

Limiting Oxygen Concentration and Minimum Inert Concentration of Fuel-air-inert Gaseous Mixtures Evaluation by means of Adiabatic Flame Temperatures and Measured Fuel-air Lower Flammability Limits

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The present paper aims to re-examine the validity of the linear correlation found between AFT^{LOC} , the adiabatic flame temperature at the apex of the flammability range of fuel-air-inert mixtures (where LOC, the Limiting Oxygen Concentration, is measured) and AFT^{LFL} , the adiabatic flame temperature at the lower flammability limit of fuel-air mixtures (LFL). New sets of experimental measurements of LFL and LOC referring to fuel-air mixtures diluted with N_2 , CO_2 , and $H_2O(vap)$ from trusted literature sources form a comprehensive database for such evaluation. Both the slope and intercept of correlations $AFT^{LOC} = a + b \cdot AFT^{LFL}$ are dependent on the nature of inert gas and on initial temperature. Based on the linear correlation between AFT^{LOC} and AFT^{LFL} , a procedure for calculation of LOC and MIC (Minimum Inert Concentration) of fuel-air-inert mixtures is presented, using measured or calculated LFL of fuel-air mixtures and their corresponding AFT. The method predicts with reasonable accuracy LOC and MIC of fuel-air-inert mixtures (relative deviations ranging between -14 and +17% when calculated and measured LOC and MIC for fuel-air-nitrogen and fuel-air-carbon dioxide at ambient initial conditions are examined).

Keywords: fuel, limiting oxygen concentration, minimum inert concentration, adiabatic flame temperature, flammability limit

The explosion limits of a fuel-oxidizer mixture are the boundaries of fuel concentration range where a locally ignited explosion (by a spark, a hot body, a pilot flame or other energy sources) can propagate in the entire amount of explosive mixture [1]. In such cases, the flame is self-sustained i.e. the evolved heat from each layer of burnt gas allows ignition of fresh gas adjacent layer. For deflagrations (explosions propagating with subsonic speeds) the flammability limits are defined: the lower flammability limit (LFL) characteristic to fuel-oxidizer systems with lean fuel amounts (fuel deficit) and the upper flammability limit (UFL) characteristic to fuel-oxidizer systems with rich fuel amounts (oxygen deficit). The flammability limits are influenced by several factors such as: the initial temperature and pressure, the presence of inert additives, the direction of flame propagation, the ignition energy, the volume and shape of the vessel [2]. Among properties characteristic of ignition stage, the flammability limits are very important; they range within primary flammability parameters, essential for safety recommendations in all domains of activity where flammable fuel-air mixtures can be formed.

The most important method to mitigate an explosion is the addition of an inert gas to the fuel-oxidizer mixture. Addition of increasing amounts of an inert gas to a flammable mixture determines the increase of the lower explosion limit and the decrease of the upper explosion limit until their values coincide and the apex of the flammability range is reached. In a fuel-oxidizer-inert mixture, the maximum oxygen concentration for which an explosion can not occur (regardless of the fuel or inert concentration) is named Limiting Oxygen Concentration

(LOC) [1]. In addition to LOC, the Minimum Inert Concentration (MIC) is defined as the minimum inert concentration that achieves a total inertization of fuel-oxidizer-inert mixture, regardless of fuel or oxidizer concentration [1]. Usually, nitrogen or carbon dioxide are used as inert additives, but argon, water vapor or exhaust gas (a mixture of N_2 , CO_2 and H_2O) are used too. The inertization effect is stronger when the inert gas has a higher heat capacity and/or the possibility to dissociate. In this respect, the aliphatic halogenated derivatives have a strong inertization action on flames. They can remove the gaseous mixtures outside of the explosion limits, even at concentrations of few percents. Their influence is explained by the ease with which these compounds generate, at high temperatures, halogen atoms which interrupt the chain of oxidation reaction. Their use is not recommended nowadays because of their high polluting action.

A key parameter for characterizing fuel-air mixtures is the Adiabatic Flame Temperature (AFT), defined as the maximum temperature reached in a flame, in the absence of energy losses. Many authors considered AFT as constant along the flammability range, no matter the amount of inert additive in the mixture [3-10]. Various threshold values of AFT^{LFL} have been set by different authors: 1860-1820 K [3], 1600 K [6], 1400 K [7], 1200 K [5], even 1000 K [4]. This criterion was extended to upper explosion limits as well, after a reexamination of adiabatic flame temperatures by including the soot among the combustion products [5]. Obviously, the criterion of constant CAFT was maintained over the entire explosion range, including also the apex of the explosion range. Other authors [11] introduced the concept of fuel-dependent threshold AFT^{LFL} : 1440 K (for

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hydrocarbons); 1505 K (for oxygenated compounds) and 1580 K (for halogenated compounds); the concept was used later by Zlochower [9] to predict LFL and UFL dependencies of several fuels on temperature.

From many studies it is seen, however, that AFT of limit mixtures vary in large limits over the whole flammability range [4, 7, 12], so that the mapping of this range and the determination of its extreme point (characterized by LOC and MIC) must rely upon other characteristic parameters, e.g., the normal burning velocity. In this respect, the choice of a limit (threshold) value for the normal burning velocity in limit fuel-air and fuel-air-inert mixtures might offer an alternative criterion for flammability limit prediction [2, 13, 14].

