



Papers

*Dedicated to Dr. Nicolae I. Ionescu
on the occasion of his 90th anniversary*

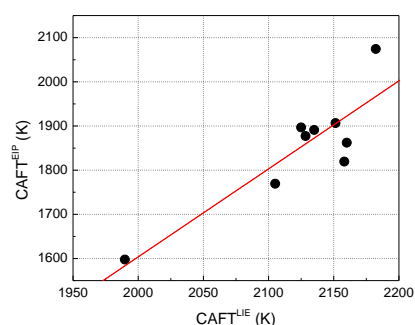
CALCULATED ADIABATIC FLAME TEMPERATURE – A TOOL FOR ASCERTAINING THE MINIMUM INERT CONCENTRATION OF FUEL-NITROUS OXIDE-INERT GASEOUS MIXTURES**

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A previous correlation of CAFT (Calculated Adiabatic Flame Temperature) found for limit fuel-air and inert-diluted fuel-air gaseous mixtures is revisited, aiming to test its validity for mixtures where air is replaced by nitrous oxide. The flammability of these mixtures is less studied when compared to fuel-air, especially in respect to the influence of inert additives on flammability limits. The paper examines several data sets reported in literature and outlines the good correlation found between the CAFT at the lower flammability limit of fuel-nitrous oxide ($CAFT^{LIE}$) and the CAFT at the extreme point of flammability range, i.e. EIP, the extreme inertization point ($CAFT^{EIP}$) of fuel-nitrous oxide-nitrogen gaseous mixtures. The correlation can be further used to predict the MIC (Minimum Inert Concentration) for nitrogen-diluted fuel-nitrous oxide gaseous mixtures, using only the lower flammability limit (LIE) of fuel-nitrous oxide and the corresponding adiabatic flame temperature ($CAFT^{LIE}$).



INTRODUCTION

Brought into contact with local sources of energy (electric sparks or hot bodies) or heated above some critical (limit) values of pressure and temperature, the fuel-oxidizer mixtures may develop an explosive combustion. The limit concentrations of fuel in fuel-oxidizer mixtures ignited by local energy sources are known as “flammability limits”, which may characterize deflagrations (explosions that propagate at a speed lower than the sound of speed characteristic to that mixture) or detonations (explosions propagating at

speeds much higher than the sound of speed). In fuel-lean mixtures, the lower flammability limit (LFL) is determined as the lowest fuel concentration where the flame ignition and propagation does not occur anymore, no matter how high the ignition energy is. In oxidizer-lean (fuel-rich) mixtures, the upper flammability limit (UFL) is determined as the highest fuel concentration where the flame ignition and propagation does not occur anymore.^{1,2} Addition of an inert gas to a fuel-oxidizer mixture results in the increase of LFL and the decrease of UFL, until the two limits merge and the mixture reaches the

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** Supplementary information on <https://www.icf.ro/rrch/> or <https://revroum.lew.ro>

extreme inertization point (called EIP). The minimum inert concentration (MIC), able to transform (turn) a flammable mixture into a non-flammable one (at constant conditions of temperature, pressure and at any fuel/oxidizer ratio) is influenced by the pressure and temperature of the flammable mixture.^{3,4} Usually, the MIC is determined at fuel-oxidizer mixtures of stoichiometric ratio, *i.e.* mixtures where both the fuel and the oxidizer burn completely (in fact, even

at the stoichiometric fuel-oxidizer ratio, the combustion is not complete since the main combustion products, CO₂ and H₂O, dissociate in the flame). At inert concentrations higher than MIC, the fuel-oxidizer mixtures cannot sustain an explosion, even at addition of extra fuel or oxidizer amounts, and can be handled as safe mixtures. A schematic representation of the flammability range is shown in Fig. 1, for CH₄-air in the presence of various inerts.⁴

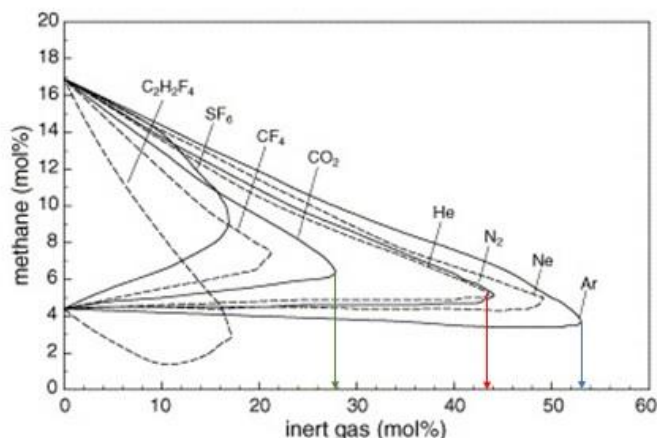
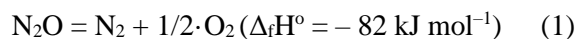


