value of the UFL is known, the number of moles of oxygen (ν_{ar}^{UFL}) is determined from Eq. (1). The energy conservation equation for the combustion process is then given by Eq. (9).

$$h_F + \nu_{ar}^{UFL} h_{ar,R} = n_{CO_2} h_{CO_2} + n_{CO} h_{CO} + n_{H_2O} h_{H_2O} + n_{H_2} h_{H_2} + 3,76 \nu_{ar}^{UFL} h_{N_2} \quad (9)$$

where h_i is the specific absolute enthalpy in molar base (kJ/mol) of the i th species. It is important to notice that $h_{ar} = h_{O_2} + 3.76 h_{N_2}$ was adopted in order to simplify the formulation.

The chemical equilibrium consideration can be implemented by using Gibbs free energy minimization or the equilibrium constant for a chosen reaction. Using the equilibrium constant approach an analytical solution for ν_{ar}^{UFL} will be obtained later. The water–gas homogeneous reaction was chosen to obtain the equilibrium equation:

Water–gas homogeneous reaction



The equilibrium equation is given in Eq. (11).

$$n_{CO_2} n_{H_2} = K_{sc} n_{H_2O} n_{CO} \quad (11)$$

where K_{sc} is the equilibrium constant. Using Eqs. (6)–(8) to express the number of moles of CO_2 , H_2O and H_2 as functions of the number of moles of CO , replacing those expressions into Eq. (11), and rearranging:

$$a(n_{CO})^2 + b n_{CO} + c = 0 \quad (12)$$

where the coefficients are:

$$a = 1 - K_{sc} \quad (13)$$

$$b = 2a \nu_{ar}^{UFL} - x_C(2a + 1) + a x_O - \frac{x_H}{2} \quad (14)$$

$$c = x_C \left(2x_C + \frac{x_H}{2} - x_O - 2 \nu_{ar}^{UFL} \right) \quad (15)$$

There are two possible solutions for Eq. (12), but only one of them will be a positive real number. The solution scheme consists on assuming a temperature value, determining the number of moles of each species in the products, checking the assumed temperature value with Eq. (9), and correcting the assumed temperature until convergence is achieved. This simple procedure was implemented in MATLAB software, where the temperature was obtained by using the “fsolve” solver. The Newton–Raphson method can be easily implemented in any other software and used to determine the adiabatic flame temperature. The implementation of the Newton–Raphson method is described in several textbooks on numerical methods [27–31].

3.1.2. Adiabatic flame temperature at the UFL for the reaction with condensate

The value of T_{UFL} for the reaction with condensate is obtained with an analogous procedure to that explained above for the case without condensate. The mass conservation equations for the reaction with condensate are:

$$x_C = n_{CO} + n_C \quad (16)$$

$$\frac{x_H}{2} = n_{H_2O} + n_{H_2} \quad (17)$$

$$x_O = n_{CO} + n_{H_2O} - 2 \nu_{ar}^{UFL} \quad (18)$$

The energy conservation equation applied to the reaction with condensate is given in Eq. (19).

$$h_F + \nu_{ar}^{UFL} h_{ar,R} = n_{CO} h_{CO} + n_C h_C + n_{H_2O} h_{H_2O} + n_{H_2} h_{H_2} + 3,76 \nu_{ar}^{UFL} h_{N_2} \quad (19)$$

The water–gas heterogeneous reaction was chosen to apply the equilibrium consideration:

Water – gas heterogeneous reaction



The equilibrium equation is given in Eq. (21).

$$n_{CO} n_{H_2} = K_{cc} n_T n_{H_2O} (p_0/p) \quad (21)$$

where K_{cc} is the equilibrium constant, p_0 is the standard atmospheric pressure, and p is the pressure of the combustion process. In the present study, both pressures are equal to 1 atm. It is convenient to write an equation for the total number of moles of the gaseous species (n_T):

$$n_T = n_{CO} + \frac{x_H}{2} + 3,76 \nu_{ar}^{UFL} \quad (22)$$

Using Eqs. (16)–(18) to express the number of moles of C , H_2O and H_2 as functions of the number of moles of CO , replacing those in Eq. (21), and rearranging, a quadratic equation for n_{CO} is obtained, identical to Eq. (12). The coefficients of that equation are shown below:

$$a = 1 + K_{cc} (p_0/p) \quad (23)$$

$$b = \frac{x_H}{2} a - x_O a + 3,76 \nu_{ar}^{UFL} (a - 1) - 2a \nu_{ar}^{UFL} \quad (24)$$

$$c = (1 - a) \left[x_H \nu_{ar}^{UFL} + 3,76 x_O \nu_{ar}^{UFL} + \frac{x_H}{2} x_O + 7,52 (\nu_{ar}^{UFL})^2 \right] \quad (25)$$

The solution scheme is identical to that described for the case without condensate.

For some compounds, both reactions produce a possible solution for the adiabatic flame temperature at the UFL. In such cases the higher temperature was chosen.

3.2. Number of moles of oxygen

Once a correlation for θ_{UFL} is established, the value of T_{UFL} will be known. Therefore, a procedure to determine the number of moles of oxygen at the UFL needs to be developed. Again there will be two processes: one for the reaction without condensate and another for the reaction with condensate. For some compounds, the same value of T_{UFL} produces two close values of the UFL, one for the reaction without condensate and the other for the reaction with condensate. In such cases, the higher value of the UFL was chosen. This criterion is in accordance with safety considerations.