Predictions of inert addition influence on LFL and UFL were issued in many other contributions [15-24], with various degrees of accuracy. Their results are generally delivered as fuel concentrations and do not include predicted values of LOC and/or MIC, since no examination of the equivalence ratio at the apex of the flammability range is done. Indeed, in most papers it was assumed that the apex of the flammability range is observed always at the stoichiometric composition of fuel-air mixtures for complete combustion to CO₂ and H₂O. Examination of a set of trusted data from Coward and Jones [25] by Britton [15] revealed that LOC of hydrocarbon-air-inert mixtures is found at a fuel equivalence ratio between 1.0 and 1.5, increasing with the number of carbon atoms. Other fuels displayed similar behavior.

According to a suggestion from Lewis and von Elbe [26], Britton assigned the difference between optimum and stoichiometric fuel concentrations to differences between the diffusivities in air of fuel versus oxygen.

Using the assumption of constant heat of combustion per mole of lower flammability limit mixture, Kondo predicted the fuel concentration for the whole flammability range of fuel-air mixtures diluted with N₂ and CO₂ and found a fair agreement of predicted limits with their measurements [17-19] made with ASTM method. From the analysis of heat balance during flame propagation, other predictions of fuel concentration in fuel-air and fuel-air-inert mixtures have been made [7-9, 10, 21, 24]. The additional hypothesis of thermal radiation loss has led to predictions of fuel concentration in limit mixtures in better agreement with experimental data, both at ambient and elevated initial temperatures, excepting however the region approaching LOC, where the assumption of complete fuel combustion fails [10].

Empirical approaches found a wide application in LOC prediction. Britton [11, 15] assumed LOC is inversely proportional to the square of net heat of oxidation and enlisted the constants for hydrocarbons and other CHON fuels:

$$LOC = \frac{ct}{(\Delta H_c / S)^2} \quad (1)$$

where *S* is the ratio of oxygen-to-fuel, as written in the stoichiometric equation of combustion. Another simple equation, equivalent to eq. (2) was used by Britton [15] and tested (with poor predictive results) by Hansen and Crowl for fuel-air-N₂ mixtures [8]:

$$LOC(\text{fuel}) = S \cdot LFL(\text{fuel}) \quad (2)$$

Indeed, eq. (3) has the disadvantage that any error in LFL is multiplied by *S* in estimating LOC. Hansen and Crowl proposed instead another method for LOC calculation in

fuel-air-diluent mixtures by approximating the boundaries of the flammability range with linear equations that are functions on fuel and oxygen concentrations at the upper and the lower flammability limits of fuel in air [8]. Their method was based on data from Lewis and von Elbe [26], extracted from Coward and Jones [25].

Predicted MIC of some fuel-air mixtures diluted with N₂, CO₂ and He/Ar were given by Bade Shrestha et al. [22] using experimental LFL and UFL of fuel-air mixtures and assuming that in each limit mixture, the fuel concentration has a threshold value allowing flame propagation. The authors extended their approach to fuel-air-inert mixtures at elevated initial temperatures up to 400°C and found a satisfactory agreement with experimental MIC (relative deviations between 1 and 9%, for hydrocarbon-air mixtures).

Another method for LOC prediction is based on group (increment) contribution of various fuels to consumed oxygen, in limit fuel-air-inert mixtures [16, 27]. Subramanian and Cangelosi used this procedure for various fuels (H₂, CO, hydrocarbons, alcohols) and enlisted group contributions after its validation against US Bureau of Mines collection of data, compiled by Zabetakis [28]. Fuβ, Molnar, Schröder and Schönbacher [16] issued a set of corrected group contributions, obtained by validation against LOC from CHEMSAFE database [29]. Their newer data were measured according the European Standard EN 1839 and are more conservative in respect to earlier data, obtained with U.S. Bureau of Mines method [25, 28].

Examination of published flammability data (LFL, UFL, LOC and MIC) is difficult considering the variety of experimental conditions and criteria to determine the limit concentration, especially in the vicinity of the flammability range apex. In fact, Zlochower and Green consider the international flammability databases as „incompatible” [21], since the current standard adopted by the European union is „a radical departure” from US standards.

An original method of calculating the limiting oxygen concentration of fuel-air-inert mixtures was recently developed, using LFL, the lower flammability limit, and the adiabatic flame temperatures (AFT) of fuel-air and fuel-air-inert limit mixtures. The method is based on the linear correlation between AFT of fuel-air-inert mixtures at the apex of the flammability range (AFT^{LOC}) and AFT of fuel-air mixtures at the lower flammability limit (AFT^{LFL}), found for systems diluted with nitrogen [12], carbon dioxide or water (vap.) [30] at ambient and at elevated initial temperatures. The examined data have been extracted from few sources: Zabetakis [28] and CHEMSAFE Database [29], where results of measurements with the German standard DIN 51649 and the European Union standard EN 1839 have been included.

The present paper aims to re-examine the validity of this correlation by including new sets of experimental measurements of LFL and LOC [5, 17-20, 31-34] at ambient initial pressure and various initial temperatures within 25–250°C. The adiabatic flame temperatures of limit mixtures have been computed with the program COSILAB by taking into account the dissociation of gases within the flame. The only requirement (restriction) of the proposed method is to examine pairwise the LFLs and LOCs obtained by means of a chosen set-up and measurement procedure. Based on the found correlation, the procedure for calculating LOC and MIC of fuel-air-inert mixtures is presented and the deviations of the predicted LOC and MIC from experimental data are examined, in comparison with predictions from other procedures.

