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Estimation of lower flammability limits of C—H compounds in air at atmospheric pressure, evaluation of temperature dependence and diluent effect

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HIGHLIGHTS

- A semi empirical method for determination of the LFLs of C—H compounds was developed.
- The method showed consistency with Le Chatelier's law for binary mixtures of C—H compounds.
- The method was extended for estimation of LFLs at moderate temperatures.
- The method was extended for estimation of LFLs when diluent is added to the mixture.

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ABSTRACT

Estimation of the lower flammability limits of C—H compounds at 25 °C and 1 atm; at moderate temperatures and in presence of diluent was the objective of this study. A set of 120 C—H compounds was divided into a correlation set and a prediction set of 60 compounds each. The absolute average relative error for the total set was 7.89%; for the correlation set, it was 6.09%; and for the prediction set it was 9.68%. However, it was shown that by considering different sources of experimental data the values were reduced to 6.5% for the prediction set and to 6.29% for the total set. The method showed consistency with Le Chatelier's law for binary mixtures of C—H compounds. When tested for a temperature range from 5 °C to 100 °C, the absolute average relative errors were 2.41% for methane; 4.78% for propane; 0.29% for *iso*-butane and 3.86% for propylene. When nitrogen was added, the absolute average relative errors were 2.48% for methane; 5.13% for propane; 0.11% for *iso*-butane and 0.15% for propylene. When carbon dioxide was added, the absolute relative errors were 1.80% for methane; 5.38% for propane; 0.86% for *iso*-butane and 1.06% for propylene.

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1. Introduction

Flammability limits need to be known for the safe operation of industrial processes which involve the use and storage of flammable compounds. The study of the flammability limits can be traced back to the early 1900s. There is still no general theory that can represent this phenomena. Experimental, theoretical, and empirical research on flammability limits continues to be developed around the world.

Original research papers that address the prediction of the lower flammability limits can be roughly divided into two groups. There are methods based on the calculated adiabatic flame temperature and methods based on Quantitative Structure–Property Relationships and neural networks. This study is part of the adiabatic flame temperature method, though instead of assuming a value of the adiabatic flame temperature, it is calculated based on a correlation that provides the ratio between the adiabatic flame temperature at the stoichiometric composition and the adiabatic flame temperature at the lower flammability limit composition.

The main advantages of the method developed in the present work are its simplicity and the possibility of extending the method for the determination of lower flammability limits at different initial temperatures, of binary fuel mixtures and of fuel–inert–air mixtures; all this can be done by applying rather simple thermal

Abbreviations: ARE, Absolute relative error for an individual compound, %; AARE, Average absolute relative error of a data set, %.

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Nomenclature

$\bar{C}_\rho$	Specific heat capacity at constant pressure, kJ/mol-K
h	Absolute enthalpy, kJ/mol
$\bar{h}_f^0$	Enthalpy of formation, kJ/mol
$\Delta\bar{h}$	Sensible enthalpy, kJ/mol
ΔH_C	Heat of combustion, kJ/mol
LFL	Lower flammability limit, %
N	Number of compounds
T	Temperature, ºC
v_{ar}	Coefficient of air quantity at the flammability limit composition
v_{ar}^s	Coefficient of air quantity at the stoichiometric composition
x_C	Number of carbon atoms in the compound
x_H	Number of monoatomic hydrogen atoms in the compound
y_i	Mole fraction of species i

Subscripts

ad	Adiabatic
ar	Air
calc	Calculated
d	Diluent
exp	Experimental
F	Fuel
LFL	Lower flammability limit
m	Mixture
P	Products
P1	Products at temperature 1
P2	Products at temperature 2
r	Reference temperature, 25ºC
R	Reactants
R1	Reactants at temperature 1
R2	Reactants at temperatura 2
R^2	Correlation factor
SS_E	Sum of squares of deviations
SS_T	Total sum of squares
STQ	Stoichiometric

Symbols

θ	Ratio of adiabatic flame temperatures

analyses. In the present work, the method is developed for C—H compounds only; however, this method can be extended for different compounds, as C—H—O compounds, for example. In comparison with other available methods, the approach presented in this work is totally related to the basic thermal analysis of the combustion of flammable mixtures. The present method does not provide a correlation that directly determines the lower flammability limits; it provides a correlation to determine the ratio of the adiabatic flame temperature at stoichiometric composition to the adiabatic flame temperature at the lower flammability limit composition. Using the correlation, the lower flammability limits can be calculated by applying the energy conservation equation with some simplifications, which are not new for the reader with basic knowledge on combustion theory. Furthermore, the method is consistent with the Le Chatelier's law, which is another advantage.

The lower flammability limits of the mixtures of C—H compounds can be accurately estimated by Le Chatelier's law using known individual lower flammability limits. It was shown that the present method is consistent with Le Chatelier's law. It has the advantage that the individual lower flammability limits do not need to be known.

The approach adopted in this study permitted the method to be expanded to include situations in which the initial temperature of the mixture is not the reference temperature, and when some diluent is added to the fuel–air mixture, making it a fuel–diluent–air mixture.

The estimation of the lower flammability limits at different initial temperatures and when there is diluent in the mixture is very important. The subject needs to be examined further. This study contributes because it helps to estimate the lower flammability limits in the two cases mentioned above, whether the lower flammability limit of the fuel–air mixture at the reference temperature is known or not.

2. Methods for estimating lower flammability limits

2.1. Methods based on a calculated flame temperature

The calculated adiabatic flame temperature (CAFT) at the lower flammability limit (LFL) was used by Vidal et al. [1] in order to estimate the LFLs of paraffinic hydrocarbons (C_nH_{2n+n}) and unsaturated hydrocarbons (C_nH_{2n}, C_nH_{2n-2}). In their study Vidal et al. [1] presented data for 25 paraffinic hydrocarbons and 10 unsaturated hydrocarbons, the CAFTs at the LFLs for each compound were determined, and the average value of the temperatures that were obtained for the paraffinic and unsaturated hydrocarbon families was used as the CAFT to determine the flammability limits. The maximum relative error obtained was 3.35%. The same data that was used to determine the average CAFT were also used to test the method's predictions.

