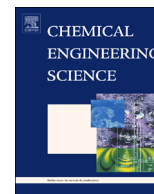




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Determination of lower flammability limits of C–H–O compounds in air and study of initial temperature dependence



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HIGHLIGHTS

- A method for determination of the LFLs of C–H–O compounds was developed.
- The method was very accurate when it was tested against experimental data.
- The temperature dependence of the LFL was studied.
- It is not always correct to assume that adiabatic flame temperature is constant.
- A method for determination of LFLs at different initial temperatures was developed.

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ABSTRACT

The main objective of this study was to develop a method that can be used to estimate the lower flammability limits of C–H–O compounds at standard temperature and pressure. In addition, a study was carried out to develop a method that can be used to determine lower flammability limits at different initial temperatures at 1 atm.

Several 374 C–H–O compounds were used to develop the method which determines the lower flammability limits at standard temperature and pressure. This group of compounds was divided into two sets, one for correlation and another for prediction. The correlation set was made up of 273 compounds while the prediction set was made up of 101 compounds. The average absolute relative error was 5.53% for the correlation set, while the squared correlation coefficient was 0.9758; the average absolute error was 5.25% and the squared correlation coefficient was 0.9699 for the prediction set; and the average absolute error was 5.43% and the squared correlation coefficient was 0.9752 for the total set. These parameters show that the method is very accurate.

The dependence of the lower flammability limit on the initial temperature was studied for a total set of 26 compounds. It was found that the adiabatic flame temperature at the lower flammability limit cannot always be assumed to be constant. A method that can be used to estimate the LFLs at different initial temperatures was developed; this method had an average absolute relative error of 1.85% and a squared correlation coefficient of 0.9987.

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1. Introduction

The flammability limits (FLs) of flammable compounds must be known for safe operation in industrial settings. Flammability limits data are available for different flammable compounds; however, there is no theory related to estimation of these limits. Therefore, semi-empirical methods to determine the flammability limits

need to be developed. Several researchers have contributed to this area using different approaches, which can be roughly divided into two main groups: a) the calculated adiabatic flame temperature approach; and b) approaches based on calculated molecular structure properties using neural networks or other techniques.

In the present study, the first objective was to determine the lower flammability limits (LFL) of C–H–O compounds by developing a method based on the calculated adiabatic flame temperature. The method is novel because it uses a correlation to determine the ratio of the adiabatic flame temperature at the stoichiometric composition and at the LFL composition.

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Most of the available experimental data on flammability limits were determined at standard temperature (25 °C); however, industrial applications may involve the use of flammable compounds at higher temperatures. Because of this, the flammability limits at different initial temperatures need to be determined.

This led to an additional objective: to study the dependence of the LFL on the initial temperature and to develop a method that can be used to estimate the LFL at different initial temperatures. In all cases, the mixture was at atmospheric pressure prior to combustion.

When estimating the LFL at different initial temperatures, in most methods, it is assumed that the adiabatic flame temperature at the LFL is not affected by the change of value of the LFL. It is considered to be constant. Although this can be assumed for some compounds, in the present study, some compounds were found to behave differently. A method that can be used to estimate the variation of the LFL with the initial temperature was developed. As mentioned before, the adiabatic flame temperature at the LFL is not constant for several compounds and the method developed provides a way to estimate this variation using the adiabatic flame temperatures at stoichiometric composition.

Determination of the upper flammability limit (UFL) will be the subject of future work.

2. Brief review of estimation methods of lower flammability limits

The research on flammability limits started decades ago. The work of Coward and Jones (1952) and Zabetakis (1965) is well known. In the study by Coward and Jones (1952), it becomes obvious that flammability limits depend on the combustion chamber's size and geometry as well as other parameters. In the study by Zabetakis (1965), there is a compilation of data on the FLs of different substances, including FLs at different initial temperatures and data for fuel–diluent–air mixtures.

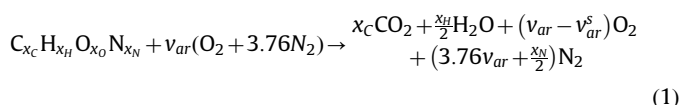
There have been several important studies using approaches based on calculated molecular structure properties. Seaton (1991) developed a second order group contribution method which considered 150 compounds and obtained an average absolute relative error (AARE) of 5.13%. Gharagheizi (2008) presented a method based on quantitative molecular properties; those properties must be calculated or found elsewhere. In the Gharagheizi study, the total number of compounds was 1056; the AARE was 7.68% and the squared correlation coefficient (R^2) was 0.9698. Pan et al. (2009) also used quantitative molecular properties. They considered 1038 compound, developing a method with an R^2 of 0.9787 and an AARE of 5.60%. Gharagheizi (2009) developed an additional method. It was based on the contributions of molecular groups and neural networks, considering 105 molecular groups; the AARE was 4.62% and the R^2 was 0.9860 for a total of 1057 compounds. Lazzús (2011) considered 42 molecular groups, for 418 compounds, and used neural networks to develop a method with an AARE of 8.60% for the correlation set and 8.50% for the prediction set. The R^2 was 0.9876 for the correlation set and 0.9819 for the prediction set. Bagheri et al. (2012) developed a method based on quantitative molecular structure properties which was applied to 1645 compounds. The method obtained an AARE of 15.86% and a R^2 of 0.9063. Albahri (2013) also used quantitative molecular structure properties for his method and obtained an R^2 of 0.9998 for 543 compounds.

The adiabatic flame temperature method has been used by several authors. This method consists of determining the LFL of a compound when the approximate value of the adiabatic flame temperature at the LFL composition is known. Works by Vidal et al.

(2006), Ma (2011) and Shebeko et al. (2002) used a fixed value of the adiabatic flame temperature for families of compounds; for instance, Vidal et al. (2006) applied the method to 25 paraffinic and unsaturated hydrocarbons. Rowley et al. (2011) determined the adiabatic flame temperature using a correlation obtained from a molecular group contribution method; they considered 509 compounds and obtained an AARE of 10.70%.

3. Determination of the lower flammability limit at standard temperature and pressure

In this section the semi-empirical method will be developed. If the adiabatic flame temperature at the lower flammability limit is known, the composition of the reactants can be calculated. This is more evident when a global reaction is used:



In Eq. (1) combustion was assumed to be complete; it was also assumed that the excess oxygen and the nitrogen are inert. The mass conservation law has been applied to the carbon, hydrogen, oxygen, and nitrogen. The oxygen content of the air at the stoichiometric composition (v_{ar}^s) is always a known parameter when the composition of the flammable compound is known. On the other hand, the oxygen content in the air at the LFL (v_{ar}) is an unknown value.

A constant pressure combustion process is considered; the energy conservation equation at adiabatic conditions, with no work crossing the system boundaries, and neglecting kinetic and potential energy variations, is written as follows:

$$h_F + v_{ar}(h_{O_2} + 3.76h_{N_2})_R = x_C h_{CO_2} + \frac{x_H}{2} h_{H_2O} + v_{ar}(h_{O_2} + 3.76h_{N_2})_P - v_{ar}^s h_{O_2} + \frac{x_N}{2} h_{N_2} \quad (2)$$

Sub-index R refers to reactants while P refers to products. It is convenient to make the following substitution:

$$h_{ar} = h_{O_2} + 3.76h_{N_2} \quad (3)$$

Assuming that the adiabatic flame temperature at the LFL (T_{LFL}) is a known parameter, Eq. (2) can be solved for v_{ar} .

$$v_{ar} = \frac{h_F + v_{ar}^s h_{O_2} - x_C h_{CO_2} - \frac{x_H}{2} h_{H_2O} - \frac{x_N}{2} h_{N_2}}{h_{ar,P} - h_{ar,R}} \quad (4)$$

Table 1
Lower flammability limits of some compounds.

Compound	Formula	CAS#	LFL (%)	References
n-Amyl alcohol	C ₅ H ₁₂ O	71-41-0	1.20	(Loba Chemie, 2015)
tert-Amyl alcohol	C ₅ H ₁₂ O	75-85-4	1.30	(Fisher Scientific, 2015)
n-Butyl alcohol	C ₄ H ₁₀ O	71-36-3	1.70	(Glassman and Yetter, 2008)
gamma-Butyrolactone	C ₄ H ₆ O ₂	96-48-0	2.00	(Glassman and Yetter, 2008)
n-Butyraldehyde	C ₄ H ₈ O	123-72-8	1.90	(International Chemical Safety Cards, 2015)
Diacetone alcohol	C ₆ H ₁₂ O ₂	123-42-2	1.40	(Kremer, 2015)
Ethyl propionate	C ₅ H ₁₀ O ₂	105-37-3	1.80	(Glassman and Yetter, 2008)
Methyl acrylate	C ₄ H ₆ O ₂	96-33-3	2.50	(Santa Cruz, 2015)
Tetrahydrofuran	C ₄ H ₈ O	109-99-9	2.00	(Glassman and Yetter, 2008)
Formic acid	CH ₂ O ₂	64-18-6	14.30	(McKetta, 1985)
iso-Amyl alcohol	C ₅ H ₁₂ O	123-51-3	1.20	(Cameo Chemicals, 2015)
tert-Butyl alcohol	C ₄ H ₁₀ O	75-65-0	1.90	(Glassman and Yetter, 2008)

Afterwards, the LFL is obtained by applying Eq. (5).

$$\text{LFL} = \frac{1}{1 + 4.76v_{ar}} 100\% \quad (5)$$

The combustion process was considered to be adiabatic; however, a similar approximation, considering a non-adiabatic temperature, was adopted by Zhao et al. (2010) and by Di Benedetto, (2013). In the present study, the combustion process is considered to be adiabatic in order to keep the estimation method simple.