LFL		LOC					Reference
[CH ₄] (vol%)	AFT (K)	[CH ₄] (vol%)	LOC (vol%)	MIC (vol%)	φ*	AFT (K)	
4.40	1357.1	5.25	10.65	43.9	0.986	1538.8	[31]
4.60	1398.8	5.30	11.00	42.2	0.964	1548.5	[29]
4.85	1450.3	6.00	11.60	40.1	1.034	1617.1	[5]
4.90	1460.5	5.25	11.63	39.2	0.903	1537.7	[18]
5.00	1480.8	6.60	12.00	36.2	1.100	1639.6	[28]

*the equivalence ratio is defined as $\phi = \frac{[fuel]/[O_2]}{([fuel]/[O_2])_{stoich}}$; the subscript "stoich" refers to

fuel-oxidant mixtures, where the fuel/oxygen ratio corresponds to the stoichiometric

combustion reaction, forming only CO₂ and H₂O.

Computing procedure

The adiabatic flame temperatures of fuel-air and fuel-inert mixtures were computed with 0-D COSILAB package [35], assuming chemical equilibrium is reached within the flame. 53 compounds were considered as combustion products. Their heat capacities, the standard enthalpies of formation at 298 K and the standard entropies at 298 K were calculated by means of NASA polynomials.

Results and discussions

Literature information on LFL, LOC and MIC is available in many papers [5, 15, 17-21, 24-26, 28-34]. Reported data were obtained mainly with standardized methods: the U.S. Bureau of Mines method [25, 28], ASTM E681 or ASTM E2079 method and their improved version issued by ASHRAE [17-19], German standard method DIN 51649 [16, 29-31], EN 1839 (European Standard) method [34]. Other methods delivered reliable data sets as well, as reported by Crawl and coworkers [5, 20] (a method using a 20 L spherical vessel with central ignition), by Zlochower and Green [21] (use of 20 L and even 120 L spherical vessels with central ignition) and by Hoppe and Jaeger [32] (Swiss method issued by ESCIS – the Expert Commission for Safety in the Swiss Chemical Industry 1994 using a 20 L sphere).

Fuel	LFL		LOC				AFT (K)
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[Added N ₂] (vol.%)	φ	
CO	12.5	1393.3	15.0	6.0	56.4	1.250	1361.5
CH ₄	5.0	1480.8	6.6	12.0	36.2	1.100	1639.6
C ₂ H ₆	3.0	1533.6	3.6	11.2	43.0	1.125	1554.7
C ₃ H ₈	2.1	1528.7	3.1	11.6	41.6	1.336	1489.9
n-C ₄ H ₁₀	1.8	1636.9	2.7	12.3	38.6	1.427	1494.3
n-C ₅ H ₁₂	1.4	1591.0	2.2	11.8	41.5	1.492	1429.7
n-C ₆ H ₁₄	1.2	1608.6	1.8	11.8	41.9	1.449	1445.9
C ₂ H ₄	2.7	1369.8	3.9	9.9	48.9	1.182	1524.2
C ₃ H ₆	2.4	1620.9	3.0	11.5	42.2	1.174	1629.5
n-C ₄ H ₈	1.6	1478.7	2.7	11.0	44.8	1.473	1443.1
i-C ₄ H ₈	1.8	1601.5	2.7	12.0	40.1	1.350	1575.6
1,3-C ₄ H ₆	2.0	1689.4	2.6	10.5	47.3	1.362	1524.5
C ₂ H ₂	2.6	1302.7	2.6	6.20	67.8	1.048	1268.5
C ₆ H ₆	1.3	1500.6	2.9	14.4	28.4	1.508	1697.2
CH ₃ OH	6.7	1561.1	8.2	9.70	45.7	1.268	1455.6
C ₂ H ₅ OH	3.30	1491.5	5.0	10.50	44.9	1.429	1399.2
(CH ₃) ₂ O	3.4	1565.5	4.0	10.5	46.0	1.143	1554.8
CH ₃ COCH ₃	2.6	1853.6	3.6	11.6	41.1	1.244	1749.4

Table 1
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR CH₄-AIR-N₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES – FROM LITERATURE

Many literature sources do not indicate the fuel concentration at the apex of the flammability range, necessary for calculation of the adiabatic flame temperature; therefore, valuable information from new publication such as NFPA 69 [33] could not be used in the present paper.

According to specific features of each method, the data are scattered between these literature sources. Even for the most studied fuel, methane, important deviations are observed between the composition of limit mixtures at the lower flammability limit and at the apex of the flammability range, as seen from table 1. In the examined data, LFLs vary between 4.4 and 5.0 vol.% and the corresponding adiabatic flame temperature varies between 1357 and 1481 K. The corresponding LOCs change from 10.65 to 12.00 vol.% and the MICs between 36.2 and 44.0 vol.%. The observed variations can be assigned to differences in ignition energy, amount of heat losses from the gas mixture to the surroundings, isobaric or isochoric conditions of testing, criteria used for ascertaining the explosion appearance, as discussed in recent papers [12, 21].

Other data sets referring to fuel-air-N₂ mixtures at ambient initial conditions are given in tables 2 and 3 where

Table 2
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-N₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES – FROM ZABETAKIS [28]

Fuel	LFL		LOC				
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[Added N ₂] (vol.%)	ϕ	AFT (K)
CH ₄	4.6	1398.8	5.3	11.0	42.2	0.964	1548.5
C ₂ H ₆	2.4	1319.5	2.7	8.7	55.8	1.086	1328.4
C ₃ H ₈	1.7	1326.8	2.4	9.3	53.2	1.290	1314.5
n-C ₄ H ₁₀	1.4	1383.2	2.0	9.6	52.2	1.354	1299.3
i-C ₄ H ₁₀	1.4	1383.2	1.8	10.3	49.1	1.136	1453.1
C ₂ H ₄	2.3	1228.9	2.6	7.6	61.1	1.026	1313.9
C ₃ H ₆	1.9	1382.6	2.6	9.3	53.0	1.258	1387.0
n-C ₄ H ₈	1.5	1415.6	2.2	9.7	51.5	1.361	1369.9
i-C ₄ H ₈	1.6	1478.7	2.0	10.6	47.4	1.132	1537.3
C ₂ H ₂	2.1	1126.8	3.7	6.2	66.7	1.492	1281.0