Zhao et al. [2] used a similar concept in order to predict the LFLs of hydrocarbon mixtures. A calculated flame temperature (CFT) method that considered heat loss by convection and radiation was used. This method was applied to binary mixtures of methane and propane; methane and *n*-butane; methane and ethylene; ethylene and propylene; and ethylene and acetylene. The method accurately estimated the experimental LFLs values of the mixtures considered. The CFTs for each pure hydrocarbon were determined by using the experimental LFLs. CFTs of the mixtures were determined by a linear combination of the molar fraction of each fuel in the mixture and their individual calculated flame temperatures at the LFL.

Ma [3] developed a thermal theory for estimating the lower flammability limits of fuel mixtures using calculations based on oxygen calorimetry and a CAFT value set at 1600 K. The results agreed well with Le Chatelier's law. In a later work, Ma et al. [4] compared correlations between estimates of the flammability limits of pure fuel and fuel–inert mixtures for nine kinds of fuel and 86 combinations.

Shebeko et al. [5] developed an analytical evaluation method for the flammability limits of gaseous mixtures; the method was also based on the CAFT, which was set at 1600 K for calculations.

Di Benedetto [6] proposed a thermal/thermodynamic theory of flammability limits. In this work, the flame temperature value is assumed to be equal to the auto-ignition temperature of the fuel. This assumption produces wider flammable ranges.

2.2. Methods based on group contribution or neural networks

Albahri [7] proposed an artificial neural network method that estimates the LFLs of different compounds with an average relative error of 2.28% for the total set; 2.3% for the training set; and 2.2% for the test set.

Bagheri et al. [8] presented two approaches to estimate the lower flammability limits of pure compounds, a multivariate model which had an average absolute error of 18.6% and a nonlinear

machine learning model which had an average absolute error of 15.3%.

Rowley et al. [9] developed a group contribution method for determining the adiabatic temperature (T_{ad}). This temperature was then used to determine the LFLs of different types of fuel. The average relative error of the training set was 10.61%; for the test set it was 10.76%; and for the combined set it was 10.67%.

Lazzús [10] developed a neural network/particle swarm method for determining the flammability limits of different fuels. The average relative error of the LFL estimates was 8.6% for the training set; 8.5% for the prediction set; and 8.6% for the total set.

Gharagheizi [11] used a group contribution method to estimate the LFLs of pure compounds. The average absolute error of the training set was 4.35%; for the test set it was 5.70%; and for the total set it was 4.62%.

Pan et al. [12] developed a relationship between quantitative structure properties in which the compounds were represented by molecular descriptors. They developed a model based on a support vector machine method to determine the LFLs of pure compounds. The average absolute relative error of the total set was 5.6% and the maximum absolute relative error was 61.86%.

Gharagheizi [13], developed a method based on molecular descriptors in order to determine a correlation for LFL determination. A total of 1056 compounds were considered, 845 in the training set and 211 in the test set. The correlation factor for the training set was 0.9698 and for the test set it was 0.9728.

3. Development of the semi-empirical method

3.1. The lower flammability limits at reference temperature

The objective of this work is to provide a simple method to estimate the LFLs of compounds containing C—H atoms. Complete combustion is assumed and the following global one-step reaction is obtained for combustion at the LFL.

$$C_{x_C}H_{x_H} + \upsilon_{ar}(O_2 + 3.75N_2) \rightarrow \; x_C CO_2 + \frac{x_H}{2}H_2O + (\upsilon_{ar} - \upsilon^s_{ar})O_2 + 3.76\upsilon_{ar}N_2. \quad (1)$$

The stoichiometric quantity of air is represented by υ^s_{ar} and determined by Eq. (2).

$$\upsilon^s_{ar} = x_C + 0.25x_H. \quad (2)$$

The relationship between LFL and the quantity of air is:

$$LFL = \frac{100}{1 + 4.76\upsilon_{ar}}. \quad (3)$$

If the adiabatic flame temperature at the LFL ($T_{ad,LFL}$) is determined beforehand and is a known parameter, the quantity of air can be calculated by applying the energy conservation equation based on the global one-step reaction given in Eq. (1), with the following assumptions:

i) The process is adiabatic.
ii) There is no another form of work than the flow work considered in enthalpies.
iii) Kinetic and potential energy variations are negligible.
iv) The sensible enthalpy of the reactants can be represented by the sensible enthalpy of air.

With these assumptions, the expression shown in Eq. (6) is obtained by isolating the desired variable υ_{ar} in the energy conservation equation.

$$\upsilon_{ar} = \frac{\upsilon^s_{ar}\Delta\bar{h}_{O_2} + \bar{h}^0_{f,F} - x_C\bar{h}_{CO_2} - 0.5x_H\bar{h}_{H_2O}}{\bar{h}_{ar,P} - \bar{h}_{ar,R}} \quad (4)$$

in which $\bar{h}_{ar} = \Delta\bar{h}_{O_2} + 3.76\Delta\bar{h}_{N_2}$, subscript P refers to products, and subscript R refers to reactants.

3.2. Estimation of the adiabatic flame temperature at the LFL

In order to correlate the adiabatic flame temperature at the LFL, the following parameters of the compounds were considered:

- Number of carbon atoms (x_C).
- Number of hydrogen atoms (x_H).
- Enthalpy of formation of the fuel ($\bar{h}^0_{f,F}$).
- Adiabatic flame temperature at the stoichiometric composition ($T_{ad,STQ}$).

The aforementioned parameters are characteristics of each compound, while $T_{ad,STQ}$ is dependent on the global reaction chosen, which in the present study is the complete combustion reaction.

Comparing the adiabatic flame temperatures at the LFL and at the stoichiometric compositions provides a ratio that can be used for correlation.

$$\theta = \frac{T_{ad,STQ}}{T_{ad,LFL}}. \quad (5)$$

This means that the task consists of determining a correlation that properly approximates the value of θ and using it to estimate $T_{ad,LFL}$ using the known value of $T_{ad,STQ}$.

3.3. Data sources for C—H compounds

A set of 120 C—H compounds was considered. LFL data was taken from Glassman and Yetter [14], Zabetakis [15], Carson and Mumford [16], Joyce and McKusick [17], CASLAB web database [18], Supplementary material from works by Lazzús [10], Gharagheizi [11], and Pan et al. [12]. Data for the enthalpies of formation of the 120 compounds were obtained from NIST chemistry web book [19]. The absolute enthalpies were calculated using the NASA Glenn coefficients obtained from McBride et al. [20]. Finally the heat capacities at constant pressure were obtained from the JANAF Thermochemical Tables [21] and adjusted to six degree polynomials.