Fig. 1 – Influence of inert gas on the explosion ranges of methane–inert gas–air mixtures, measured at 20 °C and 101 kPa, from S. Besnard, Full Flammability Test of Gases and Gas Mixtures in Air, CERN Report, 1996, as cited by Molnarne.⁴

Fuel-nitrous oxide can support (afford) both deflagrations and detonations as combustion regimes, depending on the initial composition of the flammable mixture (fuel/N₂O ratio and the presence of inert additives), pressure, temperature, strength of the ignition source and, quite often, on the presence of obstacles in the explosion vessel, able to accelerate the propagation velocity of the process. Lately, many studies were performed on flammability properties of fuel-nitrous oxide in the presence of inert gases. Among them, the studies on flammability limits and propagation characteristics of explosions in various conditions (especially, deflagrations in enclosures) are of great interest. These studies have shown that fuel-N₂O mixtures differ greatly from fuel-air mixtures as a result of the greater oxidizing potential of N₂O when compared to air. In this respect, one has to take into account the exothermal decomposition of nitrous oxide, which influences especially the fuel-lean mixtures:



The lower and upper flammability limits of fuel–N₂O deflagrations were determined in various conditions: at ambient pressure and temperature,^{5–14} at pressures and/or temperatures different from ambient,^{9,15–19} using neat fuel–N₂O mixtures and sometimes fuel–N₂O diluted with air or O₂. Minimum inert concentrations of inert-diluted fuel–N₂O mixtures (inerts: He, Ar, N₂, CO₂) were also reported^{5,7–9,19} mostly at ambient initial conditions. Few studies were conducted in standardized conditions, as recommended by the international standards.^{20,21} As a result, the delivered flammability limits and minimum inert concentrations are quite scattered, even for frequently studied mixtures of hydrogen and methane. A typical set of data referring to hydrogen and methane mixed with N₂O is given in Table 1, where the minimum nitrogen concentration (MIC) is also given. The data from Table 1 refer to several N₂-diluted fuel–N₂O mixtures. One can observe a wide range for the reported lower flammability limits for hydrogen and methane – well studied fuels, but with various techniques, most of them being far from the present standards.

Table 1

Lower flammability limit (LIE) of fuel–N₂O and minimum inert concentration (MIC) of nitrogen-diluted fuel–N₂O mixtures, at ambient (or close to ambient) initial conditions

Fuel	LIE (vol%)	Experimental conditions for determining LIE and MIC	MIC (vol%)	Reference
H ₂	4.5–5.0	Spherical vessel, V = 11.25 L; central ignition	76.0	Pfahl <i>et al.</i> ⁵
H ₂	2.5	Spherical vessel, V = 5 L, as recommended by EN 1839 T; central ignition	73.2	Meye <i>et al.</i> ⁹
H ₂	8.0	Spherical vessel, V = 4.2 L; central ignition	–	Shebeko <i>et al.</i> ¹⁰
H ₂	5.8 @700 mmHg	Vertical tube (L= 1 m); bottom ignition	–	Pannetier and Sicard ¹⁵
H ₂	3.0–3.1 @28° C	Vertical tube (L= 1 m); bottom ignition	–	Scott <i>et al.</i> ⁶
CH ₄	2.5–3.0	Spherical vessel, V = 11.25 L; central ignition	–	Pfahl <i>et al.</i> ⁵
CH ₄	1.5	Spherical vessel, V = 5 L, as recommended by EN 14756; central ignition	71.3	Meye <i>et al.</i> ⁹
CH ₄	2.0	Spherical vessel, V = 4.2 L; central ignition	–	Shebeko <i>et al.</i> ¹⁰
CH ₄	2.5	Cylindrical vessel, V = 9.4 L; central ignition	–	Koshiha <i>et al.</i> ¹²
CH ₄	4.0 @700 mmHg	Vertical tube (L= 1 m); bottom ignition	–	Pannetier and Sicard ¹⁵