Table 3
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-N₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES - FROM CHEMSAFE DATABASE [34]

Fuel	LFL		LOC				
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[Added N ₂] (vol.%)	ϕ	AFT (K)
Besnard, 1996 [31]							
CH ₄	4.4	1357.1	5.3	10.7	43.9	0.986	1538.8
C ₂ H ₆	2.4	1319.5	3.0	9.3	52.8	1.118	1374.0
C ₃ H ₈	1.8	1378.4	2.6	10.1	49.5	1.293	1379.7
i-C ₄ H ₁₀	1.5	1480.7	2.0	10.7	46.9	1.239	1366.1
n-C ₄ H ₁₀	1.4	1416.0	2.6	12.1	39.5	1.371	1507.6
Mashuga and Crowl, 1999 [5]							
CH ₄	4.9	1450.3	6.0	11.6	38.7	1.034	1632.7
C ₂ H ₄	2.6	1342.0	3.0	9.3	52.6	0.968	1480.6
Kondo, 2007 [18]							
CH ₄	4.9	1460.5	5.6	11.3	40.5	0.992	1608.6
C ₃ H ₈	2.0	1494.3	2.6	10.5	47.6	1.220	1420.9
i-C ₄ H ₁₀	1.7	1562.9	2.2	11.1	44.6	1.283	1465.5
C ₂ H ₄	2.7	1383.7	3.2	8.6	56.0	1.122	1397.3
C ₃ H ₆	2.2	1508.5	2.9	10.5	46.9	1.219	1506.9
(CH ₃) ₂ O	3.3	1534.9	4.0	9.5	50.8	1.267	1418.1
Brooks and Crowl, 2007 [20]							
CH ₃ OH	6.7	1561.1	6.8	8.6	52.2	1.186	1369.7
C ₂ H ₅ OH	3.7	1608.3	3.8	9.8	49.5	1.163	1430.5
CH ₃ CN	4.4	1819.6	5.2	12.7	34.2	1.126	1766.5
C ₇ H ₈	1.2	1562.0	1.7	11.6	43.0	1.319	1549.7

Table 4
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-N₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES - FROM LITERATURE SOURCES

results taken from U.S. Bulletin of Mines no. 627 [28] edited by Zabetakis and from a recent version of the German database CHEMSAFE [34] are listed together with their computed adiabatic flame temperatures. Some of these data have been published earlier [12], but the corresponding AFT were computed with another software (ECHIMAD), based on thermodynamic input data from other sources. The present AFT, computed with the package COSILAB, are systematically lower by 10-12 K in comparison with previously reported values [12].

Additional data sets referring to fuel-air-N₂ mixtures at ambient initial conditions are given in table 4.

Data referring to the limit composition at the apex of the flammability range of any fuel differ strongly when results from tables 2, 3 and 4 are compared, in respect to both LOCs and MICs. It is worth mentioning that most fuel-air-N₂ at the apex of the flammability range are rich mixtures, having equivalence ratios ϕ between 1.10 and 1.40¹, in contradiction with the findings of other authors which indicated $\bar{\phi} = 1.00$ at LOC for all fuels [5, 16-19].

For the 45 data sets, we found an average equivalence ratio of limit mixtures $\bar{\phi} = 1.230$. It must be outlined that the present data referring to fuel-air-N₂ flammable mixtures include not only hydrocarbons, but also oxygenated compounds and a cyano-derivative, extracted from various sources [18, 20, 28].

In our previous contributions [12, 30], we examined the adiabatic flame temperatures of limit mixtures at LFL and LOC measured pairwise by various experimental techniques. For each added inert gas and initial temperature of limit fuel-air and fuel-air-inert mixtures, we found that AFT of limit mixtures are correlated by a linear relationship:

$$AFT^{LOC} = a + b \cdot AFT^{LFL} \quad (3)$$

where **a** and **b** are constants dependent on the inert gas and on the initial temperature of flammable mixtures.

The results describing 45 flammable fuel-air-N₂ mixtures at ambient initial conditions (data from tables 2, 3 and 4) are plotted in figure 1. Examination of these data sets

¹ The equivalence ratio of any fuel-oxygen(air) mixture $\phi = ([fuel]/[O_2])/([fuel]/[O_2])_{stoich}$ is defined as a function of fuel and oxygen concentrations in the "stoichiometric" mixture, where the fuel/oxygen ratio corresponds to the stoichiometric combustion reaction, forming only CO₂ and H₂O.

reveals that the linear correlation holds with a correlation coefficient $r = 0.655$ and a probability less than 0.001 that examined data are not linearly correlated:

$$AFT^{LOC} = (639.9 \pm 147.1) + (0.564 \pm 0.099) * AFT^{LFL} \quad (4)$$

where AFT are expressed in K.

The correlation is improved in comparison to previously reported data [12], as seen from a higher correlation coefficient and lower standard deviations of slope and intercept.