The data were taken from the references in the same priority order in which they are cited. The data presented by Glassman and Yetter [14] and Zabetakis [15] were the main sources; more compounds were added from the other cited sources [10–18]. The number of compounds was limited to 120 due to the availability of their enthalpies of formation in the NIST chemistry web book [19]. Some compounds that were available in the cited references [10–12,14–18] were left out of the present study because their enthalpies of formation were not found. The proposed method needs the value of the enthalpy of formation of the fuel in order to perform the correlation procedure.

Most of the sources [10–12,14,16–18] give little or none information regarding the experimental details for the determination of the LFLs. On the other hand, the work by Zabetakis [15] provides information regarding the experimental procedures and vessel size. The data by Zabetakis [15] were preferred when another source reported a different value for the LFL of a compound.

The average values of the heat capacities at constant pressure were determined for the temperature interval ranging from 800 to 2500 K. The ideal gas standard state corresponded to 1 bar of

pressure in McBride et al. [20] and in Chase et al. [21]. Since all the calculations performed in this work assume ideal gas behaviour, the enthalpies and heat capacities depend only on temperature.

3.4. The correlation obtained

The set of 120 C—H compounds was divided in two sets of 60 compounds. The compounds were randomly ordered in a list and to each compound an order number was attributed; however, when different compounds had the same number of carbon and hydrogen atoms they were attributed consecutive order numbers. After this was done, it was decided that all the compounds with odd order numbers would be used for the correlation set and all the compounds with even order numbers would be used for the prediction set.

With the data of the correlation set, a correlation was determined for θ by using the multiple linear regression method provided in the MATLAB program. The procedure consisted of determining the adiabatic flame temperatures at the stoichiometric and LFL compositions of each compound and calculating the θ ratio. The correlation obtained is shown below.

$$\theta = a_0 + a_1\bar{h}^0_{f,\mathrm{F}} + a_2 x_\mathrm{C} + a_3 x_\mathrm{H} + a_4 \frac{x_\mathrm{C}}{x_\mathrm{H}}\bar{h}^0_{f,\mathrm{F}} \tag{6}$$

where the coefficients are: $a_0 = 1.58$, $a_1 = 6.99 \times 10^{-4}$, $a_2 = -1.12 \times 10^{-2}$, $a_3 = 7.80 \times 10^{-3}$, and $a_4 = -2.34 \times 10^{-4}$.

3.5. Expanding to C—H compound mixtures

Le Chatelier's law is very accurate when applied to binary hydrocarbon mixtures, as discussed by Kondo et al. [21] and by Zhao et al. [22], among others. For this reason, the method proposed in this study is intended to produce accurate results for binary hydrocarbon mixtures. The method proposed in the present work will be shown to be equivalent to Le Chatelier's law by comparing the estimates obtained by the two methods. The estimate of the lower flammability limit of a mixture is made in the same way as for a single fuel, but considering a mixture of fuel 1 and fuel 2, both described by their respective mole fractions, y_1 and y_2. The mole fractions are determined with respect to the fuels only, thus $y_1 + y_2 = 1$. In order to determine the value of θ for the mixture of fuels, it is necessary to determine the moles of carbon in the mixture ($x_{\mathrm{C,m}}$), the moles of hydrogen in the mixture ($x_{\mathrm{H,m}}$) and the enthalpy of formation of the mixture ($\bar{h}^0_{f,m}$), the following operations are carried out.

$$x_{\mathrm{C},m} = y_1 x_{\mathrm{C},1} + y_2 x_{\mathrm{C},2}, \tag{7}$$

$$x_{\mathrm{H},m} = y_1 x_{\mathrm{H},1} + y_2 x_{\mathrm{H},2}, \tag{8}$$

$$\bar{h}^0_{f,m} = y_1 \bar{h}^0_{f,1} + y_2 \bar{h}^0_{f,2}. \tag{9}$$

The obtained values are used to determine θ by means of Eq. (6). The adiabatic flame temperature of the mixture at stoichiometric composition is then determined and used together with θ in order to determine the adiabatic flame temperature of the mixture at the LFL composition by means of Eq. (5). The lower flammability limit is finally determined by calculating ν_{ar} with Eq. (4) and LFL with Eq. (3).

3.6. Lower flammability limits at different temperatures

The flammability limits depend on the initial temperature of the reactive mixture. The proposed method can be expanded by performing a simple thermal analysis. The following simplifications are necessary:

i) The lower flammability limits at the reference temperature are used as the basis for calculations.
ii) The difference between the initial temperatures is not excessively high, it is rather moderate.
iii) Average heat capacities at constant pressure can be used to determine the sensible enthalpies.
iv) The sensible enthalpy of the fuel can be neglected.
v) The flame temperatures for the two cases have approximately the same value.

The energy conservation equation for the global one-step reaction shown in Eq. (1) is written for the fuel at the reference temperature. Then considerations (i)–(iii) are applied and expressions for ν_{ar} and $\mathrm{LFL}_{T_{\mathrm{R1}}}$ are obtained. Only the expression for $\mathrm{LFL}_{T_{\mathrm{R1}}}$ is presented here.

$$\mathrm{LFL}_{T_{\mathrm{R1}}} = \frac{100\bar{C}_{\mathrm{P,ar}}(T_{\mathrm{P1}} - T_{\mathrm{R1}})}{\bar{C}_{\mathrm{P,ar}}(T_{\mathrm{P1}} - T_{\mathrm{R1}}) + 4.76[\Delta H_\mathrm{C} + A(T_{\mathrm{P1}} - T_{\mathrm{R1}})]} \tag{10}$$

in which T_{P1} is the adiabatic flame temperature and T_{R1} is the initial temperature. The initial temperature was considered as the reference temperature. For the other parameters appearing in Eq. (10), the expressions below are used.

