



# Estimation of upper flammability limits of C–H compounds in air at standard atmospheric pressure and evaluation of temperature dependence



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## HIGHLIGHTS

- A semi-empirical method for determining UFLs of C–H compounds was developed.
- The squared correlation coefficient obtained for the UFL determination was 0.9248.
- The method was applied to estimate UFLs of binary fuel mixtures.
- The method was extended to estimate UFLs at moderate initial temperatures.
- The estimations showed good or acceptable accuracy in all cases.

## ARTICLE INFO

### Article history:

Received 17 April 2015

Received in revised form 24 October 2015

Accepted 5 November 2015

Available online 12 November 2015

### Keywords:

Upper flammability limits

C–H compounds

Initial temperature effect

Estimation

## ABSTRACT

This study focuses on estimating the upper flammability limits of C–H compounds. A method was developed to determine the upper flammability limits in air at standard atmospheric pressure for the following cases: (a) estimation of the UFLs of pure C–H compounds at standard ambient temperature (25 °C); (b) estimation of the UFLs of binary mixtures of C–H compounds at standard ambient temperature (25 °C); (c) estimation of the UFLs of C–H compounds at different initial temperatures. The method was accurate in all cases. In case (a), for a total set of 115 compounds, the absolute average relative error was 7.27% and a squared correlation coefficient of 0.9248 was obtained. In case (b), the average absolute relative error was 5.55%; in case (c) it was 2.19%.

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## 1. Introduction

Flammability limits (FLs) are an important topic in combustion science. They are still not fully understood. Researchers focus their efforts on determining FLs experimentally and on developing methods to estimate these limits.

This study focuses on estimating the upper flammability limit (UFL) of C–H compounds in air at standard atmospheric pressure. The study has three parts: (a) a semi-empirical method was developed that can be used to estimate the UFL of a C–H compound at standard ambient temperature (25 °C), (b) UFLs of binary mixtures of C–H compounds at standard ambient temperature (25 °C) were estimated, (c) UFLs of C–H compounds at different initial temperatures were estimated. The initial pressure and the presence of a

diluent also have an effect on flammability limits. These two cases will be the subject of future study.

Numerical values of FLs depend on experimental conditions. Sometimes different values of these limits are reported. Most of the available experimental data were obtained at 1 atm and 25 °C. There are some experimental data for FLs at different initial temperatures and binary mixtures of C–H compounds.

It is easier to estimate the lower flammability limit (LFL) than the UFL. This is mainly because, for the LFL, the mixture is lean and complete combustion can be assumed. For the UFL, the mixture is rich and combustion is incomplete. In this study, the products are considered to be in chemical equilibrium. Therefore, the temperature of the products must be known in order to determine the UFL. A set of experimental data was used to obtain a correlation to estimate this temperature. The method was developed for C–H compounds but it can be extended to other types of compounds.

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## Nomenclature

$c_p$	Specific heat capacity at constant pressure, kJ/mol-K
$g_{T,i}^0$	Specific standard Gibbs function of formation of species $i$ , kJ/mol
$h$	Absolute enthalpy, kJ/mol
$h_f^0$	Enthalpy of formation, kJ/mol
$\Delta G_{T,1}^0$	Standard-state Gibbs function change of the equilibrium reaction, kJ/mol
$\Delta \bar{h}$	Sensible enthalpy, kJ/mol
$\Delta H_C$	Heat of combustion, kJ/mol
$K$	Equilibrium constant
$M$	Molecular weight (g/mol)
$n_i$	Number of moles of species $i$ (mol)
$n_T$	Total number of moles of product mixture (mol)
$N$	Number of compounds
$p_0$	Standard atmospheric pressure (1 atm)
$p$	Pressure (atm)
$s$	Specific entropy, kJ/mol K
$T$	Temperature, °C
UFL	Upper flammability limit, %
$\nu_{ar}$	Number of moles of oxygen at the flammability limit composition
$\nu_{ar}^s$	Number of moles of oxygen at the stoichiometric composition
$x_C$	Number of carbon moles in the compound
$x_H$	Number of monoatomic hydrogen moles in the compound
$y_i$	Molar fraction of species $i$

### Subscripts

ad	Adiabatic
ar	Air
calc	Calculated
F	Fuel
$m$	Mixture
P	Products
$r$	Standard ambient temperature, 25 °C
R	Reactants
$R^2$	Correlation factor
stq	Stoichiometric

### Symbols

$\theta$	Ratio of adiabatic flame temperatures
$\lambda$	Dimensionless parameter

### Abbreviations

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

## 2. Brief review of studies of UFL estimation

Garagheizi [1] obtained a correlation to estimate the UFL of pure compounds in air based on their molecular structure. The squared correlation coefficient ( $R^2$ ) was 0.9202 for the total set. The average absolute relative error (AARE) was 9.52%.

Lazzús [2] used a neural network–particle swarm method to estimate the LFL and UFL of pure compounds using a total of 42 structural groups. The AARE of the total set was 7.1% and the squared correlation coefficient was 0.9818.

Ma et al. [3] stated that experimental data of UFLs is so diverse that a universal correlation is not possible. A method to estimate

the UFL of binary mixtures was also presented which agreed well with Le Chatelier's law.

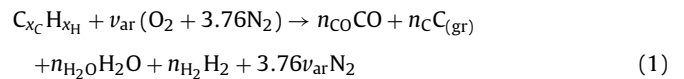
Albahri [4] developed a group contribution method to estimate the UFL of pure hydrocarbons using a total of 30 structural groups. The AARE was 11.8% and the squared correlation coefficient was 0.96.

Seaton [5] developed a group contribution method to predict LFL and UFL. For UFL estimation, the AARE was determined to be 9.68%. A squared correlation coefficient of 0.8862 was determined using experimental data and calculations presented by Seaton [5].

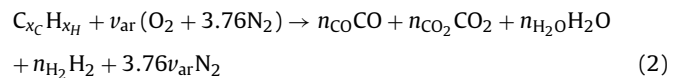
## 3. Development of the semi-empirical method

In a previous study, a method to estimate the LFL of C–H compounds [6] was developed. In the present study, the objective is to estimate the UFL of C–H compounds. Two global reactions were considered for analysis:

Global reaction with condensate



Global reaction without condensate



Two global reactions had to be used, since one is not enough to represent the combustion of all the compounds in the data set. Although a more complex global reaction could have been considered, the idea was to obtain the simplest solution possible.

The method is based on the calculated adiabatic flame temperature [7–11]. The adiabatic flame temperatures at the UFL ( $T_{UFL}$ ) and at the stoichiometric composition ( $T_{stq}$ ) of a correlation set were determined. A correlation that estimates the ratio  $T_{stq}/T_{UFL}$  was then obtained. Finally, the estimated  $T_{UFL}$  value was used to calculate the UFL.

### 3.1. Determining the adiabatic flame temperature at the UFL

At the UFL, a feasible  $T_{UFL}$  is obtained when all the moles of the species in the products are positive quantities while satisfying the mass and energy conservation equations. Both of the global reactions require another equation to complete the system and chemical equilibrium was considered for this purpose. The water–gas heterogeneous reaction is shown in Eq. (3) and the water–gas homogeneous reaction is shown in Eq. (4).