3.2.1. Number of moles of oxygen at the UFL for the reaction without condensate

In Section 3.1.1 the number of moles of CO₂, H₂O and H₂ were expressed as functions of n_{CO} . Replacing those expressions into Eq. (9) and rearranging, the following expression is obtained:

$$n_{CO} = m v_{ar}^{UFL} + n \quad (26)$$

where the coefficients are:

$$m = \frac{h_{ar,R} + 2h_{H_2} - 2h_{H_2O} - 3,76h_{N_2}}{h_{CO} - h_{CO_2} + h_{H_2O} - h_{H_2}} \quad (27)$$

$$n = \frac{h_F - x_C h_{CO_2} + (2x_C - x_O)h_{H_2O} + (x_O - \frac{x_H}{2} - 2x_C)h_{H_2}}{h_{CO} - h_{CO_2} + h_{H_2O} - h_{H_2}} \quad (28)$$

By using Eq. (26) the number of moles of CO₂, H₂O and H₂ are now expressed as functions of v_{ar}^{UFL} . Replacing the obtained expressions into Eq. (11) and rearranging:

$$a_v (v_{ar}^{UFL})^2 + b_v v_{ar}^{UFL} + c_v = 0 \quad (29)$$

where the coefficients are given by:

$$a_v = am^2 + 2am \quad (30)$$

$$b_v = 2amn + amx_O + 2an - (2a + 1)mx_C - m\frac{x_H}{2} - 2x_C \quad (31)$$

$$c_v = an^2 - (2a + 1)nx_C + (an - x_C)x_O - (n - x_C)\frac{x_H}{2} + 2x_C^2 \quad (32)$$

The quadratic equation given in Eq. (29) has an analytical solution for the number of moles of oxygen at the UFL (v_{ar}^{UFL}), and, by applying Eq. (1), the UFL is obtained. It is now evident that the reason for choosing simpler one-step global reactions was to obtain an analytical solution for v_{ar}^{UFL} .

The solution scheme implies the determination of all the coefficients which are functions of the flammable compound and T_{UFL} . A simpler routine which determines the coefficients was written in MATLAB software, where the analytical solution of the quadratic equation was also considered.

3.2.2. Number of moles of oxygen at the UFL for the reaction with condensate

In Section 3.1.2, the numbers of moles of C, H₂O and H₂ were expressed as functions of n_{CO} . Replacing those expressions into Eq. (19) and rearranging, the same expression shown in Eq. (26) is obtained. However, the coefficients are different:

$$m = \frac{h_{ar,R} + 2h_{H_2} - 2h_{H_2O} - 3,76h_{N_2}}{h_{CO} - h_{H_2} - h_{H_2O} - h_C} \quad (33)$$

$$n = \frac{h_F - x_C h_C - x_O h_{H_2O} + (x_O - \frac{x_H}{2})h_{H_2}}{h_{CO} - h_{H_2} - h_{H_2O} - h_C} \quad (34)$$

By using Eq. (26), the numbers of moles of C, H₂O and H₂ are now expressed as functions of v_{ar}^{UFL} . Replacing the obtained expressions into Eq. (21) and rearranging, the expression shown in Eq. (29) is obtained again. The coefficients for that expression are presented below:

$$a_v = am^2 - 2am + 3,76(a - 1)m - 7,52(a - 1) \quad (35)$$

$$b_v = 2amn + am\left(\frac{x_H}{2} - x_O\right) - 2an + (a - 1)(3,76[n - x_O] - x_H) \quad (36)$$

$$c_v = an^2 + an\left(\frac{x_H}{2} - x_O\right) - (a - 1)\frac{x_H}{2}x_O \quad (37)$$

The solution scheme is analogous to that described for the reaction without condensate.

The use of the reaction shown in Eq. (3) requires the application of the Newton – Raphson method to obtain a solution for v_{ar}^{UFL} . However, by using the reactions shown in Eqs. (4) and (5), the solution for v_{ar}^{UFL} is analytical.

4. Thermodynamic properties and experimental data

The thermodynamic properties of the species involved in the combustion process, were determined by using the NASA–Glenn coefficients given by McBride et al. [32]. The specific absolute enthalpies and the specific entropies (s) are used to determine the Gibbs free energies at the standard-state pressure in molar base (g^0). All these properties are functions of temperature:

$$\frac{h(T)}{RT} = -\frac{a_1}{T^2} + a_2 \frac{\ln T}{T} + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \quad (38)$$

$$\frac{s(T)}{R} = -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln T + a_4 T + a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + b_2 \quad (39)$$

$$\frac{g^0(T)}{RT} = \frac{h(T)}{RT} - \frac{s(T)}{R} \quad (40)$$

where R is the universal ideal gas constant, the coefficients a_i and b_i are the NASA–Glenn coefficients given for each compound by McBride et al. [32]. The equilibrium constants for the considered reactions are determined by using the standard-state Gibbs function change (ΔG_T^0) as shown in Eqs. (41) and (42).

Water – gas homogeneous reaction

$$K_{sc} = \exp\left(-\frac{\Delta G_{T,2}^0}{RT}\right) = \exp\left(-\frac{g_{T,CO_2}^0 - g_{T,CO}^0 - g_{T,H_2O}^0}{RT}\right) \quad (41)$$

Water – gas heterogeneous reaction

$$K_{cc} = \exp\left(-\frac{\Delta G_{T,1}^0}{RT}\right) = \exp\left(-\frac{g_{T,CO}^0 - g_{T,H_2O}^0}{RT}\right) \quad (42)$$

The experimental data of the upper flammability limits were obtained from several sources. The main sources are listed below by order of number of compounds:

- Supplementary Material by Gharagheizi [12] – UFLs of 66 compounds. This data belong to the Design Institute for Physical Properties (DIPPR).
- Lide [33] – UFLs of 56 compounds.
- CAMEO Chemicals [34] – UFLs of 17 compounds.
- Chemical Book [35] – UFLs of 15 compounds.
- PubChem [36] – UFLs of 13 compounds.
- The experimental data of 41 compounds were obtained from specific Material Safety Data Sheets; these sources are properly indicated in the [Supplementary Material](#) and in the reference section.

The total set contains 208 flammable compounds. This set was divided into a correlation set and a prediction set of 136 and 72 flammable compounds, respectively.