$$A = \nu^{\mathrm{s}}_{\mathrm{ar}}\bar{C}_{\mathrm{P,O_2}} - x_\mathrm{C}\bar{C}_{\mathrm{P,CO_2}} - \frac{x_\mathrm{H}}{2}\bar{C}_{\mathrm{P,H_2O}}, \tag{11}$$

$$\Delta H_\mathrm{C} = \bar{h}^0_{f,\mathrm{F}} - x_\mathrm{C}\bar{h}^0_{f,\mathrm{CO_2}} - \frac{x_\mathrm{H}}{2}\bar{h}^0_{f,\mathrm{H_2O}}, \tag{12}$$

$$\bar{C}_{\mathrm{P,i}} = \frac{1}{T_\mathrm{b} - T_\mathrm{a}}\int_{T_\mathrm{a}}^{T_\mathrm{b}} C_{\mathrm{P,i}}\mathrm{d}T, \tag{13}$$

$$\bar{C}_{\mathrm{P,ar}} = \bar{C}_{\mathrm{P,O_2}} + 3.76\bar{C}_{\mathrm{P,N_2}}. \tag{14}$$

The same analysis is carried out for the fuel at the desired initial temperature (T_{R2}). This produces the adiabatic flame temperature (T_{P2}). The result is shown in Eq. (15).

$$\mathrm{LFL}_{T_{\mathrm{R2}}} = \frac{100\bar{C}_{\mathrm{P,ar}}(T_{\mathrm{P2}} - T_{\mathrm{R2}})}{\bar{C}_{\mathrm{P,ar}}(T_{\mathrm{P2}} - T_{\mathrm{R2}}) + 4.76[\Delta H_\mathrm{C} + \bar{C}_{\mathrm{P,F}}(T_{\mathrm{R2}} - T_{\mathrm{R1}}) + A(T_{\mathrm{P2}} - T_{\mathrm{R1}})]}. \tag{15}$$

An expression that serves to estimate the LFLs at different temperatures is obtained by dividing Eq. (15) by Eq. (10) and applying considerations (iv) and (v).

$$\mathrm{LFL}_{T_{\mathrm{R2}}} = K^*\left(1 - \frac{T_{\mathrm{R2}} - T_{\mathrm{R1}}}{T_{\mathrm{P1}} - T_{\mathrm{R1}}}\right)\mathrm{LFL}_{T_{\mathrm{R1}}} \tag{16}$$

in which

$$K^* = \frac{(\bar{C}_{\mathrm{P,ar}}/\Delta H_\mathrm{C}(T_{\mathrm{P1}} - T_{\mathrm{R1}}) + 4.76[1 + A/\Delta H_\mathrm{C}(T_{\mathrm{P1}} - T_{\mathrm{R1}})])}{(\bar{C}_{\mathrm{P,ar}}/\Delta H_\mathrm{C}(T_{\mathrm{P2}} - T_{\mathrm{R2}}) + 4.76[1 + A/\Delta H_\mathrm{C}(T_{\mathrm{P1}} - T_{\mathrm{R1}})])}. \tag{17}$$

3.7. Lower flammability limits of diluted C—H compounds

Adding a diluent to the fuel–air mixture, producing a fuel–diluent–air mixture, has an effect on the flammability limits. The effect is more evident in the case of the upper flammability limit. However, for diluents such as CO_2, the effect on the lower flammability limit is not negligible. As more diluent is added to the fuel–diluent–air mixture, the lower flammability limit increases and the upper flammability limit reduces. At the limit oxygen concentration point, the two flammability limits have the same value, and beyond this point the fuel–diluent–air mixture becomes non-flammable.

The effect produced on flammability limits by diluting methane, propane, ethylene, propylene, methyl ether, methyl formate, 1,1-difluoroethane, and ammonia with nitrogen was studied by Kondo et al. [24]. In that study, a modification to Le Chatelier's law was

proposed to estimate the effects of dilution on flammability limits. The effect produced on the flammability limits by dilution of the aforementioned compounds with carbon dioxide was studied by Kondo et al. [25], and a modification to Le Chatelier's law was proposed again.

The approach developed in the present study is different from that proposed by Kondo et al. [24,25]. It is similar to that proposed for the initial temperature effect on the lower flammability limit. Considerations (i)–(iv) are maintained. The diluent and flammable compound are considered to be a separate mixture for simplicity. They are described by their mole fractions y^d for the diluent and y^F for the flammable compound. For the fuel–diluent mixture, $y_d + y^F = 1$. The diluent is included in the one-step global reaction and it is considered to be inert in the combustion reaction. The energy conservation equation for this new reaction is written. Considerations (i)–(iii) are applied, giving Eq. (18).

$$\mathrm{LFL_d} = \frac{100 y_F \bar{C}_{P,ar}(T_{P1} - T_{R1})}{\bar{C}_{P,ar}(T_{P1} - T_{R1}) + 4.76[y_F B_d - y_d \bar{C}_{P,d}(T_{P1} - T_{R1})]} \tag{18}$$

Dividing Eq. (18) by Eq. (10) leads to:

$$\frac{\mathrm{LFL_d}}{\mathrm{LFL}_{T_{R1}}} = \frac{y_F[\bar{C}_{P,ar}(T_{P1} - T_{R1}) + 4.76B_0]}{\bar{C}_{P,ar}(T_{P1} - T_{R1}) + 4.76[y_F B_d - y_d \bar{C}_{P,d}(T_{P1} - T_{R1})]} \frac{(T_{P2} - T_{R1})}{(T_{P1} - T_{R1})} \tag{19}$$

in which

$$B_d = \Delta H_C + \bar{C}_{P,F}(T_{R1} - T_r) + A(T_{P2} - T_r) \tag{20}$$

$$B_0 = \Delta H_C + \bar{C}_{P,F}(T_{R1} - T_r) + A(T_{P1} - T_r). \tag{21}$$

The equations above imply that the lower flammability limit of the non-diluted mixture and that of the diluted mixture are both determined at the same initial temperature.

Until this point, there is no solid basis that permits any conjecture on the value of the adiabatic flame temperature of the diluted mixture at the lower flammability limit (T_{P2}). Some investigation on the behaviour of the adiabatic flame temperature when the fuel is diluted needs to be carried out. Zabetakis [15] presents some graphs depicting the flammability limits of compounds diluted in nitrogen and carbon dioxide. Those graphs were used to obtain the lower flammability limits of the diluted compounds. The adiabatic flame temperatures were then calculated. The results are shown on Table 1. It can be seen that the adiabatic flame temperature increases as the inert content increases. This is an interesting fact that was also observed by Razus et al. [26]. It can be understood if the total moles of the inert substance and the total moles of oxygen are considered. As the diluent is added, the total moles of oxygen decrease and get closer to the stoichiometric quantity. At the same time, the total moles of the inert substance decrease with the increase of diluent. For example, the lower flammability limit of methane is reported to be 5% by Zabetakis [15]. In the fuel–air mixture, there are approximately 4 mol of O_2 and 15 mol of N_2. Since only 2 mol of O_2 can react, the other 2 mol of O_2 are treated as inert and a total of 17 mol of inert substances are present. For the fuel–diluent–air mixture with 30% N_2, with a lower flammability limit of 5.8% [15], there are 2.33 mol of O_2 and 13.92 mol of N_2, therefore there is a total of 14.25 mol of inert substances.