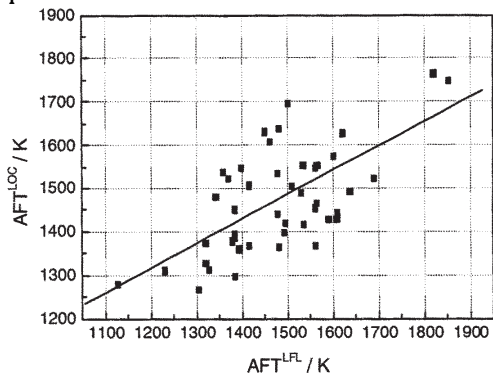


Fig. 1. Adiabatic flame temperatures of fuel-air-N₂ mixtures versus adiabatic flame temperatures of fuel-air mixtures at ambient initial pressure and temperature (45 data sets)

For fuel-air-CO₂ mixtures, the examined data from the two main reference sources (Zabetakis [28] and CHEMSAFE data base [34]) are given in tables 5 and 6. Other relevant results from literature are listed in table 7. These tables do not include the information on mixture composition at LFL and adiabatic flame temperatures AFT^{LFL}, already given in tables 2, 3 and 4. The corresponding adiabatic flame temperatures AFT^{LOC} vs. AFT^{LFL} are plotted in figure 2.

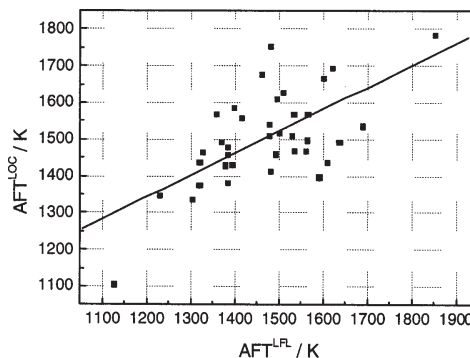


Fig. 2. Adiabatic flame temperatures of fuel-air-CO₂ mixtures versus adiabatic flame temperatures of fuel-air mixtures at ambient initial pressure and temperature (38 data sets)

Fuel	LOC				AFT (K)
	[Fuel] (vol.%)	[Oxygen] (vol.%)	[CO ₂] (vol.%)	φ	
CO	21.1	8.0	40.74	1.312	1428.8
CH ₄	7.4	14.6	22.96	1.013	1753.7
C ₂ H ₆	4.4	13.6	30.73	1.132	1568.2
C ₃ H ₈	3.9	14.3	27.89	1.362	1510.2
n-C ₄ H ₁₀	3.2	14.6	27.16	1.423	1492.1
n-C ₅ H ₁₂	2.9	14.5	27.93	1.603	1397.0
n-C ₆ H ₁₄	2.3	14.5	28.53	1.504	1437.8
C ₂ H ₄	4.5	11.8	39.21	1.140	1491.6
C ₃ H ₆	3.8	14.4	27.51	1.189	1693.5
n-C ₄ H ₈	3.2	13.8	30.97	1.392	1509.1
i-C ₄ H ₈	3.2	14.9	25.73	1.291	1665.2
1,3-C ₄ H ₆	3.3	13.1	34.21	1.390	1535.8
C ₂ H ₂	6.1	8.7	52.40	1.758	1335.3
C ₆ H ₆	2.9	14.4	28.41	1.508	1515.7
CH ₃ OH	10.3	12.0	32.46	1.287	1466.9
C ₂ H ₅ OH	6.1	13.3	30.46	1.377	1459.6
(CH ₃) ₂ O	5.4	13.2	31.64	1.228	1568.2
(CH ₃) ₂ CO	4.4	14.2	28.00	1.239	1784.9

Table 5
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-CO₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES - FROM ZABETAKIS [28]

Fuel	LOC				AFT (K)
	[Fuel] (vol.%)	[Oxygen] (vol.%)	[CO ₂] (vol.%)	φ	
CH ₄	6.4	14.0	26.8	0.914	1587.2
C ₂ H ₆	3.1	12.5	37.3	0.868	1375.2
C ₃ H ₈	2.8	12.6	37.1	1.111	1464.7
n-C ₄ H ₁₀	2.5	13.2	34.5	1.231	1457.6
i-C ₄ H ₁₀	2.6	12.8	36.3	1.320	1380.3
C ₂ H ₄	3.9	10.4	46.5	1.125	1345.6
C ₃ H ₆	3.4	12.5	37.0	1.224	1478.0
i-C ₄ H ₈	2.6	13.2	34.4	1.182	1540.2
C ₂ H ₂	7.0	6.3	63.0	2.777	1105.5

Table 6
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-CO₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES - FROM CHEMSAFE DATABASE [34]

Fuel	LOC				
	[Fuel] (vol.%)	[Oxygen] (vol.%)	[CO ₂] (vol.%)	φ	AFT (K)
Besnard, 1996 [31]					
CH ₄	6.3	13.8	27.9	0.918	1569.6
C ₂ H ₆	3.8	12.1	38.4	1.088	1437.7
C ₃ H ₈	3.2	12.8	35.7	1.238	1428.0
n-C ₄ H ₁₀	2.1	13.2	35.1	1.012	1558.6
i-C ₄ H ₁₀	3.0	13.7	31.7	1.423	1413.2
Kondo, 2007 [17]					
CH ₄	6.9	14.1	25.8	0.979	1676.0
C ₃ H ₈	3.3	13.4	33.0	1.236	1610.2
i-C ₄ H ₁₀	2.8	14.0	30.6	1.295	1497.7
C ₂ H ₄	4.0	11.3	42.2	1.065	1456.8
C ₃ H ₆	3.4	13.6	31.9	1.128	1628.3
(CH ₃) ₂ O	5.1	12.3	36.4	1.247	1467.1

A common feature is found for fuel-air-N₂ and fuel-air-CO₂ flammable mixtures at ambient initial conditions: the apex of the flammability range is observed in rich mixtures. For the examined set of data from tables 5, 6 and 7, we found an average equivalence ratio $\bar{\varphi} = 1.244$ of limit mixtures at LOC. Their adiabatic flame temperatures, as plotted in figure 2, were correlated according to equation:

$$AFT^{LOC} = (625.3 \pm 172.1) + (0.598 \pm 0.117) * AFT^{LFL} \quad (5)$$

(correlation coefficient $r_n = 0.649$ and a probability less than 0.001 that examined data are not linearly correlated). As above, the AFT are expressed in K.