An earlier compilation of experimental data was presented by Zabetakis [3] in 1965. Most of these data have been included in the aforementioned references and also in works by Glassman and Yetter [21] and by Carson and Mumford [37]. Also, Lazzús [9] and Pan et al. [13] present experimental data on the Supplementary Material of their respective works. These sources [3,9,13,21,33] are provided as an alternative to the interested reader.

The enthalpies of formation of the flammable compounds were obtained from NIST Chemistry Webbook [38], and from Vatani et al. [39].

5. The correlation for θ_{UFL}

The combustion process represented by the reaction without condensate will be used to explain the meaning of θ_{UFL} . Average

heat capacities at constant pressure ($\bar{c}_{p,i}$) are considered in the energy conservation equation given in Eq. (9). Also, the reference temperature is represented by T_r . Applying those considerations and rearranging:

$$T_{UFL} - T_r = \frac{H_{UFL} + (\bar{c}_{p,F} + 4.76 \nu_{ar}^{UFL} \bar{c}_{p,ar})(T_1 - T_r)}{n_{CO_2} \bar{c}_{p,CO_2} + n_{CO} \bar{c}_{p,CO} + n_{H_2O} \bar{c}_{p,H_2O} + n_{H_2} \bar{c}_{p,H_2} + 3.76 \nu_{ar}^{UFL} \bar{c}_{p,N_2}} \quad (43)$$

It is important to notice that the number of moles of air is equal to $4.76 \nu_{ar}^{UFL}$. An analogous procedure can be applied to the combustion process at the stoichiometric composition, obtaining the following expression:

$$T_{stq} - T_r = \frac{H_C + (\bar{c}_{p,F} + 4.76 \nu_{ar}^s \bar{c}_{p,ar})(T_1 - T_r)}{x_C \bar{c}_{p,CO_2} + \frac{x_H}{2} \bar{c}_{p,H_2O} + 3.76 \nu_{ar}^s \bar{c}_{p,N_2}} \quad (44)$$

where H_{UFL} is the heat liberated in the combustion process at the UFL and, analogously, H_C is the heat liberated at the stoichiometric combustion process:

$$H_{UFL} = \bar{h}_{f,F}^0 - n_{CO_2} \bar{h}_{f,CO_2}^0 - n_{CO} \bar{h}_{f,CO}^0 - n_{H_2O} \bar{h}_{f,H_2O}^0 \quad (45)$$

$$H_C = \bar{h}_{f,F}^0 - x_C \bar{h}_{f,CO_2}^0 - \frac{x_H}{2} \bar{h}_{f,H_2O}^0 \quad (46)$$

Recognizing that the initial temperature of the reactants is equal to the reference temperature ($T_1 = T_r$), dividing Eq. (44) by Eq. (43), expressing n_{CO_2} as a function of x_C and n_{CO} ; n_{H_2O} as a function of x_H and n_{H_2} ; and, rearranging:

$$\frac{T_{stq} - T_r}{T_{UFL} - T_r} = \frac{1 + (n_{CO} \bar{c}_{p,1} + n_{H_2} \bar{c}_{p,2} + 3.76 \nu_{ar}^{UFL} \bar{c}_{p,N_2}) / (x_C \bar{c}_{p,CO_2} + \frac{x_H}{2} \bar{c}_{p,H_2O})}{1 + 3.76 \nu_{ar}^s \bar{c}_{p,N_2} / (x_C \bar{c}_{p,CO_2} + \frac{x_H}{2} \bar{c}_{p,H_2O})} \left(\frac{H_C}{H_{UFL}} \right) \quad (47)$$

where, $\bar{c}_{p,1} = \bar{c}_{p,CO} - \bar{c}_{p,CO_2}$ and $\bar{c}_{p,2} = \bar{c}_{p,H_2} - \bar{c}_{p,H_2O}$. The denominator of the first term on the right hand side depends only on the flammable compound, while the numerator depends on the flammability limit and also on the flammable compound. The second term on the right hand side is the ratio of the heat liberated by the combustion process at the stoichiometric composition to that liberated at the UFL composition.

Therefore, the parameter θ_{UFL} is an indirect measure of the flammability limit of a given flammable compound. In obtaining a correlation for θ_{UFL} the expression given in Eq. (2) will be used. This means that T_r is dropped from the left hand side of Eq. (47). By inspection of Eq. (47), it is concluded that θ_{UFL} can be represented as a function of five parameters:

$$\theta_{UFL} = \frac{T_{stq}}{T_{UFL}} = f(x_C, x_H, x_O, \bar{h}_{f,F}^0, M_F) \quad (48)$$

The correlation for θ was obtained from the correlation set (136 flammable compounds) by applying the multiple linear regression tool of the MATLAB Software. Different variables were proposed by combining the basic parameters: x_C , x_H , x_O , $\bar{h}_{f,F}^0$ and M_F . The variables were added one by one; each time a variable was added the UFLs of the correlation set were calculated and the accuracy of the method was tested. If the method's accuracy did not increase (or if it decreased) the variable was discarded. As a result of this procedure the following variables remained in the correlation:

$$x_1 = \frac{\bar{h}_{f,F}^0}{M} b_1 \quad (49)$$

$$x_2 = \frac{\bar{h}_{f,F}^0}{x_C x_H x_O} b_2 \quad (50)$$

$$x_3 = \frac{M}{x_C x_H x_O} b_3 \quad (51)$$

$$x_4 = \frac{x_C x_O}{x_H} b_4 \quad (52)$$

The constants b_i are equal to unity and they have the purpose of making the variables x_i dimensionless. For example $b_1 = 1 \text{ kg/kJ}$. The correlation for θ_{UFL} is shown below:

$$\begin{aligned} \theta_{UFL} = & 2.7659 - \frac{5.3705}{10^2} x_1 - \frac{1.4071}{10^2} x_1^2 - \frac{1.6690}{10^4} x_1^3 \\ & - \frac{1.1561}{10} x_2 - \frac{7.1337}{10^3} x_2^2 - \frac{9.2997}{10^5} x_2^3 - \frac{6.5872}{10} x_3 \\ & + \frac{1.4739}{10} x_3^2 - \frac{7.8006}{10^3} x_3^3 + \frac{1.9024}{10^2} x_4 - \frac{1.6117}{10} x_4^{1/2} \end{aligned} \quad (53)$$

Once θ_{UFL} is determined, the procedure described in Section 3.2 is applied in order to obtain the value of the UFL for a particular compound. An example of calculation is provided in the [Supplementary Material](#).