At the limiting oxygen concentration point, the mixture is generally rich with respect to the oxygen content. The global one-step reaction proposed in this study cannot be used to determine the limiting oxygen concentration point because it can only be used when the concentration of fuel and oxygen is stoichiometric or when there is excess oxygen. In the case of a rich mixture, dissociation must be taken into account and thermochemical equilibrium calculations must be made. The determination of the limiting oxygen concentration point will be properly addressed in a future study in which the upper flammability limits of C—H compounds will be studied. Razus et al. [27] proposed a method for estimating the limiting oxygen concentration of fuel–diluent–air mixtures using methane, propane, and ethylene as fuel.

The previous analysis indicates that the temperature of the fuel–inert mixture goes up along with the volume of inert substances. The calculation with Eq. (19) will be made in three steps:

(1) Determination of the LFL considering $T_{P1} = T_{P2}$.
(2) Determination of T_{P2} by using the LFL determined in first step.
(3) Re-calculation of LFL by using the value of T_{P2} obtained in the second step.

4. Results and discussions

The method's accuracy was tested by determining the average absolute relative error (AARE) for the total set, the correlation set, and the prediction set. Eq. (22) is the AARE equation. Individual absolute relative errors were determined using Eq. (23). The correlation factor (R^2) of the method was calculated by using Eq. (24) which is presented by Montgomery [28]. The necessary parameters are the sum of squares of residuals (SS_E) and the total sum of squares (SS_T), given in Eqs. (25) and (26), respectively.

$$\mathrm{AARE} = \frac{1}{N}\sum_{i=1}^{N} \frac{|\mathrm{LFL_{exp}} - \mathrm{LFL_{calc}}|}{\mathrm{LFL_{exp}}} 100\% \tag{22}$$

$$\mathrm{ARE} = \frac{|\mathrm{LFL_{exp}} - \mathrm{LFL_{calc}}|}{\mathrm{LFL_{exp}}} 100\% \tag{23}$$

$$R^2 = 1 - \frac{SS_E}{SS_T} \tag{24}$$

$$SS_E = \sum_{i=1}^{n} \left(\mathrm{LFL_{exp}} - \mathrm{LFL_{calc}}\right)^2 \tag{25}$$

$$SS_T = \sum_{i=1}^{n} \left(\mathrm{LFL_{exp}}\right)^2 - \frac{\left(\sum_{i=1}^{n} \mathrm{LFL_{exp}}\right)^2}{n} \tag{26}$$

Table 1
Calculated adiabatic flame temperatures for some compounds diluted with N_2 and CO_2.

Inert	CH_4		C_2H_6		C_3H_8		C_5H_{12}	
	LFL	T_{ad} (K)	LFL	T_{ad} (K)	LFL	T_{ad} (K)	LFL	T_{ad} (K)
0%	5.00	1482.5	3.00	1536.1	2.10	1530.8	1.40	1594.2
10% N2	5.10	1504.1	3.00	1537.3	2.10	1532.0	1.50	1672.0
20% N2	5.30	1546.0	3.00	1538.6	2.20	1582.6	1.55	1711.1
30% N2	5.80	1647.4	3.00	1539.8	2.40	1680.8	1.60	1749.8
10% CO2	5.60	1541.0	3.20	1543.6	2.40	1611.9	1.60	1678.1
20% CO2	6.20	1592.2	3.50	1581.1	3.00	1807.0	1.80	1750.8

LFLs and diluent are expressed as volume percentages in the fuel–inert–air mixture.

Table 2
Other experimental values of LFL for some compounds and comparison with predicted LFL values.

Compound	LFL(%) Calc.	LFL(%) Exp.		ARE(%)
1-Dodecene	0.61	0.40	[10]	53.08
		0.62	[7]	1.61
		0.60	[29]	1.67
1-Decene	0.72	0.55	[10]	31.57
		0.74	[7]	2.70
		0.70	[29]	2.86
Metylacetylene	2.43	1.70	[10]	43.01
		2.10	[16]	15.71
		2.30	[30]	5.65
Cyclohexene	1.23	1.00	[10]	23.38
		1.31	[7]	6.10
		1.20	[17]	2.50
Toluene	1.18	1.40	[10]	16.05
		1.20	[7,14]	1.67
n-Heptane	1.02	1.20	[10]	15.38
		1.05	[17]	2.86
		1.00	[7]	2.00
1-Heptene	1.01	0.80	[10]	26.15
		1.00	[7,31]	1.00

Table S1 shows all of the data for the prediction set. Table S2 shows all of the data for the correlation set. These tables are in the Supplementary material. The total AARE error for the 120 compounds was 7.89%, while the AARE for the correlation set was 6.09% and the AARE for the prediction set was 9.68%. These results can be analyzed further considering the data shown on Table 2. On Table 2, the predicted LFL values that had the highest absolute relative errors are compared with experimental LFL values from different sources for the same compounds. When the minimum AREs are used to determine the AARE of the prediction set, the new value is 6.5% and the new AARE for the total set is 6.29%.

Takahashi et al. [32] studied the dependence of the flammability limits on vessel size. They found that the larger the diameter the narrower the flammable range. Coward and Jones [33] present experimental values for the flammability limits of different compounds obtained in vessels of different size and with upward, downward and horizontal flame propagation. In Table 3 some of the experimental values presented by Coward and Jones [33] for methane are depicted. It can be observed that there are differences between the values obtained and, therefore, it should not be surprising that different flammability limits have been observed for the same compound because these limits depend on the experimental conditions. Taking the later observations into account the best case scenario would be to obtain the flammability limits of all the compounds under the same experimental conditions. However, this does not happen in reality since the experimental efforts are performed by different research groups under different experimental conditions. In previous works the authors have studied the flammability limits of ethanol and some of the obtained flammability limits differ from those available in the literature [35,36].