It is not easy to estimate the value of the adiabatic flame temperature for a relatively large number of compounds (100 for example); in fact, it can be as difficult as obtaining a correlation that directly determines the LFL.

Assuming average specific heat capacities at constant pressure and rearranging the energy conservation equation, the following equation is obtained:

$$T_{LFL} - T_r = \frac{H_C + (\bar{c}_{p,F} + 4.76v_{ar}\bar{c}_{p,ar})(T_1 - T_r)}{\chi_C\bar{c}_{p,CO_2} + \frac{\chi_H}{2}\bar{c}_{p,H_2O} + 4.76v_{ar}\bar{c}_{p,ar} - v_{ar}^s\bar{c}_{p,O_2} + \frac{\chi_N}{2}\bar{c}_{p,N_2}} \quad (6)$$

In which the heat of combustion (H_C) is given in Eq. (7).

$$H_C = \bar{h}_{f,F}^0 - \chi_C\bar{h}_{f,CO_2}^0 - \frac{\chi_H}{2}\bar{h}_{f,H_2O}^0 \quad (7)$$

Considering the stoichiometric combustion of the same compound and applying the same considerations for the energy conservation equation, the following equation is obtained:

$$T_{stq} - T_r = \frac{H_C + (\bar{c}_{p,F} + 4.76v_{ar}^s\bar{c}_{p,ar})(T_1 - T_r)}{\chi_C\bar{c}_{p,CO_2} + \frac{\chi_H}{2}\bar{c}_{p,H_2O} + 3.76v_{ar}^s\bar{c}_{p,N_2} + \frac{\chi_N}{2}\bar{c}_{p,N_2}} \quad (8)$$

Assuming that the initial temperature is equal to the reference temperature ($T_1 = T_r$) and dividing Eq. (8) by Eq. (6) gives:

$$\frac{\Delta T_{stq}}{\Delta T_{LFL}} = \frac{T_{stq} - T_r}{T_{LFL} - T_r} = \frac{1 + (4.76v_{ar}\bar{c}_{p,ar} - v_{ar}^s\bar{c}_{p,O_2}) / (\chi_C\bar{c}_{p,CO_2} + \frac{\chi_H}{2}\bar{c}_{p,H_2O} + \frac{\chi_N}{2}\bar{c}_{p,N_2})}{1 + 3.76v_{ar}^s\bar{c}_{p,N_2} / (\chi_C\bar{c}_{p,CO_2} + \frac{\chi_H}{2}\bar{c}_{p,H_2O} + \frac{\chi_N}{2}\bar{c}_{p,N_2})} \quad (9)$$

As can be seen in Eq. (9), the ratio $\Delta T_{stq}/\Delta T_{LFL}$ is a measure of the ratio between the oxygen content at the LFL and the oxygen content at the stoichiometric composition. It is also shown that $\Delta T_{stq}/\Delta T_{LFL}$ is a normalized parameter because the non-unitary terms in the numerator and denominator are both divided by the same quantity.

It can be inferred that the ratio $\Delta T_{stq}/\Delta T_{LFL}$ will reveal a moderate variation when calculated for several compounds. Therefore, it is possible to obtain an accurate correlation to determine $\Delta T_{stq}/\Delta T_{LFL}$ as a function of known properties of the flammable compounds.

When the correlation procedure was performed, it was found that the simpler parameter defined in Eq. (10) can be used to

estimate the value of the adiabatic flame temperature at the LFL.

$$\theta = \frac{T_{stq}}{T_{LFL}} = f(\chi_C, \chi_H, \chi_O, \bar{h}_{f,F}^0, M_F) \quad (10)$$

Thus, the ratio θ was correlated as a function of five parameters of the flammable compounds:

1. The moles of carbon (χ_C);
2. The moles of hydrogen (χ_H);
3. The moles of oxygen (χ_O);
4. The enthalpy of formation ($\bar{h}_{f,F}^0$); and
5. The molecular weight (M_F).

The lower flammability limit of C–H–O compounds in air at standard temperature and pressure is then obtained by calculating the value of θ and using this value to estimate the adiabatic flame temperature at the lower flammability limit. Once the flame temperature has been estimated, the LFL can be determined by using Eqs. (4) and (5). The correlation obtained is used to calculate θ . It is presented in Section 6.

Note that the adiabatic flame temperature at the LFL is different from the lower flammability limit temperature (LFLT). The former is the temperature of the flame generated by the combustion of a fuel–air mixture at the LFL composition in adiabatic conditions.

The LFLT is defined as the temperature at which the concentration of a saturated vapor–air mixture is equal to the lower flammability limit. Gharagheizi et al. (2013) and Lazzús (2011) developed methods to estimate the LFLT. Brandes et al. (2007) presented experimental results regarding the LFLT.

4. Determination of the lower flammability limit at different initial temperatures at 1 atm

The initial temperature of the reactant mixture has an effect on the values of the flammability limits. The increase in the initial temperature produces a decrease in the LFL value and an increase in the UFL value. Therefore, any increase in the initial temperature of the mixture widens the flammable interval.

This section discusses the lower flammability limit's dependence on the initial temperature. A simple explanation for the decrease of the LFL can be given: when the initial temperature is increased, the energy of the reactants is also increased; thus, a quantity of the flammable compound with a quantity of energy equivalent to that increase can be “removed” from the mixture without affecting the capacity of the flames to propagate.

The adiabatic flame temperature has been used to estimate the LFL of a compound at different initial temperatures. Zabetakis

Table 2

Comparison of correlation coefficients obtained in the present work with those obtained in published articles.

	R^2 (Correlation Set)	N (Compounds)	R^2 (Prediction set)	N (Compounds)	R^2 (Total set)	Applicability
Albahri (2013)	0.9998	518	0.99997	25	0.9998	Hydrocarbons, ethers, ketones, aldehydes, alcohols, phenols, esters, amines, anhydrides, etc. ^a
Bagheri et al. (2012)	0.9061	1292	0.9083	323	0.9063	
Lazzús (2011)	0.9876	328	0.9819	90	0.9865	
Gharagheizi (2009)	0.99	846	0.971	211	0.986	
Gharagheizi (2008)	0.9698	845	0.9728	211	–	
Pan et al. (2009) ^b	0.979	830	0.979	208	–	
Seaton (1991) ^c	0.9904	150	–	–	0.9904	
Mendiburu et al. (2015)	0.9652	60	0.9239	60	0.9543	C–H compounds
This work	0.9758	273	0.9699	101	0.9752	C–H–O compounds

^a More detailed information is available in the cited articles.

^b Several models were tested, only the best is presented here.

^c the compounds were used in the correlation set.

Table 3Value of parameter I obtained at LFL_{T_1} for the 26 compounds considered in the temperature dependence study.

Compound	Formula	CAS	M_F ($\frac{g}{mol}$)	\bar{h}_f^0 ($\frac{kJ}{mol}$)	Family	H_C (kJ/mol)	I ($\frac{g/mol}{kJ}$)
Methane	CH ₄	74-82-8	16.04	-74.87	Alkane	802.30	0.81; 0.83; 0.82
Propane	C ₃ H ₈	74-98-6	44.1	-104.7	Alkane	2043.17	2.11
iso Butane	C ₄ H ₁₀	75-28-5	58.12	-134.2	Alkane	2649.01	2.62
Propylene	C ₃ H ₆	115-07-1	42.08	20.41	Alkene	1926.46	2.01
Ethylene	C ₂ H ₄	74-85-1	28.06	52.47	Alkene	1323.17	1.55; 1.63
2-Pinene ^a	C ₁₀ H ₁₆	80-56-8	136.23	-16.4	Alkene	5853.42	8.21
1-Hexyne	C ₆ H ₁₀	693-02-7	82.14	122.3	Alkyne	3692.57	5.26
Methanol	CH ₄ O	67-56-1	32.04	-205	Alcohol	672.18	1.40
Ethanol	C ₂ H ₆ O	64-17-5	46.07	-234	Alcohol	1278.52	1.93
Butanol	C ₄ H ₁₀ O	71-36-3	74.12	-277	Alcohol	2506.21	3.97
1-Octanol	C ₈ H ₁₈ O	111-87-5	130.22	-356	Alcohol	4968.61	8.19
4-Methyl-2-pentanol ^a	C ₆ H ₁₄ O	108-11-2	102.18	-344.1	Alcohol	3709.81	5.75
Dimethyl ether	C ₂ H ₆ O	115-10-6	46.07	184.1	Ether	1328.42	2.07
Methyl formate	C ₂ H ₄ O ₂	107-31-3	60.06	-336.9	Ester	933.80	2.43
Methyl Benzoate	C ₈ H ₈ O ₂	93-58-3	136.14	-269.3	Ester	3846.18	8.70
Phenetole ^a	C ₈ H ₁₀ O	103-73-1	122.17	-101.6	Ether	4255.70	7.34
Ethyl lactate ^a	C ₅ H ₁₀ O ₃	97-64-3	118.13	-695.08	ester	2481.66	6.98
Hexyl formate ^a	C ₇ H ₁₄ O ₂	629-33-4	130.19	-518.49	ester	3928.94	7.74
Octyl formate ^a	C ₉ H ₁₈ O ₂	112-32-3	158.23	-566.45	ester	5151.69	10.16
Dibutylamine ^a	C ₈ H ₁₉ N	111-92-2	129.24	-171.1	Amine	3882.81	9.66
Carbon monoxide	CO	630-08-0	28.01	-110.53		282.99	1.61; 1.49; 1.47
Ammonia	NH ₃	7664-41-7	17.03	-45.94		316.79	0.70; 0.66
2-methyl-1,3-propanediol ^a	C ₄ H ₁₀ O ₂	2163-42-0	90.12	-505.9	Glycol	2277.31	6.96
Di iso butyl phthalate ^a	C ₁₆ H ₂₂ O ₄	84-69-5	278.34	-1087.3		7869.13	22.03
Toluene	C ₇ H ₈	108-88-3	92.13	50.1	Arom. HC	3772.06	4.77
Hydrogen	H ₂	1333-74-0	2.01	0		241.83	0.43; 0.38; 0.41

^a The heat capacity at constant pressure of the flammable compound was assumed to be equal to that of air.