The equilibrium equations for these two reactions are presented in Eqs. (5) and (6), in which  $K_1$  is the equilibrium constant for the water–gas heterogeneous reaction and  $K_2$  is the equilibrium constant for the water–gas homogeneous reaction. Because the pressure is 1 atm:  $p_0/p = 1$ .

$$n_{CO}n_{H_2} = K_1 (p_0/p) n_{H_2O}n_T \quad (5)$$

$$n_{CO_2}n_{H_2} = K_2 n_{CO}n_{H_2O} \quad (6)$$

The equilibrium constants are determined by the standard-state Gibbs function change of the equilibrium reaction:

$$K_1 = \exp\left(-\frac{\Delta G_{T,1}^0}{RT}\right) = \exp\left(-\frac{g_{T,CO}^0 - g_{T,H_2O}^0}{RT}\right) \quad (7)$$

$$K_2 = \exp\left(-\frac{\Delta G_{T,2}^0}{RT}\right) = \exp\left(-\frac{g_{T,\text{CO}_2}^0 - g_{T,\text{CO}}^0 - g_{T,\text{H}_2\text{O}}^0}{RT}\right) \quad (8)$$

The NASA Glenn coefficients [18] can be used to determine specific absolute enthalpies ( $h$ ), specific entropies ( $s$ ), and the specific standard-state Gibbs function of formation ( $g_T^0$ ):

$$\frac{h(T)}{R_u T} = -\frac{a_1}{T^2} + a_2 \frac{\ln T}{T} + a_3 + a_4 \frac{T}{2} + a_5 \frac{T^2}{3} + a_6 \frac{T^3}{4} + a_7 \frac{T^4}{5} + \frac{b_1}{T} \quad (9)$$

$$\frac{s(T)}{R} = -a_1 \frac{T^{-2}}{2} - a_2 T^{-1} + a_3 \ln T + a_4 T + a_5 \frac{T^2}{2} + a_6 \frac{T^3}{3} + a_7 \frac{T^4}{4} + b_2 \quad (10)$$

$$\frac{g^0(T)}{RT} = \frac{h(T)}{RT} - \frac{s(T)}{R} \quad (11)$$

Now it is simple to obtain a numerical solution for  $T_{\text{UFL}}$ :

- (i) The mass conservation equations for each element are written and all the products are expressed in function of the moles of carbon monoxide ( $n_{\text{CO}}$ ).
- (ii) The expressions obtained for each species in the products are replaced in Eq. (5) or (6). A quadratic equation is obtained in which  $n_{\text{CO}}$  is the unknown.

$$an_{\text{CO}}^2 + bn_{\text{CO}} + c = 0 \quad (12)$$

For the global reaction with condensate and using Eq. (5):

$$a = 1 + K_1 \quad (13)$$

$$b = \frac{X_H}{2} (1 + K_1) - 2\nu_{\text{ar}} (1 + K_1) + 3.76\nu_{\text{ar}} K_1 \quad (14)$$

$$c = -(X_H + 7.52\nu_{\text{ar}}) \nu_{\text{ar}} K_1 \quad (15)$$

For the global reaction without condensate and using Eq. (6):

$$a = 1 - K_2 \quad (16)$$

$$b = 2\nu_{\text{ar}} (1 - K_2) - x_C (3 - 2K_2) - \frac{X_H}{2} \quad (17)$$

$$c = x_C \left( \frac{X_H}{2} - 2\nu_{\text{ar}} + 2x_C \right) \quad (18)$$

The coefficients (a, b and c) of the quadratic equation depend on the equilibrium constants, which in turn depend on temperature, as shown in Eqs. (7)–(11). By solving Eq. (12) along with Eqs. (13)–(15) or with Eqs. (16)–(18), two values of  $n_{\text{CO}}$  are found for each global reaction. It was not difficult to identify which one was feasible because the remaining ones were negative or produced negative moles of other species. The equilibrium constants are functions of temperature; therefore, in order to determine the number of moles of each species, an initial choice for the adiabatic flame temperature must be made.

- The energy conservation equation is used to correct the initial choice of the adiabatic flame temperature until convergence is achieved. It is written for each global reaction considering adiabatic conditions, no work crossing the boundaries of the system, and negligible variations of kinetic and potential energies.

$$h_{\text{F}} + \nu_{\text{ar}} h_{\text{ar}} = n_{\text{CO}} h_{\text{CO}} + n_{\text{C}} h_{\text{C}} + n_{\text{H}_2\text{O}} h_{\text{H}_2\text{O}} + n_{\text{H}_2} h_{\text{H}_2} + 3.76\nu_{\text{ar}} h_{\text{N}_2} \quad (19)$$

$$h_{\text{F}} + \nu_{\text{ar}} h_{\text{ar}} = n_{\text{CO}} h_{\text{CO}} + n_{\text{CO}_2} h_{\text{CO}_2} + n_{\text{H}_2\text{O}} h_{\text{H}_2\text{O}} + n_{\text{H}_2} h_{\text{H}_2} + 3.76\nu_{\text{ar}} h_{\text{N}_2} \quad (20)$$

- As shown in Eqs. (9)–(11), the absolute enthalpies and the Gibbs free energies of formation are functions of temperature. Eqs. (7) and (8) show that the equilibrium constants are also functions of temperature. Thus, the adiabatic flame temperature at the UFL is determined by solving a non-linear algebraic equation [Eq. (19) or (20)]. A simple routine that applies the Newton–Raphson method is used to solve the energy conservation equation and the result is used to correct the initial guess of temperature to determine the equilibrium constants. The procedure is repeated until convergence is achieved.

### 3.2. Determining the correlation

$T_{\text{stq}}$  and  $T_{\text{UFL}}$  are the adiabatic flame temperatures. After they had been determined, the ratio of  $T_{\text{stq}}/T_{\text{UFL}}$  was found to vary much less than the UFL. This parameter is designated as  $\theta$ .

$$\theta = \frac{T_{\text{stq}}}{T_{\text{UFL}}} \quad (21)$$

As this ratio has less variation than the UFL, it is reasonable to estimate  $T_{\text{UFL}}$  on the basis of  $\theta$ , where  $\theta$  is empirically expressed in term of four fuel parameters, namely: moles of carbon ( $x_C$ ), moles of hydrogen ( $h_C$ ), enthalpy of formation ( $\bar{h}_{f,F}^0$ ), and molecular weight ( $M_F$ ). Because this dependence proves to be nonlinear, arbitrary nonlinear functions of these four parameters ( $X_i$ ) were introduced. Using a training set of 62 compounds, a linear expression for theta in terms of the  $X_i$  was sought by performing multiple linear regression with MATLAB software.

The procedure for obtaining the correlation shown in Eq. (22) started by considering variables  $X_1$  to  $X_4$ . New variables were added one by one and the UFLs of the compounds in the correlation set were determined. A new variable  $X_i$  was accepted if it produced an increase in the squared correlation coefficient ( $R^2$ ) of the correlation set; otherwise, it was discarded. The correlation determines  $\theta$ , while  $R^2$  was determined for the calculated UFLs of the correlation set. There are several possible combinations of the four parameters that can produce new variables  $X_i$ . However, after adding  $X_{12}$  the increments in the value of  $R^2$  were not significant. Examples of discarded variables are:  $X_i = \sqrt{x_C}$ ,  $X_i = X_1 X_2 X_7$ , and  $X_i = \ln |X_9|$ .

$$\begin{aligned} &4.6364 - 0.4749X_1 + 0.0814X_2 - 0.4586X_3 - 0.5946X_4 \\ \theta = &-2.7268X_5 + 2.451X_6 - 0.0519X_7 + 0.012X_8 \\ &+ 0.0453X_9 - 0.1937X_{10} + 0.1663X_{11} - 0.072X_{12} \end{aligned} \quad (22)$$

In which

$$X_1 = (\bar{h}_{f,F}^0/298b_1); X_2 = (M_F/29b_2);$$

$$X_3 = (x_C/x_H); X_4 = X_1 X_3; X_5 = \sqrt{X_2 X_3}$$

$$X_6 = \ln(X_5); X_7 = (\bar{h}_{f,F}^0/M_F b_3); X_8 = (x_C M_F/x_H b_2);$$

$$X_9 = X_1 X_2; X_{10} = \sqrt{|X_9|}$$

$$X_{11} = \ln(X_{10}); X_{12} = X_1 X_2 X_3; b_1 = 1\text{kJ/mol}; b_2 = 1\text{g/mol}; b_3 = 1\text{kJ/g}$$

### 3.3. Determining the UFL with an estimated value of $T_{\text{UFL}}$

In order to estimate the UFL it is necessary to determine the number of moles of air ( $4.76\nu_{\text{ar}}$ ) or, the number of moles of oxygen ( $\nu_{\text{ar}}$ ). Determining  $\nu_{\text{ar}}$  is the same as determining the upper flammability limit ( $\text{UFL} = 100\%/[1 + 4.76\nu_{\text{ar}}]$ ).

On the procedure described in Section 3.1 it was known that, for one mole of fuel there were  $4.76\nu_{\text{ar}}$  moles of air. The problem, on that section, consisted on the determination of the number of moles of each product species and of the adiabatic flame temperature at the UFL ( $T_{\text{UFL}}$ ).

In the present section the number of moles of air is not known and the value of  $T_{\text{UFL}}$  is approximated by using Eq. (21) together with the values of  $\theta$  and of the stoichiometric adiabatic flame temperature ( $T_{\text{stq}}$ ). The value of  $\theta$  is determined by using Eq. (22) and the value of ( $T_{\text{stq}}$ ) is determined by the procedure described in combustion literature [12].