6. Method's accuracy and 95% confidence intervals

The procedures applied to determine the method's accuracy and the 95% confidence intervals were taken from the work by Montgomery [40]. Similar procedures were applied by Frutiger et al. [41,15].

The accuracy was tested in terms of the absolute value of the relative error (ARE), the average of the absolute values of the relative errors (AARE) and the squared correlation coefficient (R^2):

$$ARE = \frac{|UFL_{calc} - UFL_{exp}|}{UFL_{exp}} 100\% \quad (54)$$

$$AARE = \frac{1}{N} \sum_{i=1}^N ARE_i \quad (55)$$

$$R^2 = 1 - \frac{SSE}{SST} \quad (56)$$

where SSE is the sum of squares of the errors and SST is the total sum of squares, as given in Eqs. (57) and (58):

$$SEE = \sum_{i=1}^N (UFL_{calc,i} - UFL_{exp,i})^2 \quad (57)$$

$$SST = \sum_{i=1}^N (UFL_{exp,i})^2 - \frac{(\sum_{i=1}^N UFL_{exp,i})^2}{N} \quad (58)$$

The confidence intervals are constructed by using the t-distribution in terms of the confidence level (α), the degrees of freedom ($N - P$) and a scalar obtained by matrix operations as described by Montgomery [40]. The confidence intervals are obtained by applying Eq. (59) to each compound.

$$UFL_{\max(\text{ou min})} = UFL_{calc} \pm t_{\alpha/2, N-P} \sqrt{\hat{\sigma}^2 (1 + \mathbf{x}_0 (\mathbf{X}'\mathbf{X})^{-1} \mathbf{x}_0')} \quad (59)$$

The UFL_{calc} are determined by using the method described in Section 3.2, the second term of the right hand side of Eq. (59) is the method's uncertainty and it has the same units as the UFL, i.e., %. The values UFL_{\max} and UFL_{\min} are the limits of the confidence interval and they are obtained by summing, or subtracting, the uncertainty to the UFL_{calc} . The method's variance ($\hat{\sigma}^2$) is determined by Eq. (60).

$$\hat{\sigma}^2 = \frac{SSE}{N - P} \quad (60)$$

In the present article basic combustion theory has been used to relate the UFL to the adiabatic flame temperature at that limit, designated as T_{UFL} . This means that if the exact value of T_{UFL} is known, the developed method determines the exact value of the UFL. Thus, any uncertainty is related to the approximation procedure applied to determine T_{UFL} . Furthermore, the value of T_{UFL} is approximated by using the stoichiometric flame temperature, designated as T_{stq} ,

and an empirical parameter called θ . Since the value of T_{stq} is determined by basic combustion theory, it is concluded that the uncertainties must be related to the correlation used to calculate the parameter θ . Once this conclusion has been achieved, the uncertainty can be determined.

In Eq. (59), \mathbf{X} is a 136×12 matrix; the number of rows correspond to the number of compounds in the correlation set and the number of columns correspond to the number of coefficients used to determine θ in Eq. (53). The first column of \mathbf{X} is filled with ones; the transpose of this matrix is represented by \mathbf{X}' . The matrix $(\mathbf{X}'\mathbf{X})^{-1}$ is a 12×12 matrix which does not change for different flammable compounds since it is related to the correlation procedure; this matrix is provided in the [supplementary material](#).

The row vector \mathbf{x}_0 is determined for each flammable compound; it is given by Eq. (61), where the elements are determined by using Eqs. (49)–(52). The column vector \mathbf{x}_0' is the transpose of \mathbf{x}_0 .

$$\mathbf{x}_0 = \left[1 \quad x_1 \quad x_1^2 \quad x_1^3 \quad x_2 \quad x_2^2 \quad x_2^3 \quad x_3 \quad x_3^2 \quad x_3^3 \quad x_4 \quad x_4^{1/2} \right] \quad (61)$$

The parameters required to determine the confidence intervals are summarized in Table 2. The 95% confidence interval will be obtained for each compound in the correlation and prediction sets.

7. Results and discussions

The validation of the method was performed by determining the values of the AARE and R^2 . Afterwards, the 95% confidence intervals were calculated for each compound on the correlation and prediction sets. The method presents an AARE of 9.66% for the correlation set, 7.63% for the prediction set and 8.95% for the total set of flammable compounds. The value of R^2 is 0.9382 for the correlation set, 0.9188 for the prediction set, and 0.9346 for the total set of flammable compounds.

The results obtained with the developed method are depicted in Fig. 2. It shows good accuracy when applied to the determination of the UFLs of C–H–O compounds. The solid line represents the experimental data and the circles and triangles represent the calculated data from the correlation and prediction sets, respectively.

The 95% confidence intervals are shown in Fig. 3. The flammable compounds were ordered according to the values of their UFLs, from the lowest to the highest, and assigned an Index Number. Only for seven compounds the experimental values of the UFLs have fallen outside of the 95% confidence interval. In the work by High and Danner [7], the results obtained for 12 compounds are shown; the experimental UFLs of 3 compounds did not fall within the 95% confidence interval. High and Danner [7] used a set of 181 flammable compounds. It was not stated how many of these compounds had their experimental UFLs fall outside of the 95% confidence interval.