(1965) presents an equation that can be used to estimate an LFL at higher temperatures when the LFL at 25 °C is known. Considering that the flame temperature does not change for the LFL and setting the temperature at 1300 °C for paraffin hydrocarbons, the following equation was given:

$$LFL_{T_1} = LFL_{25} - \frac{LFL_{25} \cdot (T_1 - 25)}{1300 - 25} \quad (11)$$

Another estimation can be found in a study by Britton and Frurip (2003). In their study, the following equation was used to estimate the LFL at different initial temperatures:

$$LFL_{T_1} = LFL_0 \frac{T_{LFL,0} - T_1}{T_{LFL,0} - T_0} \quad (12)$$

In Eq. (12), sub-index “0” refers to the known LFL at the reference conditions, which may be 25 °C. Sub-index “1” refers to the temperature at which the LFL is going to be estimated. Both of the previous methods consider adiabatic flame temperature at the LFL to be constant. Similarly, assuming a constant flame temperature, Zlochower (2012) used the CEA-NASA code (2015) to estimate the LFL at different initial temperatures.

Kondo et al. (2011) presented experimental data for the flammability limits of 10 compounds for initial temperatures ranging from 5 to 100 °C. They considered that the heat of combustion of the fuel (Q) was constant in the range of 5 to 100 °C and used the heat capacity of the unburned mixture at 25 °C ($\bar{c}_{p,u}$) to develop the following equation to estimate the LFL at different initial temperatures:

$$LFL_{T_1} = LFL_{25} - \frac{100 \bar{c}_{p,u} (T_1 - 25)}{Q} \quad (13)$$

Zlochower (2012) presented the results obtained by his own method along with those obtained using the methods developed by Zabetakis (1965), Britton and Frurip (2003), and Kondo et al. (2011) with the experimental data for methane, ethylene, dimethyl ether and carbon monoxide. The data for dimethyl ether and methyl formate were presented by Kondo et al. (2011). They are especially relevant considering the scope of the present study.

Table 4

Summary of results obtained by applying the method developed to study the dependence of LFL on temperature.

Set	ARE _{max} (%)	ARE _{min} (%)	AARE(%)	R ²	Data points
Correlation	11.02	0.03	1.73	0.9985	82
Prediction	7.00	0.28	2.14	0.9996	27
Hydrogen	10.34	0.14	3.02	0.9828	9
Total	11.02	0.03	1.85	0.9987	118

In earlier work, Mendiburu et al. (2015) studied the case of C–H compounds. For these compounds, adiabatic flame temperature at the LFL could reliably be assumed to be constant. However, when the same assumption was applied to some alcohols, such as methanol, ethanol, butanol, and 1-octanol, the results were not as satisfactory as those obtained in the aforementioned study.

An equation that can be used to estimate the LFL at different initial temperatures can be obtained from Eq. (4) using the following procedure: a) consider average heat capacities; and b) substitute the expression obtained for v_{ar} into Eq. (5). The following expression was obtained:

$$LFL_{T_i} = \frac{100(4.76 \bar{c}_{p,ar})(T_{LFL_i} - T_i)}{4.76 \bar{c}_{p,ar}(T_{LFL_i} - T_i) + 4.76 [H_C + \bar{c}_{p,F}(T_i - T_r) + A(T_{LFL_i} - T_r)]} \quad (14)$$

Sub-index “i” refers to any initial temperature; T_{LFL_i} is the adiabatic flame temperature at the LFL of a mixture with an initial temperature T_i . Parameter “A” was introduced to simplify the equation. It is a function of fuel composition, stoichiometric air coefficient, and average heat capacities at constant pressure, as shown below:

$$A = v_{ar}^s \bar{c}_{p,O_2} - x_C \bar{c}_{p,CO_2} - \frac{x_H}{2} \bar{c}_{p,H_2O} - \frac{x_N}{2} \bar{c}_{p,N_2} \quad (15)$$

By Considering two initial temperatures, T_1 and T_2 , writing Eq. (14) for each one of those temperatures, dividing the expression obtained for T_2 by the expression obtained for T_1 , and rearranging,

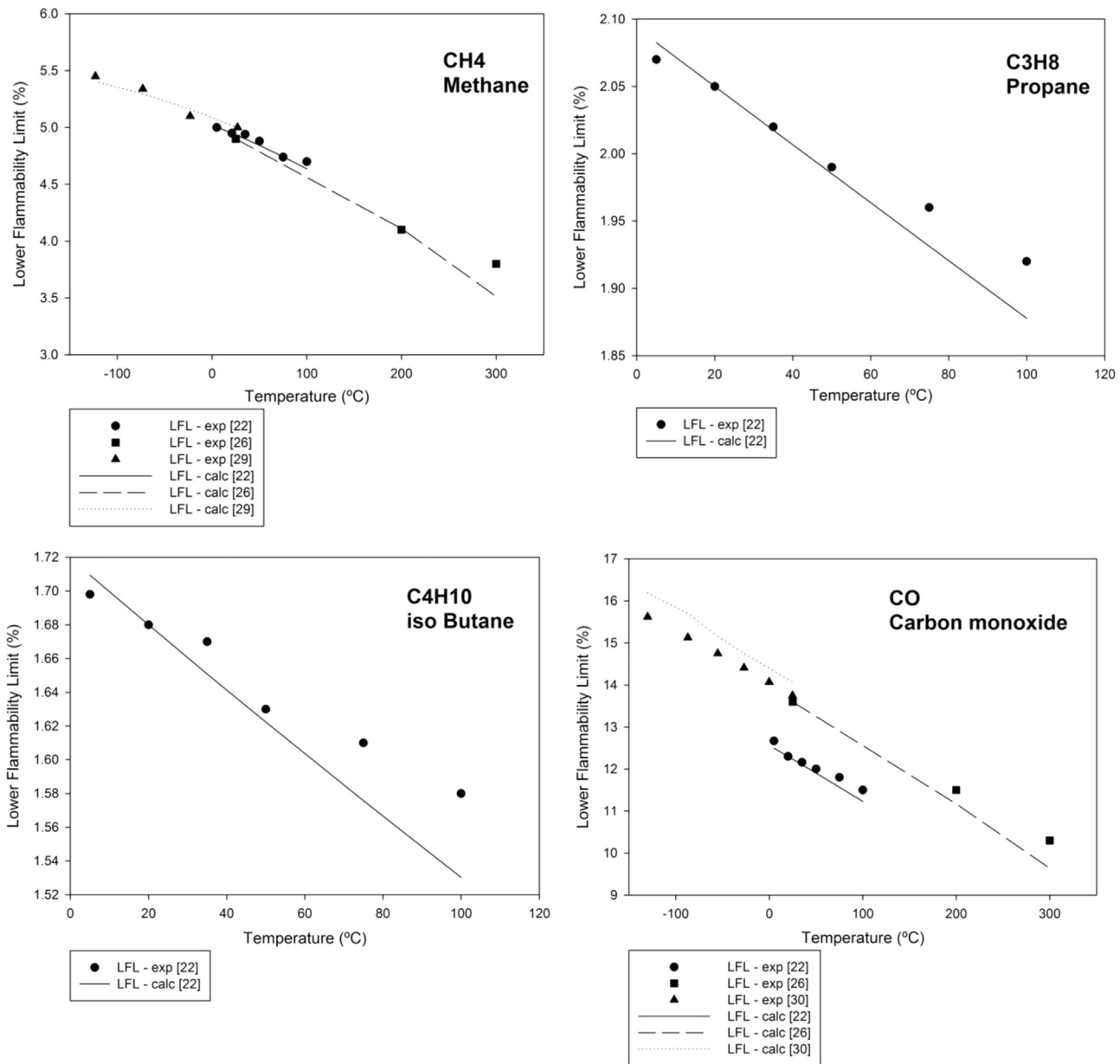


Fig. 1. Lower flammability limits of methane, propane, iso-butane and carbon monoxide at different initial temperatures.