Since the value of ( $T_{\text{UFL}}$ ) is already known (approximately) it is possible to determine the number of moles of oxygen in the reactants ( $\nu_{\text{ar}}$ ). In other words, it is possible to estimate the UFL. The value of  $T_{\text{UFL}}$  is used to determine the enthalpies in the energy conservation equation [Eq. (19) or (20)] and also the equilibrium constant [Eq. (7) or (8)]. An analytical solution for  $\nu_{\text{ar}}$  is obtained by the following procedure:

- (i) All the species in the products were expressed in terms of  $n_{\text{CO}}$  and now they are expressed in terms of  $\nu_{\text{ar}}$ . To achieve this, the energy conservation equation is used to express  $n_{\text{CO}}$  as a function of  $\nu_{\text{ar}}$ , as shown in Eq. (23). By using this expression, all the species can be written in terms of  $\nu_{\text{ar}}$ .

$$n_{\text{CO}} = m\nu_{\text{ar}} + n \quad (23)$$

For the global reaction with condensate

$$m = \frac{h_{\text{ar}} - 2h_{\text{H}_2\text{O}} + 2h_{\text{H}_2} - 3.76h_{\text{N}_2}}{h_{\text{CO}} - h_{\text{C}} - h_{\text{H}_2\text{O}} + h_{\text{H}_2}} \quad (24)$$

$$n = \frac{\bar{h}_{f,F}^0 - x_{\text{C}}h_{\text{C}} - \frac{x_{\text{H}}}{2}h_{\text{H}_2}}{h_{\text{CO}} - h_{\text{C}} - h_{\text{H}_2\text{O}} + h_{\text{H}_2}} \quad (25)$$

For the global reaction without condensate

$$m = \frac{h_{\text{ar}} - 2h_{\text{H}_2\text{O}} + 2h_{\text{H}_2} - 3.76h_{\text{N}_2}}{h_{\text{CO}} - h_{\text{CO}_2} + h_{\text{H}_2\text{O}} - h_{\text{H}_2}} \quad (26)$$

$$n = \frac{\bar{h}_{f,F}^0 - x_{\text{C}}h_{\text{CO}_2} + 2x_{\text{C}}h_{\text{H}_2\text{O}} - \frac{x_{\text{H}}}{2}h_{\text{H}_2} - 2x_{\text{C}}h_{\text{H}_2}}{h_{\text{CO}} - h_{\text{CO}_2} + h_{\text{H}_2\text{O}} - h_{\text{H}_2}} \quad (27)$$

- Now a solution can be found using Eq. (5) or (6). A quadratic equation is obtained, leading to an analytical solution for  $\nu_{\text{ar}}$ :

$$a_{\nu}\nu_{\text{ar}}^2 + b_{\nu}\nu_{\text{ar}} + c_{\nu} = 0 \quad (28)$$

For the global reaction with condensate

$$a_{\nu} = (1 + K_1)m^2 - 2(1 + K_1)m + 3.76mK_1 - 7.52K_1 \quad (29)$$

$$b_{\nu} = 2(1 + K_1)nm + \frac{x_{\text{H}}}{2}(1 + K_1)m - 2(1 + K_1)n + 3.76nK_1 - x_{\text{H}}K_1 \quad (30)$$

$$c_{\nu} = \frac{x_{\text{H}}}{2}(1 + K_1)n + (1 + K_1)n^2 \quad (31)$$

For the global reaction without condensate

$$a_{\nu} = (1 - K_2)m^2 + 2(1 - K_2)m \quad (32)$$

$$b_{\nu} = 2(1 - K_2)nm + 2(1 - K_2)n - x_{\text{C}}(3 - 2K_2)m - \frac{x_{\text{H}}}{2}m - 2x_{\text{C}} \quad (33)$$

$$c_{\nu} = (1 - K_2)n^2 - x_{\text{C}}(3 - 2K_2)n + 2x_{\text{C}}^2 + \frac{x_{\text{H}}}{2}(x_{\text{C}} - n) \quad (34)$$

### 3.4. Data sources

A set of 115 C–H compounds was considered. UFL data was taken from Glassman and Yetter [12], Zabetakis [13], Carson and Mumford [14], Joyce and McKusick [15], the CASLAB web database [16], and Supplementary material from works by Lazzús [2] and Gharagheizi [1]. Data for the enthalpies of formation of the compounds were obtained from the NIST chemistry web book [17]. Absolute enthalpies and Gibbs free energies were calculated using the NASA Glenn coefficients obtained from McBride et al. [18].

### 4. Estimation of the UFL of binary mixtures of C–H compounds

The calculation procedure is analogous to that described in the previous section. If the binary mixture is made up of fuels 1 and 2 with molar fractions  $y_1$  and  $y_2$ , respectively ( $y_1 + y_2 = 1$ ). Therefore, the value of the property  $z$  is given by Eq. (35).

$$z_m = y_1z_1 + y_2z_2 \quad (35)$$

Kondo et al. [19,20] and Zhao et al. [21] present experimental data on the FLs of binary hydrocarbon mixtures in air. These data will be used for comparison.

### 5. Estimation of the UFL at different initial temperatures

In general, as the initial temperature increases, the LFL decreases while the UFL increases. This means that the flammable range expands as the initial temperature increases.

Considering that  $\theta_1$  corresponds to some initial temperature at which the UFL value is known and that  $\theta_2$  corresponds to some initial temperature at which the UFL is going to be determined, from the definition of  $\theta$  given in Eq. (21):

$$T_{\text{UFL2}} = T_{\text{UFL1}} \frac{T_{\text{stq2}} \theta_1}{T_{\text{stq1}} \theta_2} \quad (36)$$

Sub-indexes 1 and 2 refer to the known and unknown UFL, respectively. The initial temperature at which the UFL is going to be determined is higher than the initial temperature at which the UFL is known:

If  $T_2 > T_1$  then  $T_{\text{stq2}} > T_{\text{stq1}}$  and assuming that  $\theta_1/\theta_2 \geq 1$  then  $T_{\text{UFL2}} > T_{\text{UFL1}}$ , but this is not always the case and is an unnecessary constraint. On the other hand, if  $T_2 > T_1$  then  $T_{\text{stq2}} > T_{\text{stq1}}$  and assuming that  $\theta_1/\theta_2 < 1$ , either  $T_{\text{UFL2}} > T_{\text{UFL1}}$  or  $T_{\text{UFL2}} \leq T_{\text{UFL1}}$  (depending on the numerical value of  $T_{\text{stq2}}/T_{\text{stq1}}$ ). Therefore, by assuming that  $\theta_1/\theta_2 < 1$ , there is no constraint since  $T_{\text{UFL2}}$  can be higher, lower, or equal to  $T_{\text{UFL1}}$ . Fig. 1 shows the values for  $\theta_1/\theta_2$  calculated from experimental data for different compounds and different initial temperatures. This figure confirms that for  $T_2 > T_1$ , the assumption that  $\theta_1/\theta_2 < 1$  correctly represents the experimental behavior.

Experiments have shown that higher initial temperatures lead to higher UFLs [22–25]. This means that there is less oxygen available at the UFL. This implies that for the global reaction without condensate, less carbon undergoes complete combustion and more undergoes incomplete combustion, and less heat is liberated. In addition, for global reaction with condensate, less carbon undergoes incomplete combustion and more carbon appears as condensate; thus, less heat is liberated.