Frutiger et al. [15] also determined the UFLs of several kind of compounds and determined the 95% confidence interval. In the supplementary material provided by Frutiger et al. [15] it was found that, in the case of the UFL, the minimum and maximum

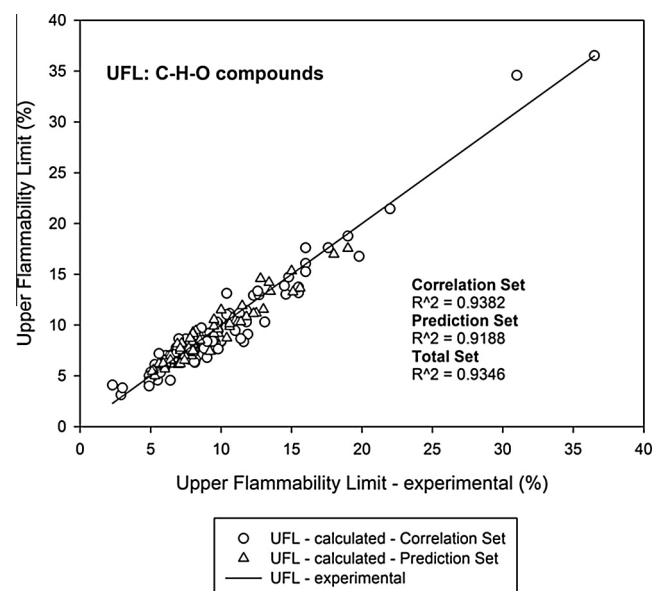


Fig. 2. Accuracy of the method for the determination of the UFLs of C–H–O compounds.

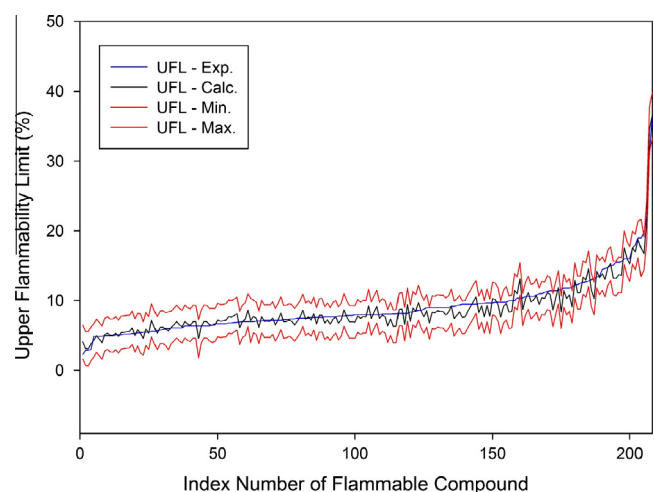


Fig. 3. Results obtained for the 95% confidence interval of the UFLs of C–H–O compounds.

uncertainties were 1.07% and 7.25%, respectively. In the present work the minimum and maximum uncertainties were 2.32% and 4.10%, respectively. It is important to notice that uncertainties have the same units as the UFL, i.e. %.

In the case of flammability limits, high uncertainties can produce unrealistic results because the minimum value of the 95% confidence interval can be a negative number. This problem was observed in the results obtained by Frutiger et al. [15] for 28 compounds in the case of the UFL and for 38 compounds in the case of the LFL. The reason for this kind of problem might be related to the heterogeneous set of compounds which were correlated in the aforementioned work. On the other hand, in the present work only C–H–O compounds were considered. The case of Diphenyl ether ($C_{12}H_{10}O$) can be taken as an example: in the present work, the calculated, minimum and maximum UFL were 5.67%, 2.95% and 8.39%, respectively; on the other hand, in the work by Frutiger et al. [15] the calculated, minimum and maximum UFL were 6.00%, –1.25% and 13.25%. A negative value appeared on the 95% confidence interval due to the high uncertainty.

Table 2

Parameters necessary to determine the 95% confidence interval for the UFL of C–H–O compounds.

Parameter	Symbol	Value
Number of data	N	136
Coefficients	P	12
Degrees of freedom	N – P	124
Variance	σ^2	1.3825
Confidence level	α	0.05 (5%)
t-distribution	$t_{0.025,124}$	1.960
$(\mathbf{X}'\mathbf{X})^{-1}$	Given in the supplementary material	

In Table 3 the method is compared with other available methods. The methods by Albahri [11], Frutiger et al. [15], Gharagheizi [12], High and Danner [7], Kondo et al. [10], Lazzús [9], Pan et al. [13] and Seaton [8] require the identification of molecular groups, or quantitative molecular properties, and, in some cases use the software developed by the respective authors. In the case of the present work, the developed method only needs the number of moles of C, H and O (x_C, x_H, x_O), the molecular weight (M), and, the formation enthalpy ($\bar{h}_{f,F}^0$). The molecular weight can also be determined by knowledge of x_C, x_H and x_O . Therefore, the developed method can be easily implemented and also it is straightforward for the reader with basic combustion knowledge.

In Table 4, it is observed that the 64.90% of the compounds presented AREs lower than 10%, 26.44% of the compounds presented AREs between 10% and 20%, and, 8.66% of the compounds presented AREs above 20%.

Another important characteristic of the UFLs is that sometimes there are different experimental data available in the literature. In order to exemplify this point, three compounds are consigned in Table 5. As stated in the introduction, the flammability criterion plays an important role on the value obtained in the experiments for the determination of the flammability limits, and it is especially important in the case of the UFL. Considering this complication, the developed method has good accuracy when applied to the determination of the UFLs of C–H–O compounds. The higher R^2 obtained in different methods for the determination of the LFLs also support the later statement. There is no easy rule to choose among these values; in the present work, the data provided by Lide [33] were accepted. In work by Lide [33], compounds with the formula $C_5H_{12}O$ present UFLs between 9.0 and 10.0%. Hence, for the UFL of Methyl *tert*-butyl ether, the value of 8.5% was adopted. In the same reference, compounds with the formula $C_4H_6O_2$ present UFLs between 8.8% and 25.0%. Thus, for the UFL of gamma-Butyrolactone, the value of 12.6% was accepted. In any practical application, a safety factor must be included.