Eq. (16) is obtained:

$$LFL_{T_2} = K \left(\frac{T_{LFL2} - T_2}{T_{LFL1} - T_1} \right) LFL_{T_1} \quad (16)$$

In which

$$K = \frac{4.76\bar{c}_{p,ar}(T_{LFL1} - T_1) + 4.76[H_C + \bar{c}_{p,F}(T_1 - T_r) + A(T_{LFL1} - T_r)]}{4.76\bar{c}_{p,ar}(T_{LFL2} - T_2) + 4.76[H_C + \bar{c}_{p,F}(T_2 - T_r) + A(T_{LFL2} - T_r)]} \quad (17)$$

After examining Eqs. (16) and (17) above, it is obvious that when the adiabatic flame temperature at the LFL is assumed to be constant, it changes the value of K and the value of the bracketed expression in Eq. (16). In some cases, these changes may be negligible. On the other hand, when the aforementioned assumption was applied to alcohols, the absolute relative error (ARE) increased with initial temperature. This means that larger AREs might occur for higher temperatures when the adiabatic flame temperature at the LFL is assumed to be a constant.

In the present study, the value of T_{LFL2} is estimated by Eq. (18), in which exponent n is determined by a correlation.

$$T_{LFL2} = T_{LFL1} \left(\frac{T_{stq1}}{T_{stq2}} \right)^n \quad (18)$$

As observed in Eq. (18), the value of n will change with the value of the adiabatic flame temperature, i.e., with the initial temperature of the mixture. It is important to notice that the values of T_{LFL1} and T_{stq1} depend on the value of T_1 and the values of T_{LFL2} and T_{stq2} depend on the value of T_2 . Therefore, the value of n can be obtained as a function of T_1 , T_2 , and a third parameter that can be used to differentiate among flammable compounds:

$$n = \frac{\ln(T_{LFL2}/T_{LFL1})}{\ln(T_{stq1}/T_{stq2})} = f(T_1, T_2, I) \quad (19)$$

If it is assumed that the reactant mixture is an ideal gas, and the vessel volume is 12 L (which is true for (Kondo et al., 2011; Rowley et al., 2010)). The number of moles of the flammable compound (n_f) for each value of LFL and for different compounds can be

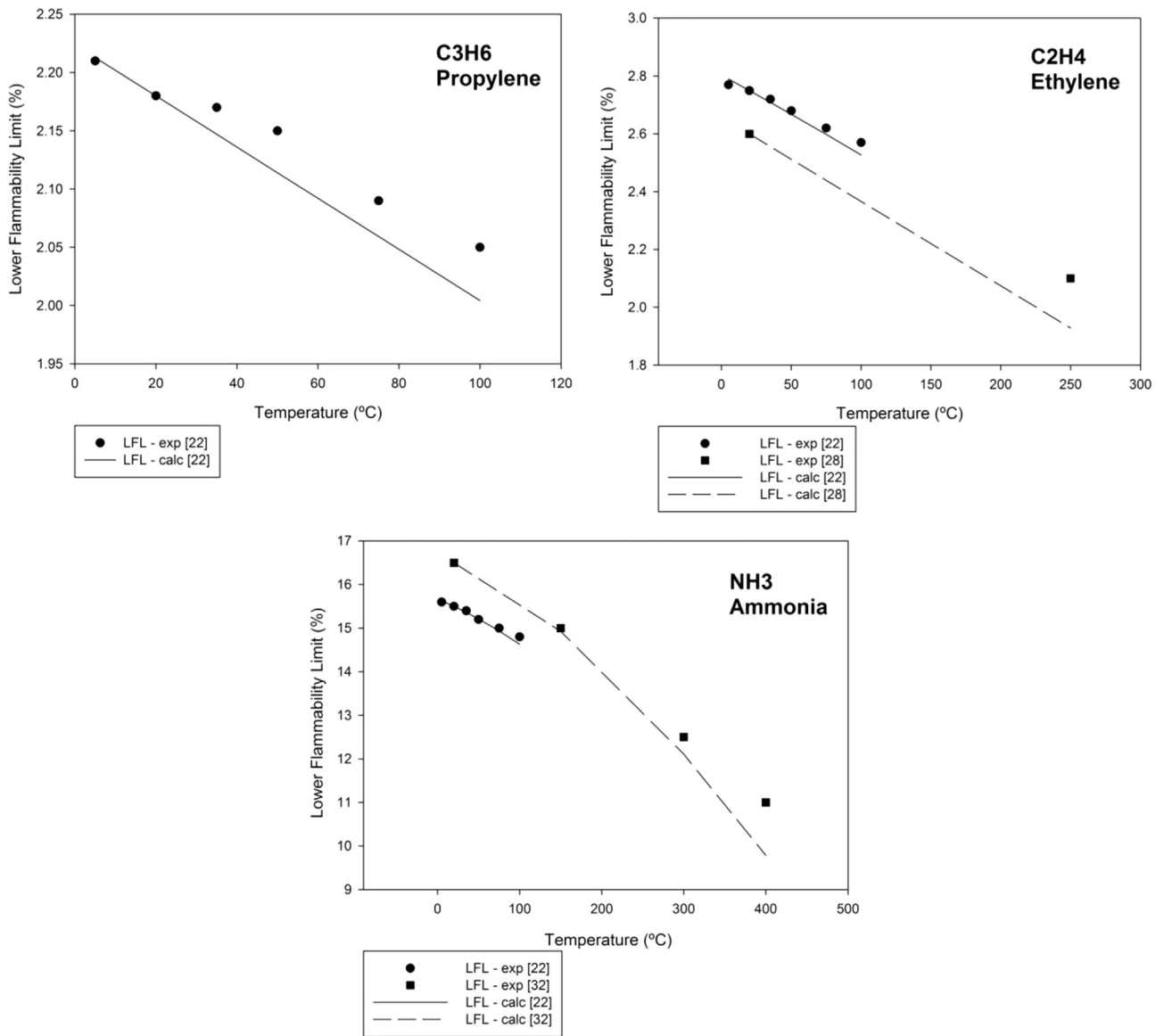


Fig. 2. Lower flammability limits of propylene, ethylene and ammonia at different initial temperatures.

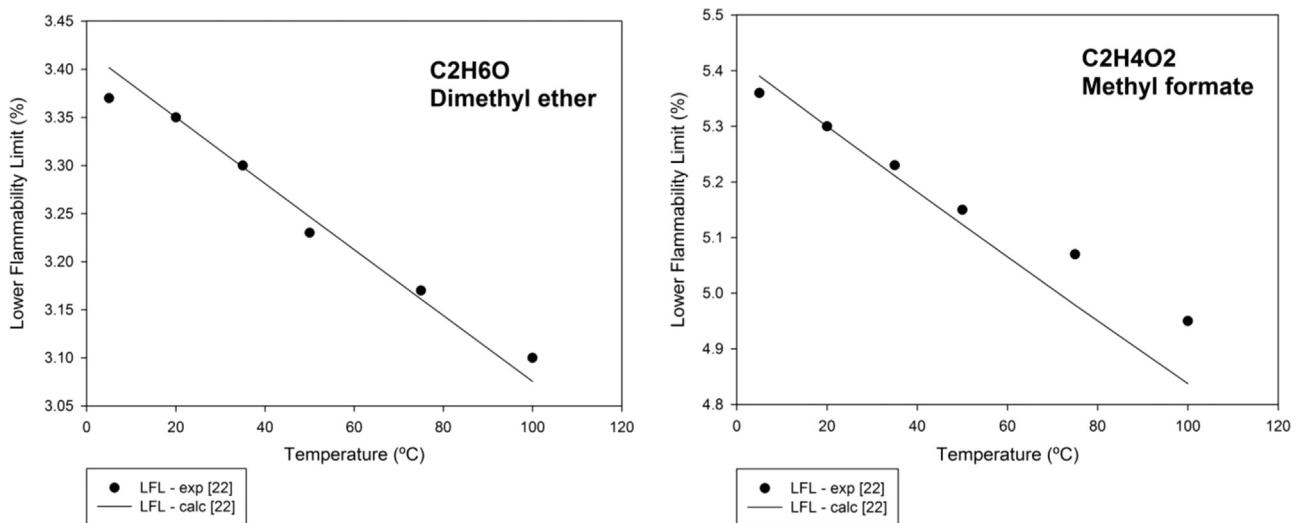


Fig. 3. Lower flammability limits of dimethyl ether and methyl formate at different initial temperatures.