Considering average heat capacities at constant pressure for the product species, the following expressions are obtained:

$$T_{\text{stq}} - T_r = \frac{\Delta h_F + \nu_{\text{ar}}^s h_{\text{ar}} - H_{\text{C}}}{\sum_{\text{stq}} n_i \bar{c}_{p,i}} \quad (37)$$

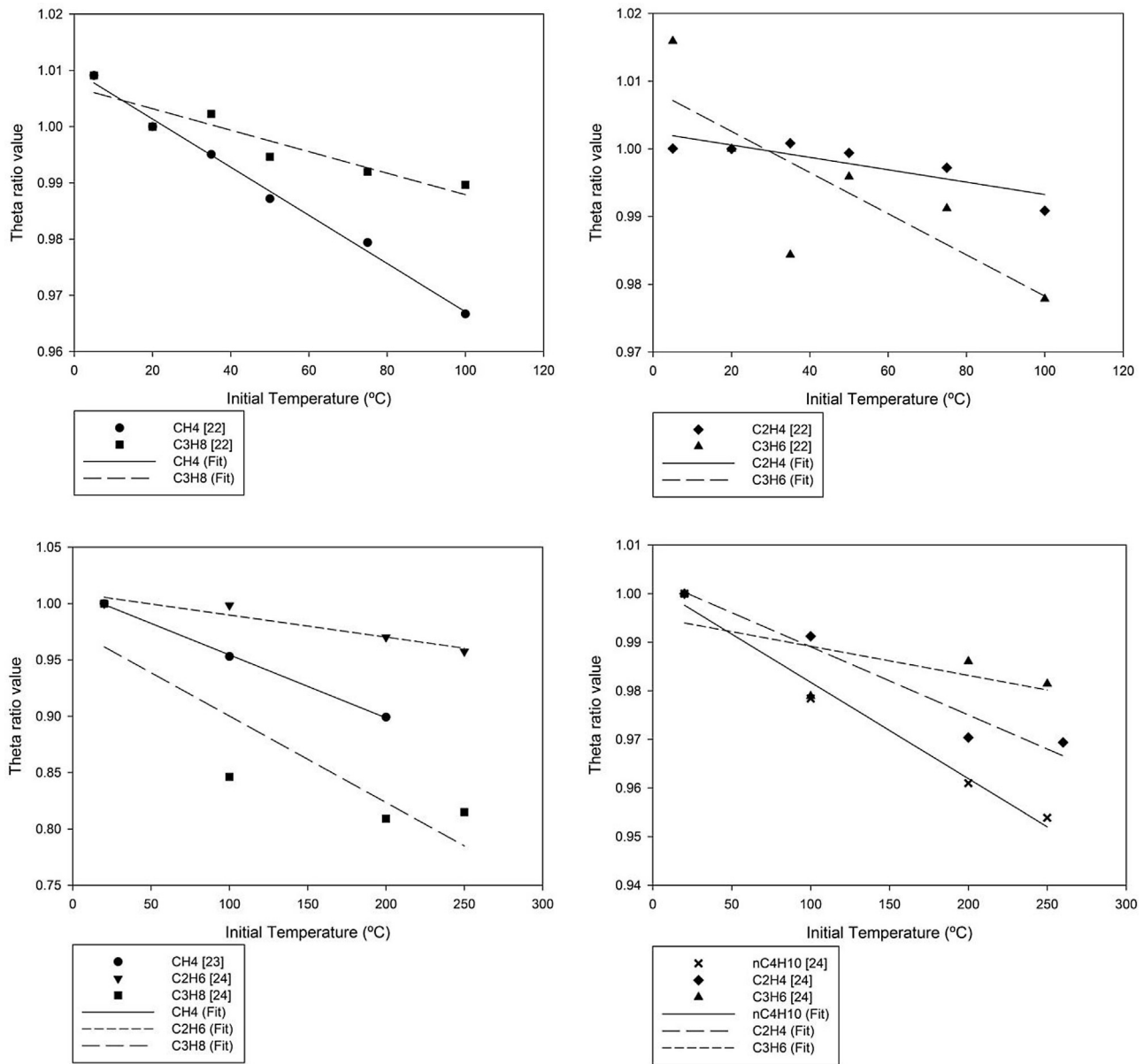


Fig. 1. Theta ratio value ( $\theta_1/\theta_2$ ) versus initial mixture temperature for methane, ethane, propane, *n*-butane, ethylene, and propylene.

$$T_{UFL} - T_r = \frac{\Delta h_F + v_{ar} h_{ar} - H_{UFL}}{\sum_{UFL} n_i \bar{c}_{p,i}} \quad (38)$$

For the stoichiometric reaction

$$H_C = x_C \bar{h}_{f,CO_2}^0 + \frac{x_H}{2} \bar{h}_{f,H_2O}^0 - h_{f,F}^0 \quad (39)$$

$$\sum_{stq} n_i \bar{c}_{p,i} = x_C \bar{c}_{p,CO_2} + \frac{x_H}{2} \bar{c}_{p,H_2O} + 3.76 v_{ar} \bar{c}_{p,N_2} \quad (40)$$

For the global reaction with condensate

$$H_{UFL} = (x_C - n_C) \bar{h}_{f,CO}^0 + \left( \frac{x_H}{2} - n_{H_2} \right) \bar{h}_{f,H_2O}^0 - h_{f,F}^0 \quad (41)$$

$$\sum_{UFL} n_i \bar{c}_{p,i} = n_C \bar{c}_{p,C} + (x_C - n_C) \bar{c}_{p,CO} + \left( \frac{x_H}{2} - n_{H_2} \right) \bar{c}_{p,H_2O} + n_{H_2} \bar{c}_{p,H_2} + 3.76 v_{ar} \bar{c}_{p,N_2} \quad (42)$$

For the global reaction without condensate

$$H_{UFL} = n_{CO_2} \bar{h}_{f,CO_2}^0 + (x_C - n_{CO_2}) \bar{h}_{f,CO}^0 + \left( \frac{x_H}{2} - n_{H_2} \right) \bar{h}_{f,H_2O}^0 - h_{f,F}^0 \quad (43)$$

$$\sum_{UFL} n_i \bar{c}_{p,i} = n_{CO_2} \bar{c}_{p,CO_2} + (x_C - n_{CO_2}) \bar{c}_{p,CO} + \left( \frac{x_H}{2} - n_{H_2} \right) \bar{c}_{p,H_2O} + n_{H_2} \bar{c}_{p,H_2} + 3.76 v_{ar} \bar{c}_{p,N_2} \quad (44)$$



Therefore, the following expression is obtained for  $\theta_1/\theta_2$ :

$$\frac{\theta_1}{\theta_2} = \frac{\sum_{UFL1} n_i \bar{c}_{p,i} \left( \int_{T_r}^{T_2} [c_{p,F} + 4.76 v_{ar} c_{p,ar}] dT - A_2 \right) \left( \int_{T_r}^{T_1} [c_{p,F} + 4.76 v_{ar}^s c_{p,ar}] dT - B \right)}{\sum_{UFL2} n_i \bar{c}_{p,i} \left( \int_{T_r}^{T_1} [c_{p,F} + 4.76 v_{ar} c_{p,ar}] dT - A_1 \right) \left( \int_{T_r}^{T_2} [c_{p,F} + 4.76 v_{ar}^s c_{p,ar}] dT - B \right)} \quad (45)$$

In which

$$B = H_C + T_r \sum_{stq} n_i \bar{c}_{p,i} \quad (46)$$

$$A_1 = H_{UFL1} + T_r \sum_{UFL1} n_i \bar{c}_{p,i} \quad (47)$$

$$A_2 = H_{UFL2} + T_r \sum_{UFL2} n_i \bar{c}_{p,i} \quad (48)$$

In Eq. (45), the ratio  $\theta_1/\theta_2$  depends on the constant pressure heat capacities of the reactants, on the number of moles of oxygen, on the initial temperature, and on the number of moles of the product species. In order to get a better idea of how to estimate the value of  $\theta_1/\theta_2$ , two more assumptions were introduced:

- (i) The heat liberated at the UFL is constant ( $H_{UFL1} = H_{UFL2}$ ).
- (ii) The variation of the number of moles of each species in the

products is negligible  $\left( \sum_{UFL1} n_i \bar{c}_{p,i} = \sum_{UFL2} n_i \bar{c}_{p,i} \right)$ .

Before accepting these two assumptions it is important to provide some more information regarding their validity. The first assumption is directly related to the method for the estimation of the flammability limits at different initial temperatures given by Zabetakis [13]. That method is based on the modified Burgess-Wheeler law. The second assumption was proposed after analyzing the results obtained for the combustion calculations of some hydrocarbons at the UFL, considering equilibrium and adiabatic conditions.

Consider the modified Burgess-Wheeler law which states that, for a given combustible the sum of the heat release at the LFL and the energy added to raise the temperature of the reactant mixture from the reference temperature to the test temperature is a constant. By applying this law Zabetakis [13] obtained an equation that allows the determination of the LFL at different initial temperatures from its value at the reference temperature. Furthermore, by assuming that the heat release at the UFL is equal to the heat release at the LFL, Zabetakis [13] obtained an equation that permits the determination of the UFL at different initial temperatures from its value at the reference temperature. In both cases Zabetakis [13] assumed that the heat release is a constant and he also assumed that the heat release is equal for both limits.