Examination of all fuel-air-N₂ and fuel-air-CO₂ flammable mixtures, at 298 K and 1 bar (a set of 83 data) reveals also a linear correlation of adiabatic flame temperatures, with a correlation coefficient $r_n = 0.641$.

$$AFT^{LOC} = (641.5 \pm 112.6) + (0.574 \pm 0.076) * AFT^{LFL} \quad (6)$$

Fuel	LFL		LOC				
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[Added inert] (vol.%)	φ	AFT (K)
N ₂							
CH ₄	4.0	1333.5	4.8	9.8	48.5	0.980	1506.9
C ₂ H ₆	2.2	1306.5	2.6	8.2	58.2	1.110	1413.1
C ₃ H ₈	1.7	1387.4	2.1	9.2	54.0	1.141	1414.2
i-C ₄ H ₁₀	1.3	1377.5	2.1	9.3	53.5	1.468	1301.3
C ₂ H ₄	2.3	1290.8	3.25	8.0	58.5	1.219	1131.7
i-C ₄ H ₈	1.4	1412.0	1.8	9.9	51.0	1.091	1543.7
CO ₂							
CH ₄	4.0	1333.5	6.1	13.0	31.9	0.938	1563.8
C ₂ H ₆	2.2	1306.5	3.7	11.3	42.5	1.146	1385.9
i-C ₄ H ₁₀	1.3	1377.5	2.9	12.6	37.0	1.496	1341.6
i-C ₄ H ₈	1.4	1412.0	2.5	13.2	34.5	1.136	1613.0
H ₂ O							
CH ₄	4.0	1333.5	6.6	12.4	34.3	1.065	1654.0
C ₂ H ₆	2.2	1306.5	3.0	10.9	45.0	0.963	1489.9
C ₃ H ₈	1.7	1397.0	2.3	12.5	38.1	0.920	1587.7
i-C ₄ H ₁₀	1.3	1377.5	2.5	12.9	36.0	1.260	1598.2
C ₂ H ₄	2.4	1326.1	3.6	10.1	48.2	1.069	1521.3
i-C ₄ H ₈	1.4	1412.0	3.0	13.4	33.1	1.343	1675.2

Table 7
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-CO₂ MIXTURES AT AMBIENT INITIAL CONDITIONS; COMPOSITION OF LIMIT MIXTURES - FROM LITERATURE SOURCES

For these 83 fuel-air-inert flammable mixtures, the average equivalence ratio at the apex of the flammability range is $\bar{\varphi} = 1.252$

Other results, collected from CHEMSAFE data base [34], refer to preheated fuel-air-inert mixture and have been included in table 8. Data for N₂- and CO₂- diluted mixtures are scattered and the corresponding AFT^{LOC} and AFT^{LFL} are in poor correlations. Only fuel-air-H₂O mixtures at 373 K could be analyzed according to equation (4). Their adiabatic flame temperatures, plotted in figure 3, were correlated according to equation:

$$AFT^{LOC} = (23.3 \pm 846.5) + (1.152 \pm 0.623) * AFT^{LFL} \quad (7)$$

(correlation coefficient $r_n = 0.679$ and a probability $P = 0.138$ that examined data are not linearly correlated). As above, the AFT are expressed in K. For these mixtures, an unique correlation equation was not observed, at least for the examined data sets.

Table 8
CALCULATED ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-INERT MIXTURES AT $T_0 = 373$ K AND $P_0 = 1$ BAR; COMPOSITION OF LIMIT MIXTURES - FROM CHEMSAFE DATABASE [34]

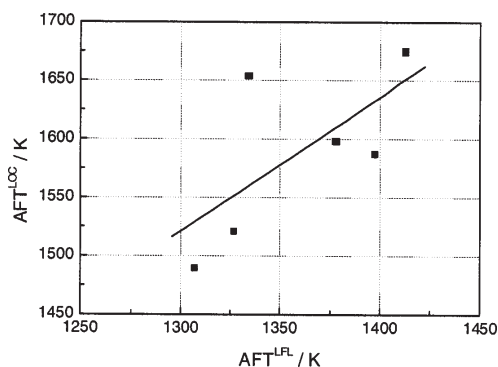


Fig. 3. Adiabatic flame temperatures of fuel-air-H₂O mixtures at $T_0 = 373$ K and $p_0 = 1$ bar (6 datasets)

Fuel	LFL		LOC				
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[H ₂ O] (vol.%)	ϕ	AFT (K)
CH ₄	3.3	1266.7	6.4	11.6	38.3	1.103	1636.0
C ₂ H ₆	1.5	1123.4	3.0	10.5	46.9	1.000	1560.0
C ₃ H ₈	1.2	1205.6	2.8	11.5	42.3	1.217	1577.3
i-C ₄ H ₁₀	1.0	1256.7	2.0	12.6	37.9	1.032	1737.4
C ₂ H ₄	1.7	1158.7	3.1	9.5	51.6	0.979	1526.8
i-C ₄ H ₈	1.2	1364.8	2.5	12.7	36.9	1.181	1746.1

Table 9
COMPOSITION OF LIMIT MIXTURES AND ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-H₂O MIXTURES AT $T_0 = 473$ K AND $P_0 = 1$ BAR; COMPOSITION OF LIMIT MIXTURES - FROM CHEMSAFE DATABASE [34]