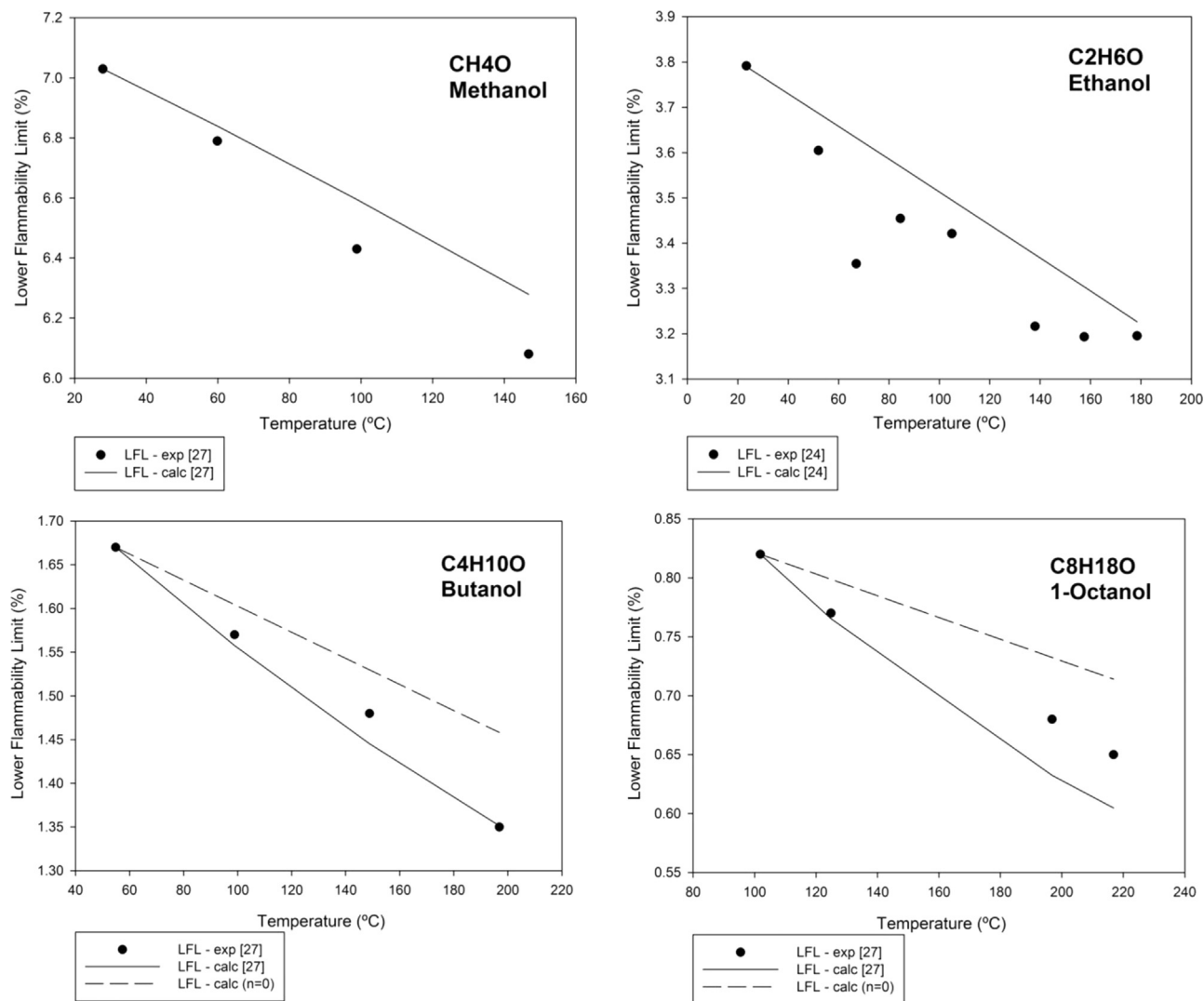


Fig. 4. Lower flammability limits of methanol, ethanol, butanol and 1-octanol at different initial temperatures.

calculated. The product of the number of moles with the heat of combustion (H_C) will be different for each flammable compound. Finally, considering the molecular weight, the following parameter can be obtained and used to differentiate among the flammable compounds:

$$I = \frac{M_F}{n_F H_C} \quad (20)$$

It can be observed that the denominator of parameter I is the total heat release at the LFL. Therefore, the parameter determines the ratio of the molecular weight to the heat release at the LFL. The value of I will change with the value of the LFL, i.e., with the value of the initial temperature of the mixture. Therefore the value of I cannot be calculated without knowing the value of the LFL. Parameter I will be calculated for each compound only at LFL_{T_1} and considered constant at any other initial temperature. This implies that the influence of the initial temperature on the value of n will be represented only by T_1 and T_2 .

5. Experimental data

Most of the experimental data concerning the lower flammability limits of C–H–O compounds at standard temperature and

pressure were obtained from [Supplementary material](#) presented in a study by [Gharagheizi \(2009\)](#). The experimental data presented by [Zabetakis \(1965\)](#) were also considered.

The experimental data for the lower flammability limits of C–H and C–H–O compounds at different initial temperatures and at 1 atm were obtained from studies by [Kondo et al. \(2011\)](#), [Coronado et al. \(2014, 2012\)](#), [Wierzbza and Wang \(2006\)](#), [Rowley et al. \(2010\)](#), [Craven and Foster \(1966\)](#), [Li et al. \(2011\)](#), [Karim et al. \(1984\)](#), [Goethals et al. \(1999\)](#), and [Ciccarelli et al. \(2006\)](#).

The enthalpies of formation were taken from [NIST Chemistry Web Book \(2015\)](#) and from [Vatani et al. \(2007\)](#). The absolute enthalpies were calculated using the NASA–Glenn coefficients, taken from [McBride et al. \(2002\)](#). The heat capacities at constant pressure for O_2 , N_2 , CO_2 , H_2O , and H_2 were calculated using the NASA–Glenn coefficients. If not otherwise specified, the specific heat capacities at constant pressure of the fuels were determined by adjusting a second degree polynomial to the data presented in the [NIST Chemistry Web Book \(2015\)](#), for a temperature ranging from 100 to 1500 K. The heat capacity of 1-octanol was obtained from the hyperbolic function given by [Maloney \(2008\)](#).

Afterwards, the average heat capacities at constant pressure were obtained using Eq. (21). For some types of fuel, the specific heat capacities at constant pressure were not found in the literature. In such cases, it was assumed that their average heat capacity

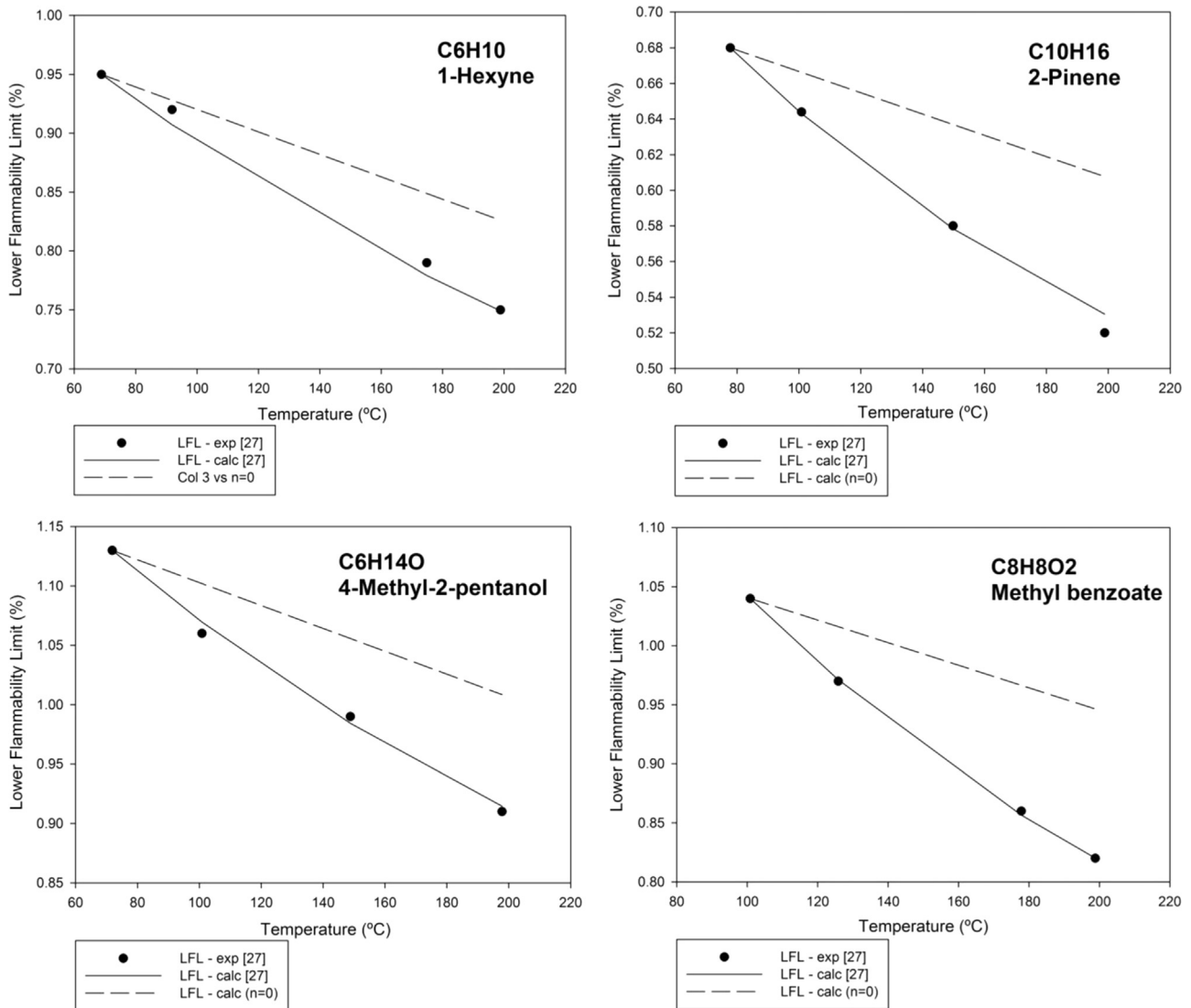


Fig. 5. Lower flammability limits of 1-hexyne, 2-pinene, 4-methyl-2-pentanol and methyl benzoate at different initial temperatures.

at constant pressure was equal to that of air.

$$\bar{c}_{p,i} = \frac{\int_{T_a}^{T_b} c_{p,i} dT}{T_b - T_a} \quad (21)$$

In the case of the product species and air, the temperature ranged from 1200 to 1800 K for all compounds except for hydrogen, in which case it ranged from 600 to 1200 K. For the fuel, the temperature range was from 298.15 K to the initial temperature of the mixture. For some compounds, the LFL values were obtained from sources other than those cited above. These compounds are listed in Table 1 and the sources are properly indicated.