In order to further explore the idea of a constant heat release at the UFL the experimental data presented by Kondo et al. [22] were used to determine the heat released at the UFL, the number of moles of product species and the adiabatic flame temperature. The calculations were performed for methane, propane, iso-butane, and ethylene by considering equilibrium and adiabatic conditions; the results are shown on Table S.3 on the Supplementary material. For initial temperatures ranging from 5 to 100 °C the following was observed:

- The value of the heat release at the UFL ( $H_{UFL}$ ) did not change to a large extent.

- Writing the enthalpy of the products in terms of average heat capacities at constant pressure, it was found that the value of  $\sum_{UFL} n_i \bar{c}_{p,i}$  did not change to a large extent.

These two observations motivated the assumptions introduced lines above. It should be observed (see Table S.3) that, the difference between the heat released at 20 °C and that released at 100 °C is always less than 10%. Although the difference between the value of  $\sum_{UFL} n_i \bar{c}_{p,i}$  at 20 °C and that at 100 °C is 17.25% for methane, it is always less than 10% for propane, iso-butane, and ethylene. Also, as will be shown in the results section (see Table 7), the maximum ARE for methane was 4.38%.

At higher initial temperatures these assumptions might become less acceptable. However, for the temperature intervals investigated in the present article (from 20 to 260 °C) the assumptions were reasonable, as will be shown in the next section.

When considering these two assumptions,  $\theta_1/\theta_2$  will be a function of the constant pressure heat capacities of the reactants, of the initial temperature, and of the number of moles of oxygen.

$$\frac{\theta_1}{\theta_2} = f(c_{p,F}, c_{p,ar}, v_{ar}, T_1, T_2) \quad (49)$$

If the number of moles of oxygen is known, the UFL at a different initial temperature would also be known. Thus, this parameter cannot be considered in the function that estimates  $\theta_1/\theta_2$ . The experimental data show that  $\theta_1/\theta_2$  can be represented by a function that decreases with the increase of the initial temperature. In the case of the reaction without condensate, a simple function that accurately estimates  $\theta_1/\theta_2$  was obtained:

$$\frac{\theta_1}{\theta_2} = \frac{c_{p,F}(T_1) + 4.76 c_{p,ar}(T_1)}{c_{p,F}(T_2) + 4.76 c_{p,ar}(T_2)} \quad (50)$$

For the case of the reaction with condensate, the value of  $\theta_1/\theta_2$  decreases slowly with the increase of the initial temperature. In order to represent this behavior, Eq. (50) was modified with a real non-integer exponent  $\lambda$ , which changes its value with the initial temperature. This led to Eq. (51), which is very accurate when used to estimate the  $\theta_1/\theta_2$  values of the compounds represented by the reaction with condensate. On Table 1, the calculated values of  $\theta_1/\theta_2$  for propylene, ethylene, *n*-butane, and ethane are compared with their respective experimental values. By inspection of Table 1 it is confirmed that Eq. (51) is very accurate.

$$\frac{\theta_1}{\theta_2} = \left[ \frac{c_{p,F}(T_1) + 4.76 c_{p,ar}(T_1)}{c_{p,F}(T_2) + 4.76 c_{p,ar}(T_2)} \right]^\lambda \quad (51)$$

$$\lambda = \frac{T_2 - T_1}{T_2} \quad (52)$$

In Eq. (50) and (51), the heat capacities correspond to the initial temperatures ( $T_1$  or  $T_2$ ), while, the temperatures in Eq. (52) must be in Kelvin. Once  $T_{UFL2}$  has been estimated, the calculation procedure described in Section 3.3 is applied, not considering the sensible enthalpies of the fuels.

**Table 1**

Comparison between  $\theta_1/\theta_2$  values obtained with experimental data  $\left[ \left( \theta_1/\theta_2 \right)_{\text{exp}} \right]$  and those obtained with Eq. (51)  $\left[ \left( \theta_1/\theta_2 \right)_{\text{Calc}} \right]$ .

$T_1$ (°C)	Propylene			Ethylene			n-Butane			Ethane		
	$\left( \theta_1/\theta_2 \right)_{\text{exp}}$	$\left( \theta_1/\theta_2 \right)_{\text{Calc}}$	ARE (%)	$\left( \theta_1/\theta_2 \right)_{\text{exp}}$	$\left( \theta_1/\theta_2 \right)_{\text{Calc}}$	ARE (%)	$\left( \theta_1/\theta_2 \right)_{\text{exp}}$	$\left( \theta_1/\theta_2 \right)_{\text{Calc}}$	ARE (%)	$\left( \theta_1/\theta_2 \right)_{\text{exp}}$	$\left( \theta_1/\theta_2 \right)_{\text{Calc}}$	ARE (%)
5	1.016	1.001	1.50	1.000	1.000	0.04	–	–	–	–	–	–
20	1.000	1.000	0.00	1.000	1.000	0.00	–	–	–	–	–	–
35	0.984	0.999	1.54	1.001	1.000	0.12	–	–	–	–	–	–
50	0.996	0.998	0.21	0.999	0.999	0.09	–	–	–	–	–	–
75	0.991	0.994	0.29	0.997	0.996	0.15	–	–	–	–	–	–
100	0.978	0.989	1.14	0.991	0.992	0.09	–	–	–	–	–	–
20	1.000	1.000	0.00	1.000	1.000	0.00	1.000	1.000	0.00	1.000	1.000	0.00
100	0.979	0.989	1.03	0.991	0.992	0.06	0.978	0.985	0.70	0.998	0.989	0.98
200	0.986	0.968	1.82	0.970	0.976	0.58	0.961	0.958	0.31	0.970	0.969	0.11
250	0.981	0.958	2.41	0.969 <sup>a</sup>	0.969 <sup>a</sup>	0.01 <sup>a</sup>	0.954	0.945	0.88	0.958	0.959	0.17
AARE (%)		0.99		0.11		0.47		0.32				

<sup>a</sup> These values correspond to an initial temperature of 260 °C.

**Table 2**

Moles of oxygen needed to convert all carbon to CO and moles of oxygen available at the known UFL.

Fuel	Formula	CAS#	$(v_{\text{ar}})_{\text{CO}}$	$(v_{\text{ar}})_{\text{UFL1}}$	$O_2^{\text{ex}}$ (%)	Selected Eq.
Methane	CH <sub>4</sub>	74-82-8	0.50	1.13	[22] 126.00	Eq. (50)
Propane	C <sub>3</sub> H <sub>8</sub>	74-98-6	1.50	1.13	[23] 126.00	Eq. (50)
				1.85	[24] 23.33	
Propylene	C <sub>3</sub> H <sub>6</sub>	115-07-1	1.50	1.83	[22] 22.00	Eq. (51)
				1.47	[24] -2.00	
iso-Butane	C <sub>4</sub> H <sub>10</sub>	75-28-5	2.00	2.45	[22] 22.50	Eq. (50)
n-Butane	C <sub>4</sub> H <sub>10</sub>	106-97-8	2.00	2.00	[24] 0.07	Eq. (51)
Ethylene	C <sub>2</sub> H <sub>4</sub>	74-85-1	1.00	0.48	[22] -52.00	Eq. (51)
				0.39	[24] -61.00	
Ethane	C <sub>2</sub> H <sub>6</sub>	74-84-0	1.00	1.06	[24] 6.00	Eq. (51)

The calculated value of  $\theta_1/\theta_2$  decreases faster when calculated with Eq. (50) than when calculated with Eq. (51). Now the choice of Eq. (50) or (51) must be established. This is related to the global reaction that can represent the process for a particular compound. For example, for methane, only the global reaction without condensate produces realistic values; on the other hand, for ethylene, only the reaction with condensate produces realistic values. Considering the moles of oxygen needed to convert all the carbon to carbon monoxide  $(v_{\text{ar}})_{\text{CO}}$  and the moles of oxygen available at the known UFL  $(v_{\text{ar}})_{\text{UFL1}}$ , the percentage of excess oxygen ( $O_2^{\text{ex}}$ ) is determined as shown in Eq. (53).

$$O_2^{\text{ex}} = \frac{(v_{\text{ar}})_{\text{UFL1}} - (v_{\text{ar}})_{\text{CO}}}{(v_{\text{ar}})_{\text{CO}}} 100\% \quad (53)$$

Table 2 shows the values of  $O_2^{\text{ex}}$  and the equations selected to determine  $\theta_1/\theta_2$  for the experimental results of Kondo et al. [22], Vanderstraeten et al. [23] and Van Den Schoor [24]. The case of ethane may need further explanation: oxygen excess was 6.32% and both equations were tested. It was found that Eq. (51) more accurately estimated the value of  $\theta_1/\theta_2$ . Assuming that the formation processes take place at 298.15 K for liberated heat: when CO is formed instead of CO<sub>2</sub>, there is a difference of -282.995 kJ/mol, while, when C as graphite is formed instead of CO, there is a difference of -110.527 kJ/mol. This affects the value of  $T_{\text{UFL}}$ , which affects the value of  $\theta$ , as can be inferred from Eqs. (37)–(45). For higher initial temperatures, the value of  $\theta_1/\theta_2$  decreases faster for the reaction without condensate than for the reaction with condensate. Therefore, when the process is represented by the reaction without condensate, Eq. (50) is used. For the other case Eq. (51) is used.