A special case that needs to be considered is Squalane. Squalane's experimental LFL is 0.2% [10,11] and the LFL predicted by the method developed in the present work is 0.32%. This gives an ARE of 62.35%. However, the results of other authors for this compound should be considered. Gharagheizi [11] used this compound in the training set of his model and obtained a calculated LFL value of 0.28%. Pan et al. [12] presented predicted LFL values of 0.26, 0.30 and 0.24, determined by using different methods. Squalene was also part of the training set in work by Pan et al. [12]. The experimental conditions for the determination of the LFL of squalene are not reported, therefore, this matter cannot be further discussed in the present work.

Considering the average absolute relative errors obtained and the previous discussions, it can be concluded that the method developed here is well suited to predict the lower flammability limits in air, at atmospheric pressure, of pure compounds containing only carbon and hydrogen atoms in their molecular structure.

Also note that the experimental LFL value for *iso*-butane used to evaluate the results in this method was 1.8%; however, Kondo et al. [22] found a value of 1.68% for the LFL of *iso*-butane. The method developed in this work predicts a value of 1.6733% for the LFL of *iso*-butane. Another interesting point is that Zhao et al. [23] found an LFL of 1.72% for *n*-Butane. In this study, the experimental value used for comparison was 1.9% and the predicted value was 1.6655%.

The correlation factors (R^2) were obtained by applying Eqs. (24)–(26). For the correlation set R^2 was 0.9652, for the prediction set it was 0.9239 and for the total set it was 0.9543. Therefore, the correlation factor is always above 0.90. The correlation factors were determined for the prediction of LFL and not for the prediction of

Table 3
Experimental values for the flammability limits of methane obtained in vessels of different sizes and with different flame propagation as presented by Coward and Jones [33].

Tube Size			Flame Propagation	LFL (%)	UFL (%)	ΔLFL[a] (%)	ΔUFL[a] (%)
Diameter (cm)	Length (cm)	Volume (L)					
10.2	96	7.84	Upward	5.00	15.00	0.00	0.00
2.5	150	0.74	Upward	5.80	13.20	16.00	12.00
7.5	150	6.62	Downward	5.95	13.35	19.00	11.00
2.5	150	0.74	Downward	6.30	12.80	26.00	14.67
7.5	150	6.62	Horizontal	5.40	13.95	8.00	7.00
2.5	150	0.74	Horizontal	6.20	12.90	24.00	14.00

[a] The variations are determined with respect to LFL = 5% and UFL = 15%.

Table 4
Comparison of correlation factors obtained in the present work with those obtained in published articles.

References	R^2 (Train Set)	N (train)	R^2 (Test Set)	N (Test)	R^2 (Total Set)	Applicability
Albahri [7]	0.9998	518	0.99997	25	0.9998	Hydrocarbons, ethers, ketones,
Bagheri et al. [8]	0.9061	1292	0.9083	323	0.9063	aldehydes, alcohols, phenols,
Lazzús [10]	0.9876	328	0.9819	90	0.9865	esters, amines, anhydrides, etc.*
Gharagheizi [11]	0.99	846	0.971	211	0.986	[7,8,10,11,13]
Gharagheizi [13]	0.9698	845	0.9728	211	–	
This Work	0.9652	60	0.9239	60	0.9543	Hydrocarbons [this work]

* For more detailed information the reader is referred to the cited articles.

Table 5
Comparison of the proposed method with Le Chatelier's law.

Mixture	LFL(%)		LFL (%)	ARE (%)	LFL (%)	ARE (%)	LFL (%)	ARE (%)
	Exp		Le Chatelier[c]		Le Chatelier[d]		This work	
0.20C3H8 + 0.80C4H10[a]	1.73	[22]	1.74	0.58	1.74	0.58	1.74	0.58
0.40C3H8 + 0.60C4H10[a]	1.79	[22]	1.80	0.56	1.83	2.23	1.83	2.23
0.60C3H8 + 0.40C4H10[a]	1.86	[22]	1.87	0.54	1.92	3.23	1.92	3.23
0.80C3H8 + 0.20C4H10[a]	1.94	[22]	1.95	0.52	2.02	4.12	2.02	4.12
0.25CH4 + 0.75C3H8	2.45	[23]	2.46	0.41	2.49	1.63	2.49	1.63
0.50CH4 + 0.50C3H8	2.97	[23]	2.99	0.67	3.00	1.01	3.00	1.01
0.75CH4 + 0.25C3H8	3.84	[23]	3.81	0.78	3.78	1.56	3.78	1.56
0.25CH4 + 0.75C4H10[b]	2.05	[23]	2.07	0.98	2.00	2.44	2.00	2.59
0.50CH4 + 0.50C4H10[b]	2.56	[23]	2.59	1.17	2.51	1.95	2.51	1.95
0.75CH4 + 0.25C4H10[b]	3.49	[23]	3.47	0.57	3.36	3.72	3.36	3.72
AARE (%)				0.68		2.25		2.25

[a] *iso*-Butane.[b] *n*-Butane.[c] Le Chatelier's law used with individual experimental LFL values.[d] Le Chatelier's law used with individual calculated LFL values.

θ, because the main objective of the present work is to determine the LFLs of C—H compounds and not to obtain a correlation for θ.

In Table 4 the correlation factors obtained in the present work are compared with those presented in published articles. Also, some of the types of compounds for which the models were developed are listed in Table 4. As it can be observed, the present work focuses only on hydrocarbons; however, the real strength of the presented procedure lies in the fact that it can be easily extended to obtain similar correlations for other types of compounds (alcohols for example).

It may be important to clarify why the correlation procedure was performed for θ and not for the LFLs themselves. Actually, a simple correlation as the one obtained for θ was also obtained for the LFLs of the correlation set (60 compounds), but the R^2 of this correlation was 0.5918 (for the correlation set). This means that a simple correlation involving the number of moles of carbon, the number of moles of hydrogen and the enthalpy of formation is not suitable for direct determination of the LFLs. At this point the idea of correlating the adiabatic flame temperature at the lower flammability limit was considered; however, the results were not satisfactory.

Another property of the fuel is its adiabatic flame temperature at stoichiometric composition and at given conditions. By dividing this temperature by the adiabatic flame temperature at the LFL composition the parameter θ was found, and it was observed that this parameter (or dimensionless number) does not vary as much as the LFLs or as the adiabatic flame temperatures at the LFL composition. Thus, the idea of performing the correlation for θ and then determine the LFLs by applying the energy conservation equation was considered as a good approach and resulted in the present work.