6. Determination of the correlations

This section is divided into two subsections. The first subsection deals with the determination of a correlation that will be used to calculate the value of θ [see Eq. (10)]. Once the values of θ and of T_{stq} are known, the value of T_{LFL} can be calculated using Eq. (10). The second subsection deals with the determination of a correlation which will be used to calculate the value of n [see Eq. (18)].

Once the values of n , T_{LFL1} , T_{stq1} , and T_{stq2} are known, the value of T_{LFL2} can be calculated using Eq. (18).

6.1. Correlation for determination of θ

A total set of 374 C–H–O compounds was considered. The total set was divided into two smaller sets: a correlation set with 273 compounds and a prediction set with 101 compounds. The adiabatic flame temperatures at stoichiometric composition and at the LFL composition of the 273 compounds on the correlation set were determined. Afterwards, the values of θ were calculated. The MATLAB multiple linear regression tool was used to obtain the correlation shown below.

$$\theta = 1.664032 - 1.048146 \times 10^{-01} \left(\frac{\bar{h}_{f,i}^0}{\bar{h}_{f,av}^0} \right) + 9.721391 \times 10^{-02} \left(\frac{M_i}{M_{av}} \right) - 1.174598 \times 10^{-01} \left(\frac{x_C}{x_H} \right) - 8.340052 \times 10^{-03} \left(\frac{x_C}{x_O} \right) + 2.648944 \times 10^{-02} \left(\frac{x_C x_O}{x_H} \right) \quad (22)$$

In which the values of the average enthalpy of formation ($\bar{h}_{f,av}^0$) and the average molecular weight (M_{av}) were determined using the total set of compounds: $\bar{h}_{f,av}^0 = -457 \text{ kJ/mol}$ and $M_{av} = 146 \text{ g/mol}$.

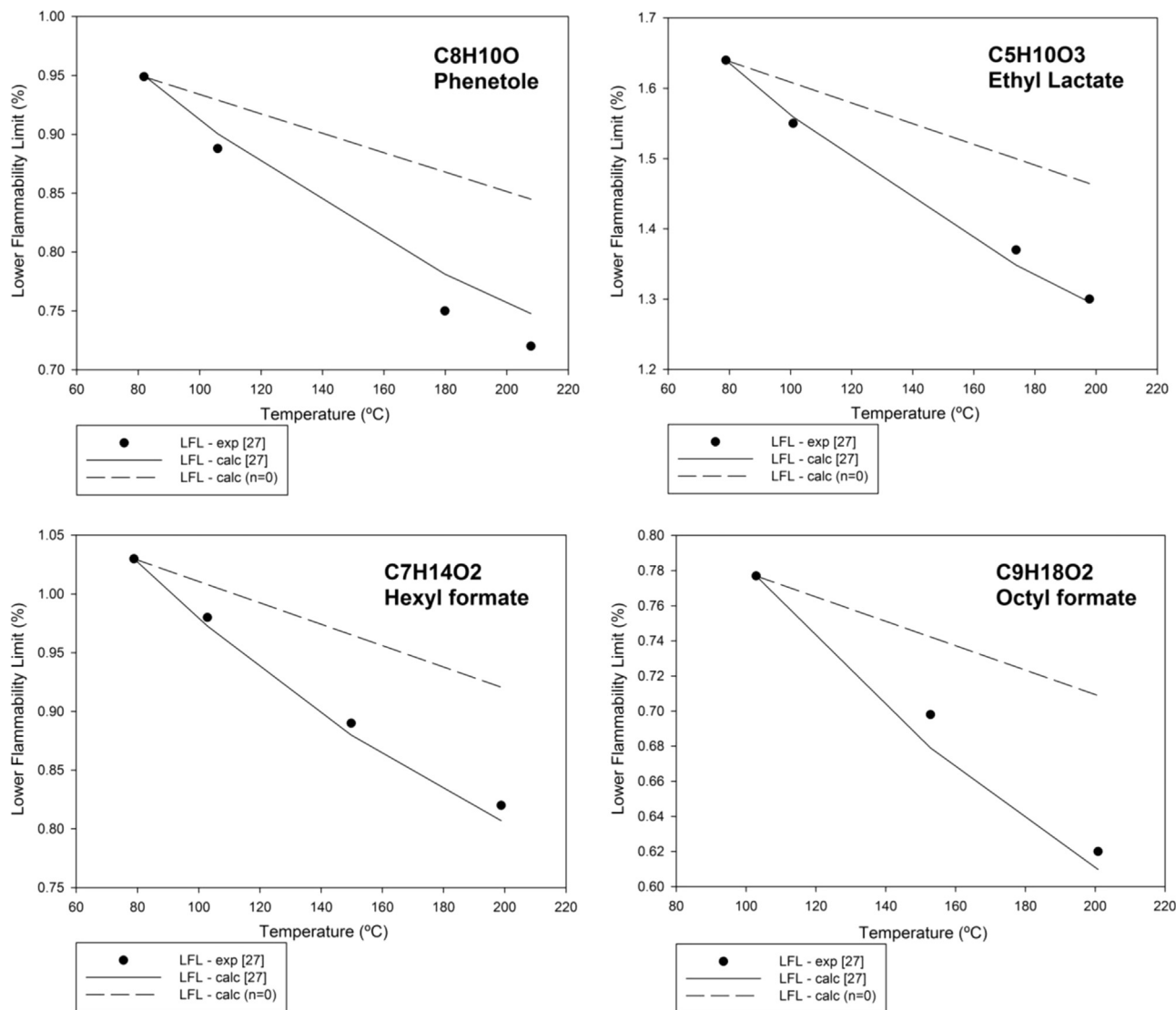


Fig. 6. Lower flammability limits of phenetole, ethyl lactate, hexyl formate and octyl formate at different initial temperatures.

The results obtained by this method are presented in Table 2 and will be discussed in the next section.

6.2. Correlation for the determination of n

A total of 26 flammable compounds were considered. The values of parameter I calculated at the LFL_{T1} for each of these compounds are shown in Table 3. For some compounds, there is more than one experimental data source. For instance, the reference values for methane taken from Kondo et al. (2011) is 4.95% at 21 °C; in Wierzb and Wang (2006) it is 4.90% at 25 °C; and in Li et al. (2011), it is 5.00% at 26.85 °C. Each one of those experimental values is considered a reference point. Therefore, there are three values of I on Table 3.

Of the 26 compounds, hydrogen was the only one which behaved differently. The adiabatic flame temperature at the LFL increases when the initial mixture's temperature increases. This does not agree with the behavior of the other 25 compounds. For this reason, hydrogen was studied separately. Two correlations were obtained, one for the hydrogen and the other for the remaining 25 compounds.

Considering all the experimental data available for the 25 compounds, there are 140 experimental points. Among these points, 31 are considered to be reference points for which the LFL is known. Two sets were formed from the remaining 109

experimental points, a correlation set with 82 experimental points and a prediction set with 27 experimental points. The values of n were determined for the correlation set. The MATLAB multiple linear regression tool was used to produce the correlation shown in Eq. (23). There are 12 experimental points for hydrogen. Three of these were considered reference points. The remaining 9 experimental points were used to determine the correlation shown in Eq. (24). The procedure applied was the same described above.

6.2.1. For all studied compounds except hydrogen

$$n = -1.0035 + 4.3961 \left(\frac{\Delta T}{10^3} \right) + 3.8690 \left(\frac{\Delta T^2}{10^7} \right) + 7.1888 \left(\frac{I}{10} \right) - 8.7834 \left(\frac{I^2}{10^3} \right) - 2.1928 \left(\frac{\Delta T \times I}{10^3} \right) \quad (23)$$

6.2.2. For hydrogen

$$n = -748.49 + 2.7457 \left(\frac{\Delta T}{10^2} \right) - 1.3549 \left(\frac{\Delta T^2}{10^5} \right) + 3711.2(I) - 4590.7(I)^2 - 5.3504 \left(\frac{\Delta T \times I}{10^2} \right) \quad (24)$$

In the above equations, parameter I is determined using Eq. (20) considering a volume of 12 L, as explained in Section 4. The

value of ΔT is the difference between temperatures T_2 and T_1 . The constants in Eqs. (23) and (24) are assumed to have units such that n is dimensionless. The results obtained by this method are presented in Table 4 and will be discussed in the next section.

$$\Delta T = T_2 - T_1 \quad (25)$$

7. Results and discussion

The correlation shown in Eq. (22) was applied to estimate the value of the T_{LFL} , and the lower flammability limits were calculated. 273 C–H–O compounds were considered in the correlation set. The average absolute relative error (AARE) of this set was 5.53% and the squared correlation coefficient (R^2) was 0.97587.