## 6. Results and discussion

When estimating the UFL of pure C–H compounds in air at atmospheric pressure, the correlation set (62 compounds) had an AARE of 7.93%, while the prediction set (53 compounds) had an AARE of 6.49%. The squared correlation coefficients were 0.9158 and 0.9045 for the correlation and prediction sets, respectively. For the total set, the AARE was 7.27% and the squared correlation coefficient was 0.9247.

On Table 3, the results obtained with the model developed in this study are compared to results obtained by other models. The AAREs on Table 3 show that the model developed in this study is accurate. The squared correlation coefficients lead to the same conclusion. The results of relevant calculations (including UFLs) performed for the correlation and test sets are presented on Tables S.1 and S.2 in the Supplementary material.

When the method developed in this study was applied, the deviations were within the experimental error. Experimental procedures will sometimes produce different results. A description of experimental procedures can be found in works by Coronado et al. [26,27].

To clarify this statement, the determination of the UFL of pure C–H compounds in air at 1 atm is again considered. Table 4 lists the compounds which had AREs above 20%, while Table 5 shows some compounds for which different experimental UFL values have been reported. The model developed in section 3 was applied to 115 compounds. Seven of them had AREs above 20%. In other words, 93.91% of the total set had AREs below 20%. Table 5 shows some experimental values which have differences of more than 20%.

Ethylene is interesting because a UFL of 36% is reported by Zabetakis [13]. This UFL probably corresponds to the propagation of cool flames. Craven and Foster [34] have compiled different values of the UFL of ethylene. Among these values, a UFL of about 17% was reported. This UFL probably corresponds to the propagation of

**Table 3**

Comparison of results obtained by the model developed for this study with those obtained by other models.

Model	Total set	Training set	Test set	AARE (%)	R <sup>2</sup>	Type of compound
This work	115	62 (53.91%)	53 (46.09%)	7.27	0.9248	C–H
Garagheizi [1]	865	693 (80.11%)	172 (19.89%)	9.52	0.9002	Various
Lazzús [2]	418	328 (78.47%)	90 (21.53%)	7.10	0.9818	Various
Albahri [4]	477	464 (97.28%)	13 (2.72%)	11.80	0.9600	C–H
Seaton [5]	141	–	–	9.68	0.8862	Various

**Table 4**

Group of C–H compounds for which ARE was above 20%.

Compound	Formula	CAS #	UFL-exp (%)	UFL-calc (%)	ARE (%)
1,2,3,4-Tetrahydronaphthalene	C <sub>10</sub> H <sub>12</sub>	119-64-2	5.00	6.38	27.60
<i>m</i> -Terphenyl	C <sub>18</sub> H <sub>14</sub>	92-06-8	3.70	4.60	24.32
<i>a</i> -Methyl styrene	C <sub>9</sub> H <sub>10</sub>	98-83-9	6.10	7.40	21.31
Styrene	C <sub>8</sub> H <sub>8</sub>	100-42-5	6.10	8.51	39.51
Ethylene	C <sub>2</sub> H <sub>4</sub>	74-85-1	36.00	14.43	59.92
Pinane	C <sub>10</sub> H <sub>18</sub>	473-55-2	7.20	5.60	22.22
<i>o</i> -Terphenyl	C <sub>18</sub> H <sub>14</sub>	84-15-1	3.80	4.59	20.79

**Table 5**

Some compounds for which different values of UFL have been reported.

Compound	Formula	CAS#	UFL-Exp (%)	Diff (%)
Amylene	C <sub>5</sub> H <sub>10</sub>	513-35-9	9.00 [14]	7.70 [28] 14.44
Butadiene(1,3)	C <sub>4</sub> H <sub>6</sub>	106-99-0	11.50 [14]	16.30 [29] 29.45
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	110-82-7	7.80 [13]	8.40 [30] 7.14
Decahydronaphthalene	C <sub>10</sub> H <sub>18</sub>	91-17-8	4.90 [2]	5.40 [31] 9.26
2,3-Dimethyl pentane	C <sub>7</sub> H <sub>16</sub>	565-59-3	7.00 [14]	6.70 [15] 4.29
1,3-Cyclopentadiene	C <sub>5</sub> H <sub>6</sub>	542-92-7	7.60 [32]	14.60 [33] 47.95
<i>n</i> -Nonane	C <sub>9</sub> H <sub>20</sub>	111-84-2	2.90 [15]	5.6 [2] 48.21
Ethylene	C <sub>2</sub> H <sub>4</sub>	74-85-1	36.00 [13]	32.30 [2] 10.28
				17.00 [34] 52.78

**Table 6**

Calculated and experimental UFLs of binary mixtures of C–H compounds.

Mixture	UFL-calc	UFL-exp	ARE (%)
50% CH <sub>4</sub> + 50% C <sub>3</sub> H <sub>8</sub>	12.91	12.10 [19]	6.69
75% CH <sub>4</sub> + 25% C <sub>3</sub> H <sub>8</sub>	14.19	13.50 [19]	5.11
50% CH <sub>4</sub> + 50% C <sub>3</sub> H <sub>6</sub>	13.05	12.60 [19]	3.57
75% CH <sub>4</sub> + 25% C <sub>3</sub> H <sub>6</sub>	14.26	13.80 [19]	3.33
50% C <sub>3</sub> H <sub>8</sub> + 50% C <sub>3</sub> H <sub>6</sub>	10.83	10.50 [19]	3.14
25% C <sub>3</sub> H <sub>8</sub> + 75% C <sub>3</sub> H <sub>6</sub>	10.28	10.50 [19]	2.10
20% C <sub>3</sub> H <sub>8</sub> + 80% C <sub>4</sub> H <sub>10</sub> <sup>a</sup>	8.91	8.20 [20]	8.66
40% C <sub>3</sub> H <sub>8</sub> + 60% C <sub>4</sub> H <sub>10</sub> <sup>a</sup>	9.25	8.60 [20]	7.56
60% C <sub>3</sub> H <sub>8</sub> + 40% C <sub>4</sub> H <sub>10</sub> <sup>a</sup>	9.62	9.00 [20]	6.89
80% C <sub>3</sub> H <sub>8</sub> + 20% C <sub>4</sub> H <sub>10</sub> <sup>a</sup>	10.02	9.40 [20]	6.60
25% CH <sub>4</sub> + 75% C <sub>4</sub> H <sub>10</sub> <sup>b</sup>	9.91	9.48 [21]	4.54
50% CH <sub>4</sub> + 50% C <sub>4</sub> H <sub>10</sub> <sup>b</sup>	11.58	10.83 [21]	6.93
75% CH <sub>4</sub> + 25% C <sub>4</sub> H <sub>10</sub> <sup>b</sup>	13.60	12.71 [21]	7.00
		AARE (%)	5.55

<sup>a</sup> iso-Butane.<sup>b</sup> *n*-Butane.

normal flames. As shown on Table 4, the UFL calculated for ethylene is 14.43%. Therefore, it can be inferred that the model works better for normal flame propagation. Since the experimental data used to obtain the correlation for  $\theta$  correspond to the propagation of normal flames, it makes sense that the model predicts the UFLs accordingly. Furthermore, a correlation obtained from experimental data that corresponds to the propagation of cool flames can be used to determine the UFLs for such cases. For ethylene, the  $\theta$  value at a UFL of 36% is 2.1209, while at a UFL of 17%, it is 1.7644. The correlation gives a value of 1.7399.