The existence of different experimental values of the UFL of a compound should be considered from the point of view of the actual phenomena. As state by Coward and Jones [4], the UFLs determined with upward flame propagation are generally higher than those determined with downward flame propagation. An interesting case is that of ethylene: the UFL is 34.0% for upward flame propagation and 15.5% for downward flame propagation [4]. This difference is related to buoyancy effects and probably to cool flames phenomena.

On the other hand, the LFL of ethylene is 3.2% for upward flame propagation and 3.3% for downward flame propagation [4]. The experimental data available to this day is a compilation of flammability limits obtained by different researchers who applied different experimental configurations and also different flammability criteria. Therefore, it is not a coincidence that the

Table 4

Distribution of AREs obtained with the developed method.

ARE intervals	C–H–O compounds	
	Number of compounds	Percentage of total
$ARE \geq 20\%$	18	8.66%
$10\% \leq ARE < 20\%$	55	26.44%
$ARE < 10\%$	135	64.90%

methods developed for the LFLs perform better than those developed for the UFLs, since LFLs are less sensible to the experimental configuration or to the flammability criteria. Further discussion on this matter can be found in works by Lovachev et al. [42] and by Britton [43].

The experimental determination of the flammability limits does not contemplate the measurement of the product gas composition. The determination of that composition would help in the development of new methods which apply the available combustion theory. Thus, future experiments on flammability limits could be performed in order to obtain product gas compositions.

The method developed by Albahri [11] for the determination of the UFL presented a correlation coefficient of 0.96. In the same article, a method for the determination of the LFL was also presented, and its correlation coefficient was 0.93. In most published works the accuracy for the determination of the LFL is higher than the accuracy for the determination of the UFL. The higher accuracy of the methods for the determination of the LFLs is related to the homogeneity of the available experimental data.

The method by Lazzús [9] presented an R^2 of 0.9776 for the total set of flammable compounds. This method requires the identification of 42 structural molecular groups and the use of the artificial neural network developed by the author. On the other hand, the method developed in the present work needs information of five parameters, and more important, it is supported by basic combustion theory and chemical equilibrium.

The methods by Seaton [8], Kondo et al. [10], Pan et al. [13] and Frutiger et al. [15] presented R^2 values of 0.8862, 0.4197, 0.7540 and 0.91, respectively. The developed method presents better accuracy than the aforementioned methods, although, only slightly better in the case of the work by Frutiger et al. [15]. The developed method showed a lower value of the AARE than most of the methods cited in Table 3, for the total set of compounds.

The method developed in the present work can be implemented in any software which allows basic operations. The analytical solution obtained for ν_{ar}^{UFL} makes the method simple since it is not necessary to apply any numerical methods in order to use it. The Newton–Raphson method was used to obtain the values of T_{UFL} of the correlation set; however, that was only necessary during the method's development and it is not necessary for its application.

Table 3

Comparison of method's accuracy with other published methods.

Reference	Correlation set			Prediction set			Total set			Applicability
	R^2	N	AARE (%)	R^2	N	AARE (%)	R^2	N	AARE (%)	
Albahri [11]	–	464	–	–	13	–	0.9600	477	11.80	Hydrocarbons, ethers, ketones, aldehydes, alcohols, others
Frutiger et al. [15]	–	–	–	–	–	–	0.9100	351	15.90	
Gharagheizi [12]	0.9188	693	9.55	0.9263	172	9.58	0.9209	865	9.56	
High and Danner [7]	–	–	–	–	–	–	–	181	26.40	
Kondo [10]	–	–	–	–	–	–	0.4197	238	19.14	
Lazzús [9]	0.9780	328	7.00	0.9771	90	7.50	0.9776	418	7.10	C–H
Pan et al. [13]	0.7582	465	19.42	0.7320	114	18.43	0.7540	579	19.23	
Seaton [8]	–	–	–	–	–	–	0.8862	141	9.68	
Mendiburu et al. [14]	0.9158	62	7.93	0.9045	53	6.49	0.9248	115	7.27	
Present work	0.9382	136	9.66	0.9188	72	7.63	0.9346	208	8.95	

Table 5

Some compounds for which different experimental values of the UFL are reported.

Compounds	Formula	CAS#	UFL _{exp} (%)	UFL _{calc} (%)	UFL _{min} (%)	UFL _{max} (%)
Gamma-butyrolactone	C ₄ H ₆ O ₂	96-48-0	6.9	13.34	10.95	15.72
			12.6			
Propionic anhydride	C ₆ H ₁₀ O ₃	123-62-6	9.5	8.48	6.11	10.85
			11.9			
Methyl <i>tert</i> -butyl ether	C ₅ H ₁₂ O	1634-04-4	8.50	8.50	6.17	10.83
			15.1			

The results obtained by the developed method, for 89 compounds of the correlation set and 53 compounds of the prediction set, are presented in Tables S.1 and S.2 of the supplementary material. The following parameters are consigned in those tables: molecular weight (M), formation enthalpy ($\bar{h}_{f,i}^0$), adiabatic flame temperature at the stoichiometric composition (T_{stq}), adiabatic flame temperature at the UFL composition (T_{UFL}), experimental and calculated values of the UFL, (UFL_{exp}) and (UFL_{calc}), absolute values of the relative errors (ARE), average of the absolute values of the relative errors ($AARE$), Minimum value of the UFL for the 95% confidence interval (UFL_{min}) and maximum value of the UFL for the 95% confidence interval (UFL_{max}).