Fuel	LFL		LOC				
	[Fuel] (vol.%)	AFT (K)	[Fuel] (vol.%)	[Oxygen] (vol.%)	[Added inert] (vol.%)	ϕ	AFT (K)
N ₂							
C ₂ H ₆	1.7	1244.2	2.0	6.5	67.0	1.066	1294.2
C ₃ H ₈	1.2	1248.6	1.8	7.2	63.9	1.250	1313.7
i-C ₄ H ₁₀	0.9	1231.4	1.8	7.2	63.9	1.625	1209.0
i-C ₄ H ₈	1.0	1274.3	1.6	7.9	60.7	1.246	1419.2
CO ₂							
C ₂ H ₆	1.7	1244.2	3.1	9.9	49.7	1.096	1385.2
C ₃ H ₈	1.2	1248.6	2.6	11.1	44.4	1.180	1461.1
i-C ₄ H ₁₀	0.9	1231.4	2.1	11.5	43.0	1.187	1487.6
C ₃ H ₆	0.9	1054.7	3.1	10.8	45.4	1.292	1378.1
i-C ₄ H ₈	1.0	1274.3	2.8	11.6	41.9	1.453	1451.7

Table 10
COMPOSITION OF LIMIT MIXTURES AND ADIABATIC FLAME TEMPERATURES AT THE LOWER FLAMMABILITY LIMIT (LFL) AND AT THE APEX OF THE FLAMMABILITY DOMAIN (LOC) FOR FUEL-AIR-INERT MIXTURES AT $T_0 = 523$ K AND $P_0 = 1$ BAR; COMPOSITION OF LIMIT MIXTURES - FROM CHEMSAFE DATABASE [34]

Diluent	T_0 / K	Linear correlations $AFT^{LOC} = a + b \cdot AFT^{LFL}$			
		a / K	b	r_n	Nr. of points
N ₂	298	639.9 ± 147.1	0.564 ± 0.099	0.655	45
	523	-4630.0 ± 595.6	4.753 ± 0.477	0.991	4
CO ₂	298	625.2 ± 172.1	0.598 ± 0.117	0.649	38
	523	1033.4 ± 306.5	0.330 ± 0.253	0.602	5
H ₂ O	373	855.0 ± 298.6	0.528 ± 0.220	0.731	6
	473	481.2 ± 331.4	0.935 ± 0.269	0.867	6

Table 11
THE BEST-FIT PARAMETERS OF CORRELATIONS BETWEEN THE ADIABATIC FLAME TEMPERATURES OF LIMIT MIXTURES

At initial temperatures $T_0 = 473$ K and 523 K, only few reliable data could be gathered. Results extracted from CHEMSAFE data base are listed in tables 9 and 10. The fit parameters of linear equations correlating AFT^{LOC} and AFT^{LFL} of the preheated mixtures are given in table 11.

The examination of equations (5) and (6) valid for limit fuel-air-N₂ and fuel-air-CO₂ mixtures shows they have close values of slopes and intercepts (within the confidence intervals, they are practically equal). It seems that an unique correlation exists between the AFT of limit mixtures at the inertization point (when various diluents are used) and the AFT of limit mixtures at LFL, as given by eq. (7). It follows that for a fuel-air mixture characterized by an

unique value of the AFT^{LFL} , an unique value of AFT^{LOC} is obtained, no matter of the nature of diluent gas. Obviously, the amount of diluent (N₂ or CO₂) necessary to bring a fuel-air mixture to the inertization point (MIC) varies significantly: typical MIC of nitrogen range between 37 - 50% and typical MIC of CO₂ range between 25 - 40%.

At elevated initial temperatures, the scatter of available data, revealed by the large standard errors of slopes and intercepts listed in Table 9, is quite large and cannot sustain the idea of an unique correlation between AFT^{LOC} and AFT^{LFL} regardless of added diluent. More experimental support may offer a future development of the present method.

According to CHEMSAFE Database, C_3H_8 -air has the LFL = 1.7 vol%. The AFT of this mixture at 298 K and 1 bar is 1326.8 K. The corresponding AFT^{LOC} of the C_3H_8 -air- CO_2 limit mixture, at 298 K and 1 bar, according to equation (6) is 1418.7 K. The average equivalence ratio of fuel-air- CO_2 mixtures at 298 K is 1.244. Five C_3H_8 -air- CO_2 gaseous mixtures with this equivalence ratio and various CO_2 contents have the AFT listed below.

Nr.	[O_2] (vol%)	[C_3H_8] (vol%)	[N_2] from air (vol%)	[CO_2] (vol%)	AFT (K)
1	10.0	2.49	37.70	49.81	1168.9
2	11.0	2.74	41.47	44.79	1258.4
3	12.0	2.99	45.24	39.77	1349.7
4	13.0	3.23	49.01	34.76	1445.0
5	14.0	3.48	52.78	29.74	1540.9

The adiabatic flame temperatures of these 5 mixtures depend linearly on O_2 and CO_2 concentrations:

$$AFT/K = (235.9 \pm 10.0) + (93.06 \pm 0.82) \cdot [O_2]/(\text{vol}\%) \quad (r_n = 0.999)$$

$$AFT/K = (2090.3 \pm 6.8) - (18.55 \pm 0.17) \cdot [CO_2]/(\text{vol}\%) \quad (r_n = 0.999)$$

$$AFT = 1418.7 \text{ K corresponds to } [O_2] = 12.7 \text{ vol}\% \text{ and } [CO_2] = 36.20 \text{ vol}\%.$$

The relative deviation* of calculated to measured LOC (12.8 mol%) is $RD = -0.78\%$.