Table 6 shows the results obtained by applying the model to binary mixtures of C–H compounds. The calculated UFL values are compared with experimental data from published articles [19–21]. An AARE of 5.55% was found for a set of 13 binary mixtures. The maximum average relative error (ARE) was 8.66% and the minimum

**Table 7**

Values obtained for AARE, maximum ARE, and minimum ARE for the initial temperature dependence.

Compound	AARE (%)	ARE-max (%)	ARE-min (%)
Methane	1.34	4.38	0.25
Ethane	1.70	4.06	0.43
Propane	3.61	10.98	0.15
iso-Butane	4.77	7.84	0.38
<i>n</i> -Butane	2.32	3.17	1.04
Ethylene	0.53	2.07	0.02
Propylene	2.87	8.30	0.19

was 2.10%. Therefore, the model agrees well with experimental data for binary mixtures of C–H compounds.

The results obtained for the estimation of UFLs at different initial temperatures are shown in Figs. 2–4. Table 7 also shows the AAREs, the maximum ARE, and the minimum ARE obtained for the compounds studied. The results show that the method accurately determines the UFL of C–H compounds at different initial temperatures.

In Fig. 1, the theta ratio values ( $\theta_1/\theta_2$ ) calculated from the experimental data show that when assuming  $\theta_1/\theta_2 < 1$ , the experimental behavior is accurately forecast. The other case ( $\theta_1/\theta_2 \geq 1$ ) implies that at any  $T_2 > T_1$ , the adiabatic flame temperature would be  $T_{UFL2} > T_{UFL1}$ . However, when assuming  $\theta_1/\theta_2 < 1$ , such cases can also be represented ( $T_{UFL2} > T_{UFL1}$ ). For example, consider the experimental data for ethylene and propylene presented by Van Den Schoor [24]. The results for the estimated adiabatic flame temperatures at the UFL ( $T_{UFL-calc}$ ) determined by using Eqs. (51) and (36) along with  $T_{UFL-exp}$  and the ratios  $(\theta_1/\theta_2)_{exp}$  calculated from the experimental values of the UFL are shown on Table 8. For these two compounds,  $\theta_1$  and  $T_{UFL1}$  determined with the UFL at 20 °C are always lower than  $\theta_2$  and  $T_{UFL2}$  determined at higher initial tem-



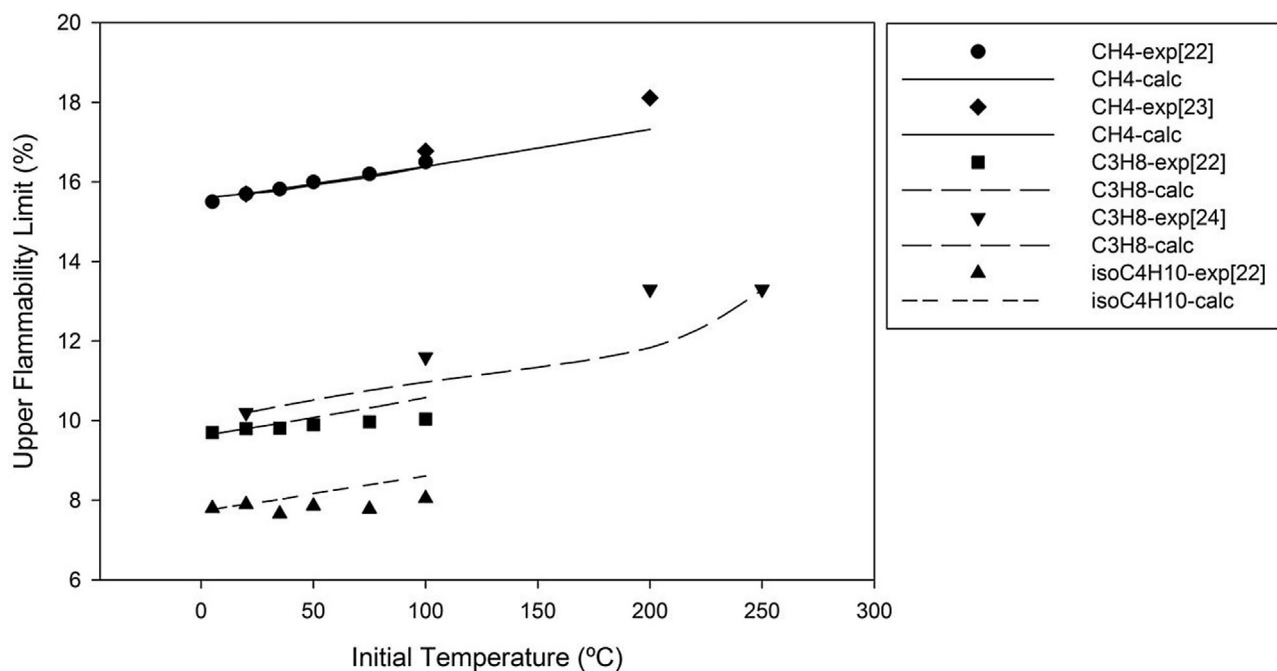


Fig. 2. Comparison of estimated and experimental UFLs of methane, propane, and iso-butane at different initial temperatures.

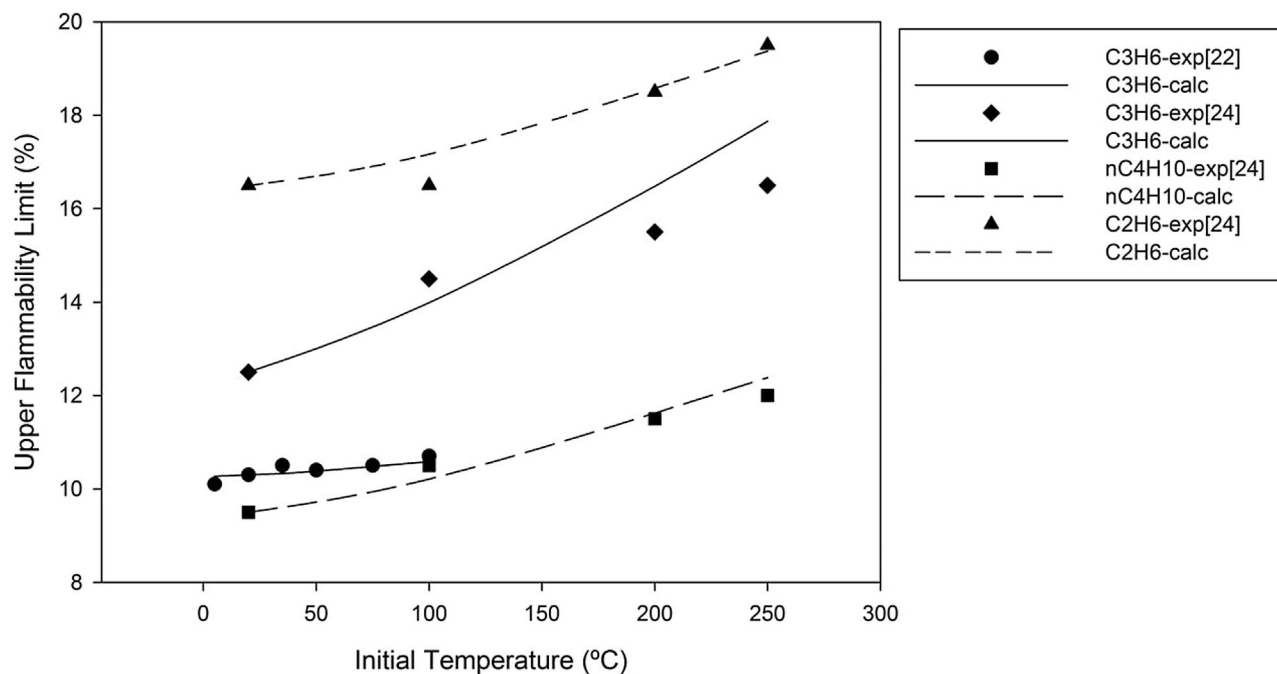


Fig. 3. Comparison of estimated and experimental UFLs of propylene, *n*-butane, and ethane at different initial temperatures.

peratures. This can be closely estimated by assuming  $\theta_1/\theta_2 < 1$ , calculating the value with Eq. (51), and finally determining  $T_{UFL2}$  with Eq. (36).

