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

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ABSTRACT

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

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

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

1. Introduction

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

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

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

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

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

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

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Abbreviations

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

Symbols

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

Subscripts

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

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

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

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

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

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

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

i) The lower flammability limit (LFL) decreases with the increase of the initial mixture temperature. That is, the ratio n_{ar}/n_F increases in value.
ii) The upper flammability limit (UFL) increases with the increase of the initial mixture temperature. In other words, the ratio n_{ar}/n_F decreases in value.
iii) The flammability limits vary linearly with the increase of the mixture initial temperature. The slope of the function is negative for the LFL and positive for the UFL. Eq. (2) represents this behavior:

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

3. The modified Burgess − Wheeler Law

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

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

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

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

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