101 C–H–O compounds were considered for the prediction set. The AARE was 5.25% and the squared correlation coefficient was 0.96996. When these parameters were calculated for the total set (374 compounds), the value of the AARE was 5.43% and the squared correlation coefficient was 0.97527. The complete data set and the relevant variables including the experimental and calculated LFLs are presented on Tables S.1 and S.2 of Supplementary material. Table 2 shows a comparison between the R^2 obtained by the method developed in the present work and the R^2 obtained by

other methods. Some published methods have higher R^2 values; however, the main advantage of the present method is that it is simpler. For instance, in order to use the method developed by Seaton (1991), 38 second-order molecular groups must be identified. The method developed by Gharagheizi (2008) establishes a correlation with four quantitative molecular structure properties, while the method developed by Bagheri et al. (2012) establishes a correlation with three quantitative molecular structure properties. Those properties are calculated by using Hyperchem software followed by Dragon software. Pan et al. (2009) also used four quantitative molecular structure properties. However, after the values of those properties have been calculated, the code developed by the authors must be used. Similarly, the methods developed by Gharagheizi (2009), Lazzús (2011) and Albahri (2013) also require the use of code developed by the authors. The present method is simpler because it relies solely on basic combustion knowledge and uses widely known parameters that can easily be obtained from the literature.

As was expected, using a dimensionless parameter θ led to a simple correlation which accurately predicts the ratio of T_{stq} to T_{LFL} . Since the stoichiometric adiabatic flame temperature (at given initial conditions) has a unique value for a particular compound, the corresponding adiabatic flame temperature at the LFL

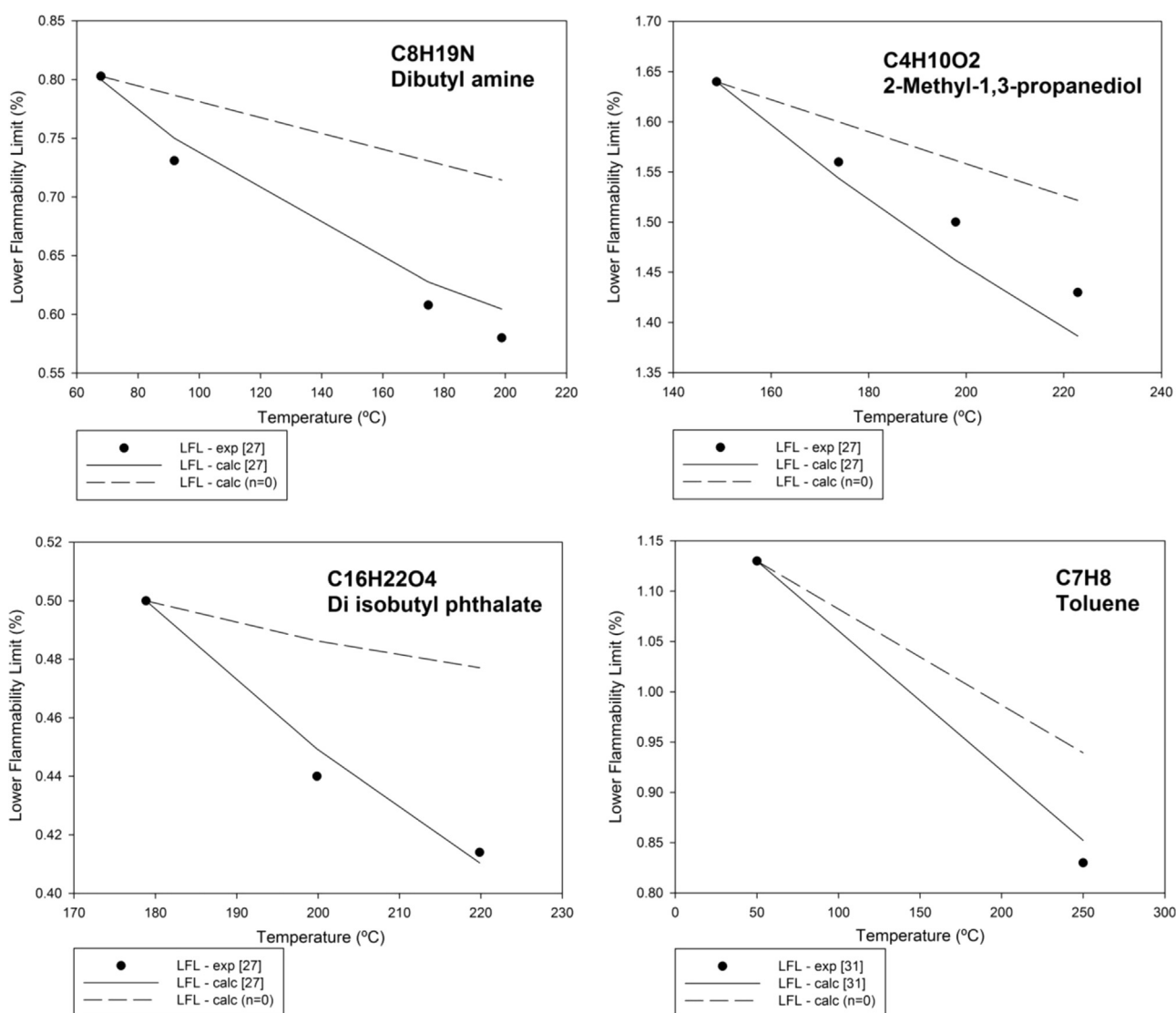


Fig. 7. Lower flammability limits of di-butyl amine, 2-methyl-1,3-propanediol, di-iso-butyl phthalate and toluene at different initial temperatures.

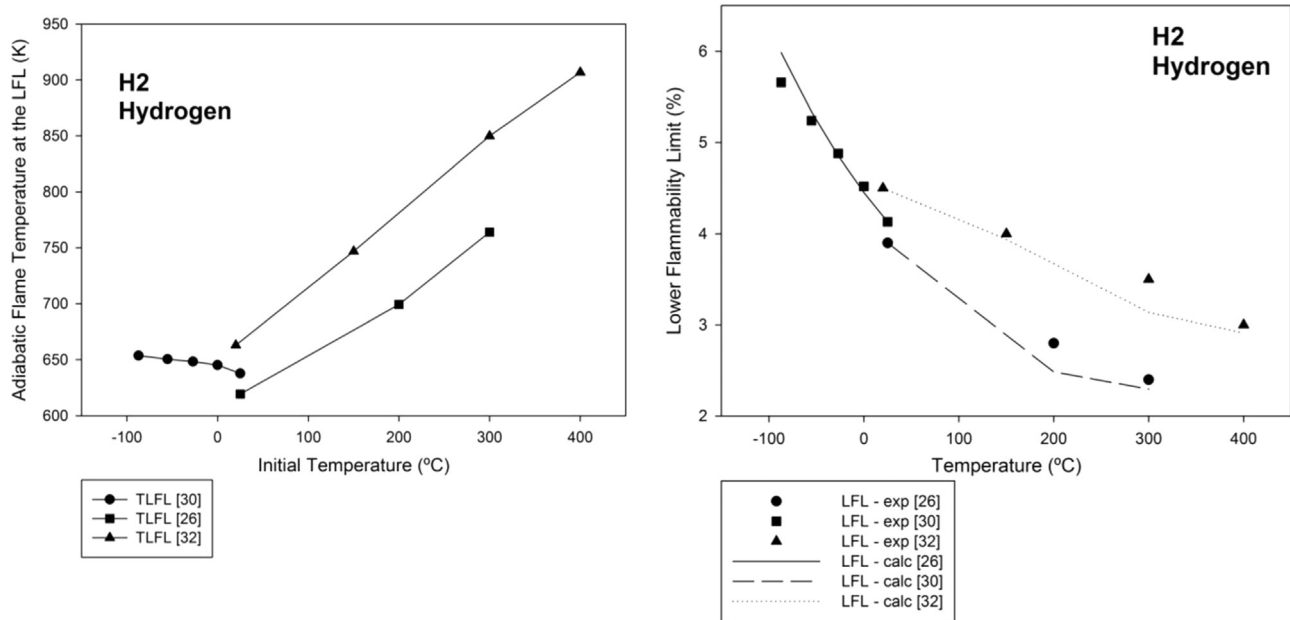


Fig. 8. Adiabatic flame temperatures at the experimental LFLs and calculated LFLs of hydrogen at different initial temperatures.

Table 5

Comparison of results obtained for hydrogen with the method developed in the present work by calculating n with Eq. (24) and considering $n = 0$.

T_i (°C)	LFL _{exp} (%)	LFL _{calc} (%) [$n = \text{Eq.}(24)$]	ARE (%) [$n = \text{Eq.}(24)$]	LFL _{calc} (%) [$T_{LFL1} = T_{LFL2}$]	ARE (%) [$T_{LFL1} = T_{LFL2}$]	Ref.
25	3.90	–	–	–	–	(Wierzba and Wang, 2006)
200	2.80	2.74	2.26	1.75	37.65	
300	2.40	2.26	5.68	0.55	77.23	
20	4.50	–	–	–	–	(Ciccarelli et al., 2006)
150	4.00	3.94	1.52	2.88	27.95	
300	3.50	3.14	10.34	1.06	69.58	
400	3.00	2.91	2.91	–0.12	103.98	
24.85	4.13	–	–	–	–	(Karim et al., 1984)
–87.15	5.66	5.74	1.45	5.55	1.89	
–55.15	5.24	5.33	1.74	5.14	1.85	
–27.15	4.88	4.93	1.13	4.79	1.92	
–0.15	4.52	4.53	0.14	4.44	1.66	

will also have a unique value. The method developed determines the LFL of a C–H–O compound through the use of six parameters ($x_C, x_H, x_O, \bar{h}_{f,F}^0, M_F, T_{stq}$) and by applying a simple thermal analysis to the combustion process assuming complete combustion and adiabatic conditions in order to estimate the value of T_{LFL} .