An interpretation for θ can be obtained by following the procedure indicated below:

- Writing the enthalpy of the products obtained from the complete combustion of the fuel–air mixture at the stoichiometric composition, by considering average heat capacities at constant pressure:

$$H_{P,STQ} = \left(x_C \bar{C}_{P,CO_2} + \frac{{}^{x}H}{2}\bar{C}_{P,H_2O} + 3.76\nu^{s}_{ar}\bar{C}_{P,N_2}\right)(T_{STQ} - T_r). \quad (27)$$

- Writing the enthalpy of the products obtained from the complete combustion of the fuel–air mixture at the lower flammability limit composition, by considering average heat capacities at constant pressure:

$$H_{P,LFL} = \left(x_C \bar{C}_{P,CO_2} + \frac{{}^{x}H}{2}\bar{C}_{P,H_2O} + 3.76\nu^{s}_{ar}\bar{C}_{P,N_2} + (\nu_{ar} - \nu^{s}_{ar})\bar{C}_{P,ar}\right)(T_{LFL} - T_r). \quad (28)$$

- Dividing Eq. (27) by Eq. (28):

$$\frac{H_{P,STQ}}{H_{P,LFL}} = \left(\frac{x_C \bar{C}_{P,CO_2} + ({}^{x}H/2)\bar{C}_{P,H_2O} + 3.76\nu^{s}_{ar}\bar{C}_{P,N_2}}{x_C \bar{C}_{P,CO_2} + ({}^{x}H/2)\bar{C}_{P,H_2O} + 3.76\nu^{s}_{ar}\bar{C}_{P,N_2} + (\nu_{ar} - \nu^{s}_{ar})\bar{C}_{P,ar}}\right)\left(\frac{T_{STQ} - T_r}{T_{LFL} - T_r}\right). \quad (29)$$

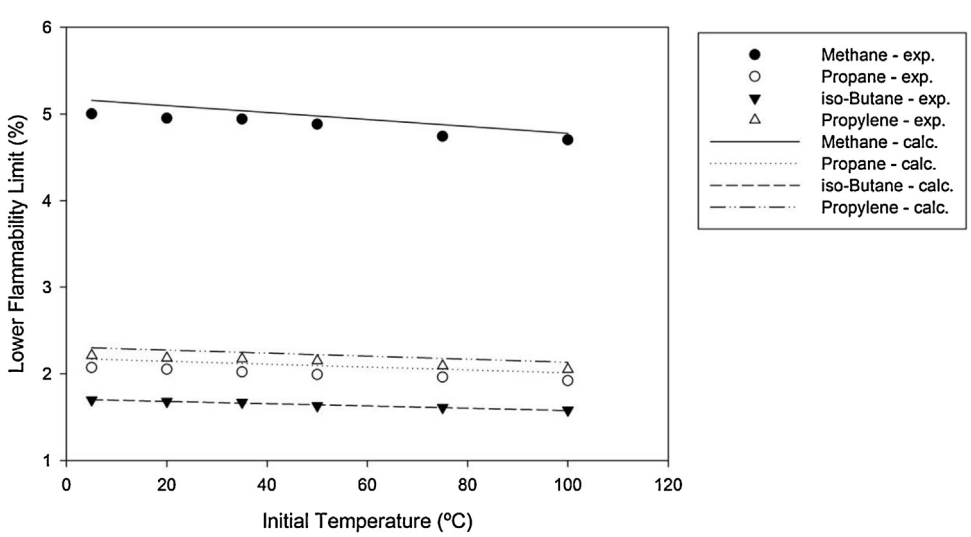

Fig. 1. Temperature dependence of the lower flammability limits of some hydrocarbons. Experimental data from Kondo et al. [34].

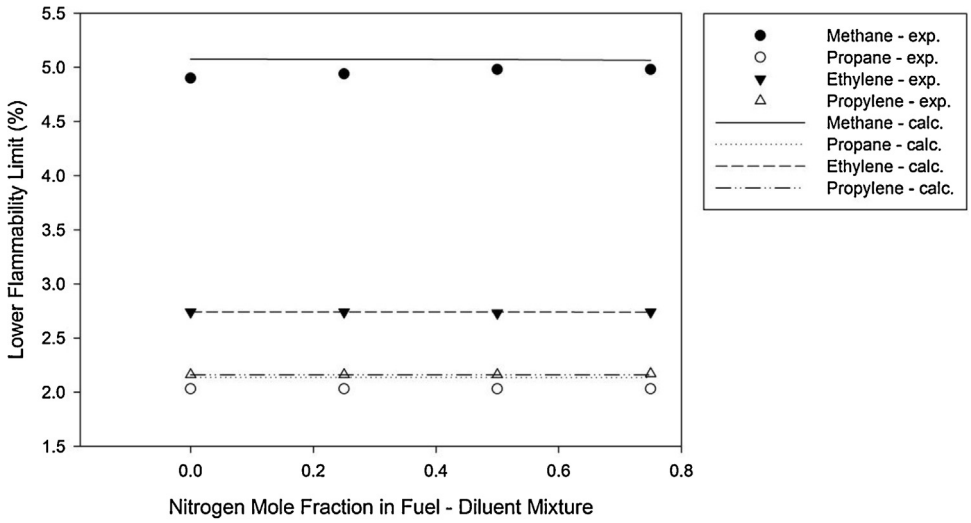

Fig. 2. Effect of dilution with nitrogen (N_2) on the lower flammability limits of some hydrocarbons. Experimental data from Kondo et al. [24].

- Now if the second term on the right-hand side of Eq. (29) is considered, the following is observed:

$$\frac{T_{STQ} - T_r}{T_{LFL} - T_r} = \frac{1 - (T_r/T_{STQ})}{(1/\theta) - (T_r/T_{STQ})}. \tag{30}$$

Therefore, θ is a measure of the ratio of the enthalpy of the products obtained for the combustion of the fuel–air mixture at the stoichiometric composition to the enthalpy of the products obtained for the combustion of the fuel–air mixture at the LFL composition, when considering complete combustion of the C—H compounds at constant pressure and adiabatic conditions. If the combustion process is adiabatic and at constant pressure the key parameters that determine the products enthalpy are the moles of carbon (x_C), the moles of hydrogen (x_H) and the enthalpy of formation ($\tilde{h}_f^0$). Because of this θ was correlated by using the three aforementioned parameters.