## 7. Conclusions

A semi-empirical equilibrium method for estimating the upper flammability limits of C–H compounds was developed. A correlation set of 62 compounds and a prediction set of 53 compounds

were considered. The squared correlation coefficient for the total set was 0.9248, while the average absolute relative error was 7.27%.

The method was used to estimate the UFL of binary mixtures of C–H compounds. The model was accurate, with an average absolute relative error of 5.55%.

The influence of the initial temperature on the UFL value was analyzed and a procedure to estimate the UFLs was developed. The results were satisfactory; the average absolute relative error was 2.19%.

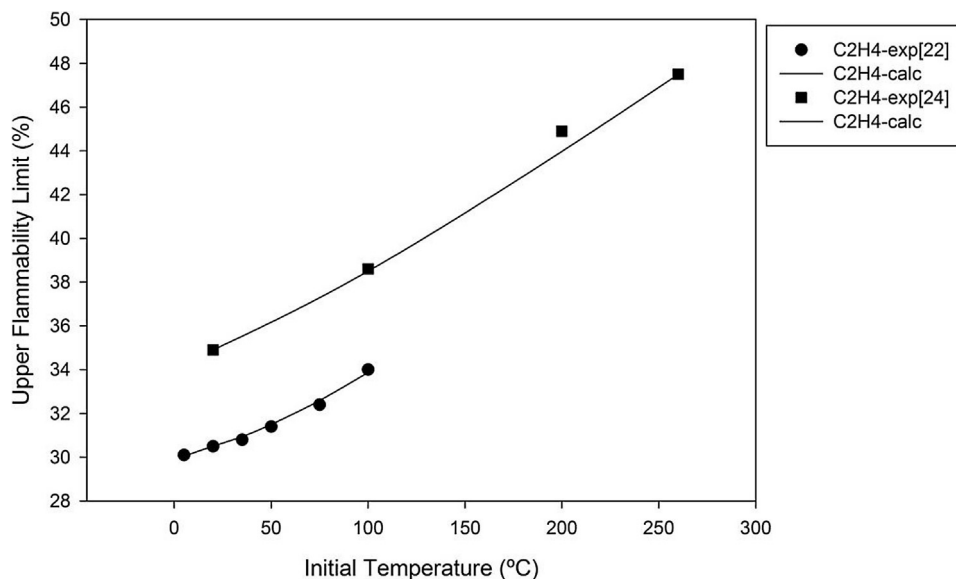


Fig. 4. Comparison of estimated and experimental UFLs of ethylene at different initial temperatures.

Table 8

Comparison between adiabatic flame temperatures determined using experimental UFLs for ethylene and propylene [24] and adiabatic flame temperatures estimated using Eqs. (51) and (36).

T (°C)	UFL-exp (%)	$T_{UFL-exp}(K)$	$(\theta_1/\theta_2)_{exp}$	$T_{UFL-calc}(K)$
Ethylene [24]				
20	34.90	1216.1	1.000	1216.1
100	38.60	1229.7	0.991	1230.4
200	44.90	1240.2	0.970	1247.4
260	47.50	1259.7	0.969	1259.8
Propylene [24]				
20	12.50	1264.6	1.000	1264.6
100	14.50	1266.4	0.979	1279.4
200	15.50	1312.4	0.986	1288.5
250	16.50	1325.0	0.981	1293.1

## 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.2015.11.008>.

## References

- [1] F. Gharagheizi, J. Hazard. Mater. 167 (2009) 507–510.
- [2] J.A. Lazzús, Thermochim. Acta 512 (2011) 150–156.
- [3] T. Ma, Q. Wang, M.D. Larrañaga, Fire Saf. J. 56 (2013) 9–19.
- [4] T.A. Albahri, Chem. Eng. Sci. 58 (2003) 3629–3641.
- [5] W.H. Seaton, J. Hazard. Mater. 27 (1991) 169–185.
- [6] A.Z. Mendiburu, J.A. Carvalho, C.R. Coronado, J. Hazard. Mater. 285 (2015) 409–418.
- [7] M. Vidal, W. Wong, W.J. Rogers, M.S. Mannan, J. Hazard. Mater. 130 (2006) 21–27.
- [8] F. Zhao, W.J. Rogers, M.S. Mannan, J. Hazard. Mater. 174 (2010) 416–423.
- [9] T. Ma, Fire Saf. J. 46 (2011) 558–567.
- [10] Y.N. Shebeko, W. Fan, I.A. Bolodian, V.Y. Navzenya, Fire Saf. J. 37 (2002) 549–568.
- [11] A. Di Benedetto, Chem. Eng. Sci. 99 (2013) 265–273.
- [12] I. Glassman, R.A. Yetter, Combustion, fourth ed, Elsevier, New York, 2008.
- [13] M.G. Zabetakis, Flammability characteristics of combustibles gases and vapors, Bur. Mines Bull. 627 (1965).
- [14] P. Carson, C. Mumford, Hazardous Chemicals Handbook, second ed, Butterworth Heinemann, New York, 2002.
- [15] R. Joyce, B.C. McKusick, Health and safety information, in: D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 2005, pp. 2462–2519.
- [16] CASLAB Web Database <http://www.caslab.com/Chemical-Search> (accessed 20.10.14.).
- [17] NIST Chemistry Web Book <http://webbook.nist.gov/chemistry> (accessed 20.10.14.).
- [18] B.J. McBride, M.J. Zehe, S. Gordon, NASA Glenn coefficients for calculating thermodynamic properties of individual species, NASA/TP-2002-211556, 2002.
- [19] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, A. Sekiya, J. Hazard. Mater. 155 (2008) 440–448.
- [20] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, A. Sekiya, J. Hazard. Mater. 148 (2007) 640–647.
- [21] F. Zhao, W.J. Rogers, M.S. Mannan, Process Saf. Environ. Prot. 87 (2009) 94–104.
- [22] S. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, J. Hazard. Mater. 187 (2011) 585–590.
- [23] B. Vanderstraeten, D. Tuerlinckx, J. Berghmans, S. Vliegen, E. Van't Oost, B. Smit, J. Hazard. Mater. 56 (1997) 237–246.
- [24] F. Van Den Schoor, Influence of pressure and temperature on flammability limits of combustible gases in air (2007) Thesis. <<https://lirias.kuleuven.be/bitstream/1979/870/1/thesis.pdf>>.
- [25] H.F. Coward, G.W. Jones, Limits of flammability of gases and vapors, Bur. Mines Bull. 503 (1952).
- [26] C.R. Coronado, J.A. Carvalho Jr., J.C. Andrade, E.V. Cortez, F.S. Carvalho, J.C. Santos, A.Z. Mendiburu, J. Hazard. Mater. 241 (2012) 42–54.
- [27] C.R. Coronado, J.A. Carvalho Jr., J.C. Andrade, A.Z. Mendiburu, E.V. Cortez, F.S. Carvalho, B. Gonçalves, J.C. Quintero, E.I. Gutiérrez Velásquez, M.H. Silva, J.C. Santos, M.A.R. Nascimento, J. Hazard. Mater. 280 (2014) 174–184.
- [28] TCI America <https://www.spectrumchemical.com/MSDS/TCI-M0708.pdf> (accessed: 26.02.15.).
- [29] BOC. <https://www.boconline.co.uk/internet.lg.lg.gbr/en/images/butadiene-13410.55533.pdf> (accessed: 26.02.15.).
- [30] MEGS <http://www.megs.ca/MSDS/Pdf/Cyclohexane.PDF> (accessed: 15.02.15.).
- [31] CAMEO Chemical <http://cameochemicals.noaa.gov/chemical/504> (accessed: 25.02.15.).
- [32] B.E. Poling, G.H. Thomson, D.G. Friend, R.L. Rowley, W.V. Wilding, Perry's Chemical Engineers Handbook, in: J.O. Maloney (Ed.), 8th ed., McGraw-Hill, USA, 2008, p. 517.
- [33] D. Hönicke, R. Födisch, P. Claus, M. Olson, Cyclopentadiene and Cyclopentene, Ullmans Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2011.
- [34] A.D. Craven, M.G. Foster, Combust. Flames 10 (1966) 95–100.