8. Conclusion

A method for the determination of the upper flammability limits of C–H–O compounds was developed and validated with experimental data. The method was developed by applying basic combustion theory and chemical equilibrium. Furthermore, the solution for the upper flammability limit is analytical, making the method simple and easy to implement.

The developed method showed good accuracy when compared with other published methods and when applied to the determination of the upper flammability limits of C–H–O compounds. It presented an AARE of 8.95% and a R^2 of 0.9346 for the total set of 208 compounds.

A procedure to determine the 95% confidence interval for the UFLs was established and, among the 208 compounds, only 7 of them presented experimental values of the UFL which fall slightly outside of the 95% confidence interval.

The method showed to be simpler than other published ones because it requires fewer properties than most published methods. Another important characteristic is that the developed method can be extended for any family of compounds as long as a correlation for the parameter θ_{UFL} can be established.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2016.10.009>.

References

- [1] Coronado C, Carvalho JA, Andrade JC, Cortez EV, Carvalho FS, Santos JC, et al. Flammability limits: a review with emphasis on ethanol for aeronautical applications and description of the experimental procedure. *J Hazard Mater* 2012;241–242:32–54. doi: <http://dx.doi.org/10.1016/j.jhazmat.2012.09.035>.
- [2] Coronado CJR, Carvalho JA, Andrade JC, Mendiburu AZ, Cortez EV, Carvalho FS, et al. Flammability limits of hydrated and anhydrous ethanol at reduced pressures in aeronautical applications. *J Hazard Mater* 2014;280:174–84. doi: <http://dx.doi.org/10.1016/j.jhazmat.2014.07.063>.
- [3] Zabetakis MG. Flammability characteristics of combustible gases and vapors. US Dept Inter Bur Mines 1965:1–129. doi: <http://dx.doi.org/10.2172/7328370>.
- [4] Coward HF, Jones GW. Limits of flammability of gases and vapors. US Dept Inter Bur Mines 1952:1–155. doi: <http://dx.doi.org/10.1021/jie4004943>.
- [5] Cui G, Yang C, Li Z, Zhou Z, Li J. Experimental study and theoretical calculation of flammability limits of methane/air mixture at elevated temperatures and pressures. *J Loss Prev Process Ind* 2016;41:252–8. doi: <http://dx.doi.org/10.1016/j.jlp.2016.02.01>.
- [6] Schröder V, Molnar M. Flammability of gas mixtures Part 1: Fire potential. *J Hazard Mater* 2005;121:37–44. doi: <http://dx.doi.org/10.1016/j.jhazmat.2005.01.032>.
- [7] High MS, Danner RP. Prediction of upper flammability limit by a group contribution method. *Ind Eng Chem Res* 1987;26:1395–9. doi: <http://dx.doi.org/10.1021/ie00067a021>.
- [8] Seaton WH. Group contribution method for predicting the lower and the upper flammable limits of vapors in air. *J Hazard Mater* 1991;27:169–85. doi: [http://dx.doi.org/10.1016/0304-3894\(91\)80028-M](http://dx.doi.org/10.1016/0304-3894(91)80028-M).
- [9] Lazzús JA. Neural network/particle swarm method to predict flammability limits in air of organic compounds. *Thermochim Acta* 2011;512:150–6.
- [10] Kondo S, Urano Y, Tokuhashi K, Takahashi A, Tanaka K. Prediction of flammability of gases by using F-number analysis. *J Hazard Mater* 2001;82:113–28. doi: [http://dx.doi.org/10.1016/S0304-3894\(00\)00358-7](http://dx.doi.org/10.1016/S0304-3894(00)00358-7).
- [11] Albahri TA. Flammability characteristics of pure hydrocarbons. *Chem Eng Sci* 2003;58:3629–41. doi: [http://dx.doi.org/10.1016/S0009-2509\(03\)00251-3](http://dx.doi.org/10.1016/S0009-2509(03)00251-3).
- [12] Gharagheizi F. Prediction of upper flammability limit percent of pure compounds from their molecular structures. *J Hazard Mater* 2009;167:507–10. doi: <http://dx.doi.org/10.1016/j.jhazmat.2009.01.002>.
- [13] Pan Y, Jiang J, Wang R, Cao H, Cui Y. Prediction of the upper flammability limits of organic compounds from molecular structures. *Ind Eng Chem Res* 2009;48:5064–9. doi: <http://dx.doi.org/10.1021/ie900193r>.
- [14] Mendiburu AZ, de Carvalho JA, Coronado CR. Estimation of upper flammability limits of C–H compounds in air at standard atmospheric pressure and evaluation of temperature dependence. *J Hazard Mater* 2016;304:512–21. doi: <http://dx.doi.org/10.1016/j.jhazmat.2016.10.058>.
- [15] Frutiger J, Marcarie C, Abildskov J, Sin G. Group-contribution based property estimation and uncertainty analysis for flammability-related properties. *J Hazard Mater* 2016;318:783–93. doi: <http://dx.doi.org/10.1016/j.jhazmat.2016.06.018>.
- [16] Mendiburu AZ, de Carvalho JA, Coronado CR, Chumpitaz GA. Determination of lower flammability limits of C–H–O compounds in air and study of initial temperature dependence. *Chem Eng Sci* 2016;144:188–200. doi: <http://dx.doi.org/10.1016/j.ces.2016.01.031>.
- [17] Vidal M, Wong W, Rogers WJ, Mannan MS. Evaluation of lower flammability limits of fuel–air–diluent mixtures using calculated adiabatic flame temperatures. *J Hazard Mater* 2006;130:21–7. doi: <http://dx.doi.org/10.1016/j.jhazmat.2005.07.080>.
- [18] Di Benedetto A. The thermal / thermodynamic theory of flammability: the adiabatic flammability limits. *Chem Eng Sci* 2013;99:265–73. doi: <http://dx.doi.org/10.1016/j.ces.2013.05.056>.
- [19] Rowley JR, Rowley RL, Wilding WV. Estimation of the lower flammability limit of organic compounds as a function of temperature. *J Hazard Mater* 2011;186:551–7. doi: <http://dx.doi.org/10.1016/j.jhazmat.2010.11.039>.
- [20] Mendiburu AZ, De Carvalho JA, Coronado CR. Estimation of lower flammability limits of C–H compounds in air at atmospheric pressure, evaluation of temperature dependence and diluent effect. *J Hazard Mater* 2015;285:409–18. doi: <http://dx.doi.org/10.1016/j.jhazmat.2014.10.058>.
- [21] Glassman I, Yetter RA. *Combustion*. 4th ed. New York: Elsevier; 2008.
- [22] Turns SR. *An introduction to combustion: concepts and applications*; 2000. pp. 676.
- [23] Kondo S, Takizawa K, Takahashi A, Tokuhashi K. On the temperature dependence of flammability limits of gases. *J Hazard Mater* 2011;187:585–90. doi: <http://dx.doi.org/10.1016/j.jhazmat.2011.01.037>.
- [24] Mishra DP, Rahman A. An experimental study of flammability limits of LPG / air mixtures q. *Fuel* 2003;82:863–6. doi: [http://dx.doi.org/10.1016/S0016-2361\(02\)00325-3](http://dx.doi.org/10.1016/S0016-2361(02)00325-3).
- [25] Liaw H-J, Chen K-Y. A model for predicting temperature effect on flammability limits. *Fuel* 2016;178:179–87. doi: <http://dx.doi.org/10.1016/j.fuel.2016.03.034>.
- [26] ASTM E-681. Standard test method for concentration limits of flammability of chemicals (vapors and gases). *Am Soc Test Mater* 2010; 9: 1–12. doi: <http://dx.doi.org/10.1520/E0681-09R15.2>.