The proposed method and Le Chatelier's law were used to determine the lower flammability limits of propane–*iso*-butane, methane–propane, and methane–*n*-Butane mixtures. The results are shown on Table 5, which also shows a comparison with experimental results by Kondo et al. [22] and Zhao et al. [23]. Le Chatelier's law was used with the experimental individual LFL values and the calculated individual LFL values. In the second case, the ARE obtained by applying Le Chatelier's law has the same value as the ARE obtained by applying the method proposed in this work. The AARE obtained with Le Chatelier's law using individual experimental LFL values was 0.68%, the maximum ARE was 1.17%, and the minimum ARE was 0.41%. When the method proposed in this work and Le Chatelier's law used calculated individual LFL values, the results were the same: AARE of 2.25%, maximum ARE of 4.12%, and minimum ARE of 0.58%. The relative error can be attributed to the deviation of the calculated individual LFL values with respect to the experimental individual LFL values. As measured by the AARE, the method can accurately predict the lower flammability limits of binary mixtures of C—H compounds. The proposed method yields the same results that would be obtained with Le Chatelier's law. The tangible difference is that the proposed method does not require the input of individual LFL values while Le Chatelier's law requires the individual LFL values.

The temperature dependence of the lower flammability limits of methane, *iso*-butane, propane, and propylene was tested by applying the relations obtained in Section 3.7. The results are shown in Fig. 1, which also shows the experimental results obtained by Kondo et al. [34]. For methane, the AARE was 2.41%; for propane, the AARE was 4.78%; for *iso*-butane, the AARE was 0.29%; and for

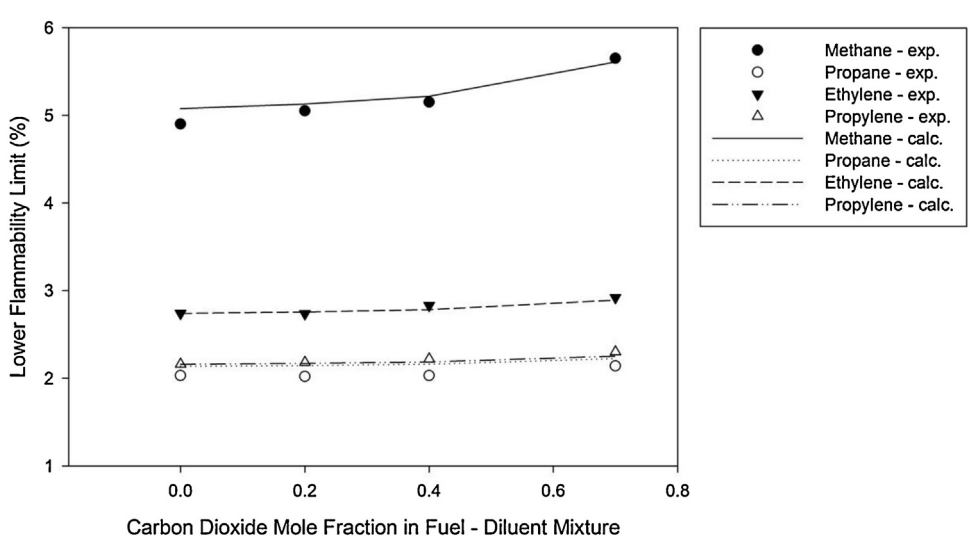

Fig. 3. Effect of dilution with carbon dioxide (CO_2) on the lower flammability limits of some hydrocarbons. Experimental data from Kondo et al. [25].

propylene, the AARE was 3.86%. The maximum ARE among these results was 5.19%. It was obtained for propane at 50 °C. The minimum ARE was 0.01%. It was obtained for *iso*-butane at 20 °C. The method could accurately predict the temperature dependence of the lower flammability limit. Note that the reference temperature was 25 °C. Fig. 1 shows that the method was tested for temperature from 5 °C to 100 °C.

Finally, the effect of adding diluent to the fuel–air mixture was tested by considering two diluents: nitrogen and carbon dioxide. The hydrocarbons considered were methane, propane, ethylene, and propylene. For methane and propane, the reference LFL value was determined by the proposed method in order to test the total algorithm. For ethylene and propylene, the reference LFL value was taken from Kondo et al. [24,25] in order to test the accuracy of the estimation proposed in Section 3.7.

The results obtained for dilution with nitrogen and experimental data from Kondo et al. [24] are shown in Fig. 2, while the results obtained for dilution with carbon dioxide and experimental data from Kondo et al. [25] are shown in Fig. 3.

In the case of dilution with nitrogen, the AAREs obtained were 2.48% for methane, 5.13% for propane, 0.11% for ethylene, and 0.15% for propylene. The maximum ARE was 5.17% for propane, while the minimum ARE was 0.01% for ethylene.

For dilution with carbon dioxide, the AAREs obtained were 1.80% for methane, 5.38% for propane, 0.86% for ethylene, and 1.06% for propylene. The maximum ARE was 6.36% for propane, while the minimum ARE was 0.49% for propylene.

It is clear that the total algorithm is accurate, starting from the determination of the reference LFL value. The AREs found are mostly due to the deviation between the calculated value of the reference LFL and the experimental value of the reference LFL. However, when the experimental value is used as the reference LFL, the AREs are minor and within the experimental error. The estimation method proposed in Section 3.7 agrees with experimental values very well.

5. Conclusions

A semi-empirical method based on determining the adiabatic flame temperature at the lower flammability limit was developed to be applied to C—H compounds. It was validated with experimental data. The model has shown good accuracy. It can be used to estimate the lower flammability limits of C—H compounds in air at 25 °C and 1 atm.

The method also showed to be consistent with the Le Chatelier's Law when applied to binary mixtures of C—H compounds. As it is known the Le Chatelier's Law is very accurate when used to determine the lower flammability limits of C—H compounds and therefore the method is also accurate for this purpose.

The semi-empirical method was expanded to assess the dependence of lower flammability limits on the initial mixture temperature. The method developed was rather simple and agreed closely with experimental data.

Finally, the effect of diluents on lower flammability limits was considered and an extension of the initial method was developed. The total algorithm closely agreed with experimental data, while the method developed for assessment of the diluents effect very closely agreed with experimental data.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.10.058.

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