25 compounds were considered to study the dependence of LFL on the initial mixture's temperature. The correlation set was made up of 82 experimental points, it had an AARE of 1.73%, a squared correlation coefficient of 0.9985, a maximum ARE of 11.02%, and a minimum ARE 0.03%. The prediction set was made up of 27 experimental points. It had an AARE of 2.14%, a squared correlation coefficient of 0.9996, a maximum ARE of 7.00%, and a minimum ARE of 0.28%. As mentioned above, a correlation for hydrogen was obtained separately with a total of 9 experimental points. The AARE was 3.02%, the squared correlation coefficient was 0.9828, the maximum ARE was 10.34%, and the minimum ARE was 0.14%. The maximum ARE for the total set of 118 experimental points was 11.02%, the minimum ARE was 0.03%, the AARE was 1.85%, and the squared correlation coefficient of 0.9987. A summary of the results obtained by the method for determining the LFL at different initial temperatures of the mixture is shown on Table 4. Table S3 of Supplementary material shows all the relevant variables along with the calculated and experimental LFLs. The values of I on Table S3 were calculated for the experimental LFLs; however, it should

be pointed out that only the value of I at LFL_{T1} is used in Eqs. (23) and (24). The calculated and experimental LFLs for each compound are shown in Figs. 1–8.

Considering that T_{LFL} does not change when the mixture's initial temperature changes is equivalent to assuming that n is equal to zero for any initial temperature. In published studies (Zabetakis, 1965; Zlochower, 2012; Mendiburu et al., 2015), that consideration had accurate results for methane, propane, iso-butane, ethylene, propylene, carbon monoxide, ammonia, and dimethyl ether. However this is not true for all compounds, as can be observed on Figs. 4–7. For 15 of the 26 compounds studied, considering T_{LFL} to be constant is not adequate. The data on Table 5 show that the consideration produced errors for hydrogen at high temperatures. For a hydrogen–air mixture at an initial temperature of 400 °C, the experimental value of the LFL is 3.00%. At the same conditions, the method developed in the present study produces a calculated LFL value of 2.91%; on the other hand, assuming that T_{LFL} is constant produces a calculated LFL value of –0.12%.

Figs. 1–8 might seem to indicate that ARE values for some compounds are high. It might seem to be true for iso-butane, propylene, ethanol and 1-octanol, for example. However, these observations should be contrasted with the data provided on Table S3. The maximum ARE for iso-Butane is 3.15%; for propylene, it is 2.23%; for ethanol, it is 8.29%; and for 1-octanol, it is 6.96%. Those errors are not particularly high. Note that the R^2 of the method

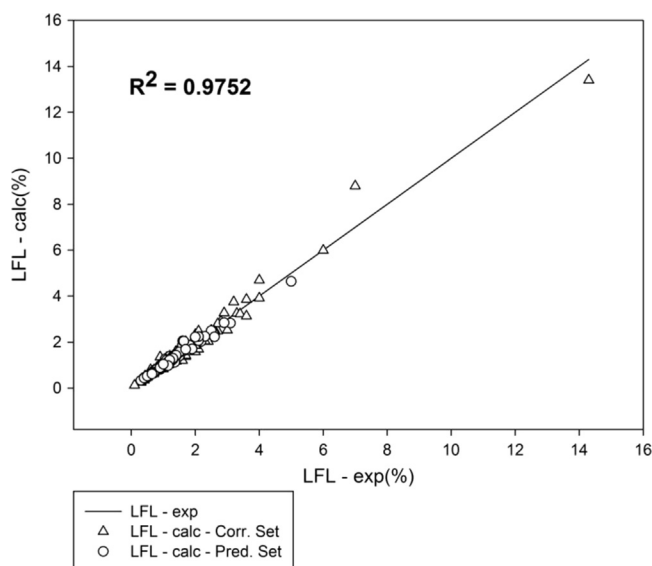


Fig. 9. Comparison of experimental data with the LFLs calculated by the method described in Section 3.

was 0.9987, which means that the method is very accurate when calculating the LFLs at different initial temperatures.

Hydrogen was studied separately. Fig. 8 shows the adiabatic flame temperatures at the experimental LFLs and the calculated LFLs for this compound. The adiabatic flame temperature at the LFL for hydrogen has a different trend; when the initial temperature is below 0 °C, the value of T_{LFL} decreases as the initial temperature increases; on the other hand, when the initial temperature is above 0 °C, the value of T_{LFL} increases as the initial temperature increases. The experimental and calculated LFLs for hydrogen are also shown in Fig. 8. Considering that few experimental points were used to obtain the correlation presented in Eq. (24), it should be used carefully for initial mixture temperatures outside of the interval ranging from -87 to 400 °C.

Finally, Figs. 9 and 10 show the comparison of the experimental LFLs to the calculated LFLs for both methods developed in the present work. Fig. 9 shows the results obtained by the method for determining the LFLs of C–H–O compounds at standard temperature and pressure. Fig. 10 shows the results obtained by the method for determining the LFLs of flammable compounds at different initial mixture temperature and atmospheric pressure. In both cases, it can be seen that the experimental LFLs are very close to the calculated LFLs.

8. Conclusions

A method that can be used to calculate the lower flammability limits of C–H–O compounds was developed. This method is based on the use of a correlation to determine the ratio between the adiabatic flame temperature at the stoichiometric composition and the adiabatic flame temperature at the LFL. Using this ratio, a simple thermal analysis was applied in order to determine the lower flammability limits at standard temperature and pressure. For a total set of 374 C–H–O compounds, the average absolute relative error (AARE) was 5.43% and the squared correlation coefficient (R^2) was 0.9752; thus, the method developed was very accurate when compared to experimental data.

The dependence of the lower flammability limit on the initial temperature of the mixture was studied for 26 compounds. It was found that assuming a constant adiabatic flame temperature at the LFL is only partially accurate. A method to determine the LFL of a

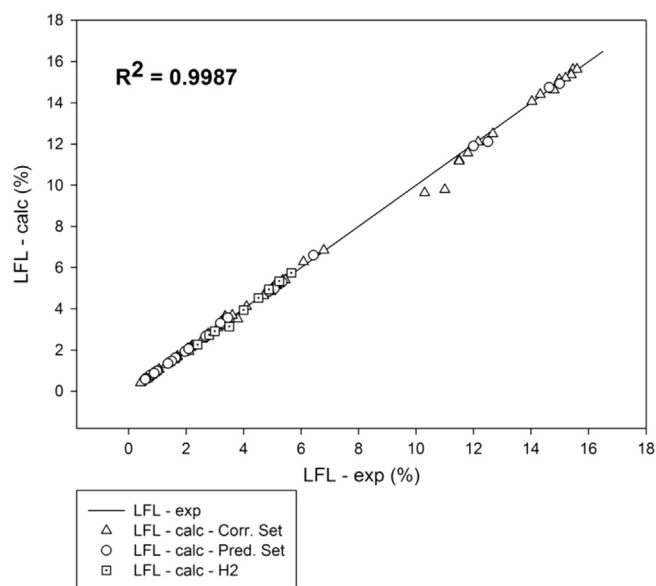


Fig. 10. Comparison of experimental data with the LFLs calculated by the method described in Section 4.

flammable compound at different initial temperatures was developed. This method was very accurate. The average absolute relative error (AARE) was 1.85% and the squared correlation coefficient (R^2) was 0.9987 for the total set made up of 118 experimental points.

Nomenclature

c_p	Specific heat capacity at constant pressure, kJ/mol-K
\bar{c}_p	Average specific heat capacity at constant pressure, kJ/mol-K
h^0	Absolute enthalpy, kJ/mol
\bar{h}_f^0	Enthalpy of formation, kJ/mol
ΔH_C	Heat of combustion, kJ/mol
LFL	Lower flammability limit, %
T	Temperature, °C
v_{ar}	Oxygen content of the air at the flammability limit composition
v_{ar}^s	Oxygen content of the air at the stoichiometric composition
x_C	Number of carbon atoms in the compound
x_H	Number of monoatomic hydrogen atoms in the compound
x_O	Number of monoatomic oxygen atoms in the compound

Subscripts

ar	Air
$calc$	Calculated
exp	Experimental
F	Fuel
LFL	Lower flammability limit
P	Products
r	Reference temperature, 25 °C
R	Reactants
R^2	Squared Correlation Coefficient
stq	Stoichiometric
U	Unburned
I	Initial temperature
Av	Average

Symbols

θ Ratio of adiabatic flame temperatures

Abbreviations

ARE Absolute relative error for an individual compound, %
 AARE Average absolute relative error of a data set, %
 FL Flammability limit
 LFL Lower Flammability limit
 LFLT Lower Flammability limit temperature
 UFL Upper Flammability limit
 A,K,I Parameters

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.ces.2016.01.031>.

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