- [27] Chapra SC. Applied numerical methods with MATLAB for engineers and scientists. 3rd ed. New York: McGraw Hill; 2012. doi: <http://dx.doi.org/10.1017/CBO9781107415324.004>.
- [28] Beers KJ. Numerical methods for chemical engineering - applications in matlab. New York: Cambridge University Press; 2006. doi: <http://dx.doi.org/10.1017/CBO9780511812194>.
- [29] Kiusalaas J. Numerical methods in engineering with MATLAB, 40. New York: Cambridge University Press; 2005. doi: <http://dx.doi.org/10.1017/CBO9780511614682>.
- [30] Otto SR, Denier JP. An introduction to programming and numerical methods in MATLAB. USA: Springer; 2005. doi: <http://dx.doi.org/10.1007/1-84628-133-4>.
- [31] Yang WY, Cao W, Chung T-S, Morris J. Applied numerical methods using MATLAB®. USA: Wiley-Interscience; 2005. doi: <http://dx.doi.org/10.1002/0471705195>.
- [32] McBride BJ, Zehe MJ, Gordon S. NASA Glenn coefficients for calculating thermodynamic properties of individual species. NASA 2002:287.
- [33] Lide DR, editor. CRC handbook of chemistry and physics. New York: CRC Press; 2005. doi: <http://dx.doi.org/978-1466571143>.
- [34] CAMEOChemicals. CAMEO chemicals version 2.6; 2016. <https://cameochemicals.noaa.gov/> [accessed September 1, 2016].
- [35] ChemicalBook. Chemical book; 2016. <http://www.chemicalbook.com/> [accessed September 1, 2016].
- [36] PubChem. PubChem compound; 2016. <https://www.ncbi.nlm.nih.gov/pccompound> [accessed September 1, 2016].
- [37] Carson P, Mumford C, editors. Hazardous chemicals handbook. London: Butterworth Heinemann; 2002. doi: [http://dx.doi.org/10.1016/S0950-4230\(95\)90017-9](http://dx.doi.org/10.1016/S0950-4230(95)90017-9).
- [38] National institute of standards and technology. NIST chemistry web book n.d. <http://webbook.nist.gov/chemistry/> [accessed April 14, 2016].
- [39] Vatani A, Mehrpooya M, Gharagheizi F. Prediction of standard enthalpy of formation by a QSPR model. Int J Mol Sci 2007;8:407–32. doi: <http://dx.doi.org/10.3390/i8050407>.
- [40] Montgomery DC. Design and analysis of experiments. 5th ed. USA: John Wiley & Sons, Inc.; 2001.
- [41] Frutiger J, Marcarie C, Abildskov J, Sin G. A comprehensive methodology for development, parameter estimation, and uncertainty analysis of group contribution based property models-an application to the heat of combustion. J Chem Eng Data 2016;61:602–13. doi: <http://dx.doi.org/10.1021/acs.jced.5b00750>.
- [42] Lovachev LA, Babkin VS, Bunev VA, V'Yun AV, Krivulin VN, Baratov AN. Flammability limits: an invited review. Combust Flame 1973;20:259–89. doi: [http://dx.doi.org/10.1016/S0010-2180\(73\)80180-4](http://dx.doi.org/10.1016/S0010-2180(73)80180-4).
- [43] Britton LG. Two hundred years of flammable limits. Process Saf Prog 2002;21:1–11. doi: <http://dx.doi.org/10.1002/prs.680210104>.
- [44] Lyondell. gamma-Butyrolactone. <http://www.ukchems.com/msds/LyondellGBLMSDS.pdf> [accessed September 1, 2016].
- [45] EVONIK. Methyl tert-butyl ether. http://www13.evonik.com/asp/documents/safetysummary/2964_Safety_Summary_Report.pdf [accessed September 1, 2016].
- [46] Organics A. Methyl tert-butyl ether. http://www.clayton.edu/portals/690/chemistry/inventory/MSDS_t.butyl_methyl_ether.pdf [accessed September 1, 2016].