The relative deviation of calculated to measured MIC (35.7 mol%) is $+1.4\%$.

*The relative deviations of predicted LOC values from experimental ones are defined as

$$RD = 100 \cdot [(LOC)_{calc} - (LOC)_{meas}] / (LOC)_{meas}$$

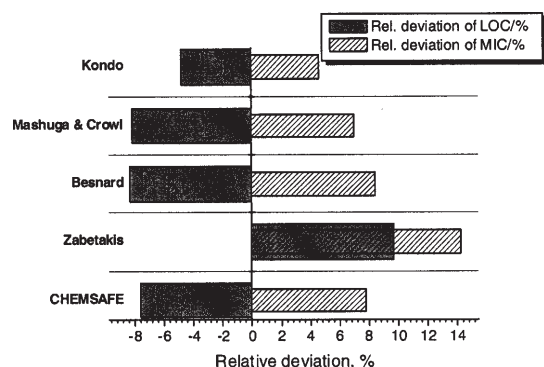


Fig. 4. Relative deviations (%) between calculated and measured LOC and MIC respectively, for CH_4 -air- N_2 mixtures at 298 K and 1 bar

The predictive power of the found correlations (5) and (6) can be examined by using the protocol for inverse calculations, described in the Appendix of the present paper. One example is given in table 12.

The relative deviations of predicted versus experimental LOC values range between -8 and +10% for CH_4 -air- N_2 mixtures at ambient initial conditions, as shown in figure 4. For these mixtures, the relative deviations of the predicted MIC versus the experimental MIC range between -14 and +8%. For CH_4 -air- CO_2 mixtures at ambient initial conditions, the relative deviations of predicted versus experimental LOC values range between -7 and +7%; the relative deviations of predicted versus experimental MIC values range between -11 and +17%.

For other fuel-air- N_2 flammable mixtures at ambient initial conditions, the relative deviations of predicted versus experimental LOC values range between -8% and +14% according to 2 literature sources [28, 34], as seen from figure 5. Relative deviations between -7 and +7% were obtained between calculated and measured LOCs of fuel-air- CO_2 flammable mixtures at ambient initial conditions. For the same fuels, the relative deviations of predicted MIC values from experimental ones range between -10 and +12%.

Table 12
LOC AND MIC ESTIMATION FOR PROPANE-AIR- CO_2 MIXTURES, AT 298 K AND 1 BAR

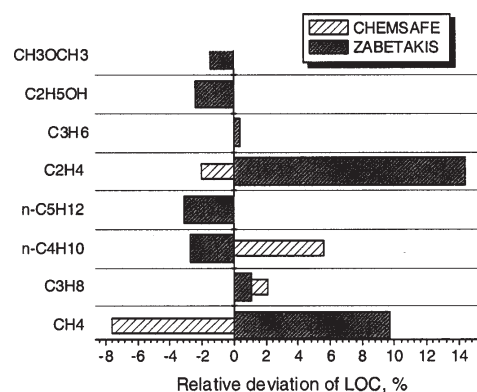


Fig. 5. Relative deviations (%) between calculated and measured LOC, for several fuel-air- N_2 mixtures at 298 K and 1 bar

According to other predictive methods, the relative deviations between the calculated and the measured LOC range between +20 and -20% [8, 15, 16, 20, 21]. It must be outlined that LOC predictions of other authors show a fair agreement only with data sets which were the basis of the corresponding method. In comparison with these results, we consider our method has a good predictive ability especially for fuel-air-diluent flammable mixtures at ambient initial conditions, since it includes series of data reported by different authors, measured with various methods according to actual international standards. Few data on flammable fuel-air-diluent mixtures at temperatures higher than ambient are available in literature; publication and analysis of additional information may form the basis for improving the predictions of the present method.

Conclusions

The widely available collections of recommended flammability data indicate only the Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) values, at various initial pressures and/or temperatures. This scarce information can be completed by using the present method of estimating the fuel and the oxygen concentration at the apex of the flammability range, based upon the values of LFL and the Calculated Adiabatic Flame Temperatures,

both at LFL and LOC. The method was developed for systems at ambient initial temperature and it was validated for mixtures at temperatures higher than ambient, containing diluents as N_2 , CO_2 and H_2O (vapour).

The relative deviations between calculated and measured LOC and MIC range between -14 and +17%. Better predictions could be obtained by extending the number of investigated systems. It is important to notice the difficulty to use the present method for compounds which are unstable or may decompose even in the absence of an oxidant (e.g. acetylene or ethylene oxide). Under such conditions, LOC and MIC should be determined by experiment.

The method has the advantage to include series of data reported by different authors, measured with various methods, according to actual international standards. According to this specific feature, inclusion of new data sets obtained with alternative or with improved procedures is possible and may contribute to a better predictive power.

Appendix - Procedure for LOC estimation by using adiabatic flame temperatures of limit mixtures

- measurement of LFL of fuel-air mixture, at various initial temperatures and/or pressures;

- calculation of AFT^{LFL} with any program able to provide adiabatic flame temperatures;

- calculation of AFT^{LOC} by means of the equation $AFT^{LOC} = a + b \cdot AFT^{LFL}$, valid for the examined initial temperature;

- calculation of inert, fuel and air concentrations for the mixture characterized by the value of AFT^{LOC} determined at step (iii).

This involves a supplementary computation of adiabatic flame temperatures, for fuel-air-inert systems with a constant fuel/oxygen ratio (equivalence ratio) and various inert concentrations. Such values allow calculation of fuel, air and inert concentrations at LOC, by interpolation.

An important step: calculation of φ , the average equivalence ratio for fuel-air-inert mixtures at the inertization point, for each examined initial temperature.

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