Among recent data sets reporting both the lower flammability limit and MIC, the most comprehensive set was reported by Meye *et al.*,⁹ from measurements at ambient initial pressure and various initial temperatures, using standard methods and various fuels: hydrocarbons, alcohols, carbonylic compounds, esters. The present study examines these data, with the scope of finding a correlation between the adiabatic flame temperature of fuel-nitrous oxide mixtures at LIE and the adiabatic flame temperature of nitrogen-diluted fuel-nitrous oxide, with a composition at the extreme flammability point (extreme inertization point, or EIP), where MIC are measured. Such empirical correlation was already found for fuel-air and inert-diluted fuel-air mixtures (inerts: N₂ and CO₂), at various initial temperatures²²⁻²⁴ and could be successfully used for predicting the composition of inert-diluted fuel-air flammable mixtures. It helps the long and tedious process of measuring the whole flammability domain, avoiding thus a waste of time and resources. This procedure is also helpful in formulating safety recommendations for all domains of activity where nitrous oxide is used.

Computing program

The adiabatic flame temperatures of fuel–N₂O and fuel–N₂O–N₂ mixtures were calculated with

COSILAB package²⁵ for ambient initial conditions of all gaseous mixtures. The program is based on a general algorithm meant to compute the equilibrium composition of products for any fuel-oxidizer gaseous mixture using the thermodynamic criterion of chemical equilibrium: the minimum of Gibbs energy, at constant temperature and pressure, or the minimum of Helmholtz energy, at constant temperature and volume. Fifty-three compounds have been considered as combustion products. In the present case the computations were run for constant pressure combustion.

RESULTS AND DISCUSSION

A typical set of results regarding the composition of limit mixtures, taken from the report of Meye *et al.*⁹ is shown in Table 2, along with the corresponding CAFTs. Only the data describing mixtures at ambient initial temperature and pressure were examined. It is important to mention that the extreme inertization point (EIP) was found for stoichiometric fuel-nitrous oxide-nitrogen mixtures,⁹ in contrast with fuel – air – nitrogen mixtures which had the EIP in the range of fuel-rich mixtures, usually at an equivalence ratio $\phi = 1.10$.²²⁻²³

Table 2

The composition of limit mixtures and the calculated adiabatic flame temperatures (CAFT) at LIE and at the extreme inertization point (EIP)

Fuel	[Fuel] at LIE (vol%)	CAFT ^{LIE} (K)	[Fuel] at EIP (vol%)	[N ₂ O] at EIP (vol%)	[N ₂] at EIP (vol%)	CAFT ^{EIP} (K)
Hydrogen	2.5	1989.8	13.4	13.4	73.20	1597.6
Methane	1.5	2074.9	5.75	23.0	71.25	1944.0
Propane	0.76	2125.0	2.22	22.2	75.58	1896.8
n-Hexane	0.47	2160.0	1.14	21.7	77.16	1862.2
Ethylene	1.2	2135.0	3.38	20.3	76.32	1891.0
Methanol	2.33	2105.1	6.23	18.7	75.07	1769.3
Ethanol	1.30	2182.3	3.58	21.5	74.92	2074.4
2-Propanol	0.88	2128.4	2.44	22.0	75.56	1877.2
Acetone	1.04	2151.4	2.76	22.1	75.14	1906.6
Dioxane	0.85	2158.1	1.99	19.9	78.11	1819.4

Examination of data from Table 2 reveals a wide range of CAFT of studied fuels at their lower flammability limit when mixed with nitrous oxide: almost 200 K, from 1989.8 K for H₂ – N₂O to 2182.3 K for C₂H₅OH – N₂O. A similar wide range of CAFT at the extreme inertization points is found, from 1597.6 K for H₂ – N₂O – N₂ up to 2074.4 K for C₂H₅OH – N₂O – N₂. This set of data shows that both the lower flammability limits and the extreme inertization points of fuel-nitrous oxide gaseous mixtures have no constant adiabatic temperature. However, a correlation exists between the two characteristic flame temperatures.

The plot of CAFT^{EIP} versus CAFT^{LIE} is shown in Fig. 2, for 9 out of 10 compounds listed in Table 2. The data for methane were left aside and will be further used to test the prediction method of MIC, as described in previous papers.²²⁻²⁴

The line correlating the data is:

$$\text{CAFT}^{\text{EIP}}/\text{K} = (1.992 \pm 0.412) \cdot (\text{CAFT}^{\text{LIE}}/\text{K}) - (2380 \pm 876) \quad (2)$$

with the correlation coefficient $r_n = 0.877$ (9 points).

Using equation (2), we can calculate the adiabatic flame temperature of CH₄–N₂O–N₂ mixture at its extreme inertization point, using

CAFT^{LIE} = 2074.9 K for CH₄–N₂O mixture at LIE. The result is CAFT^{EIP} = 1753.2 K.

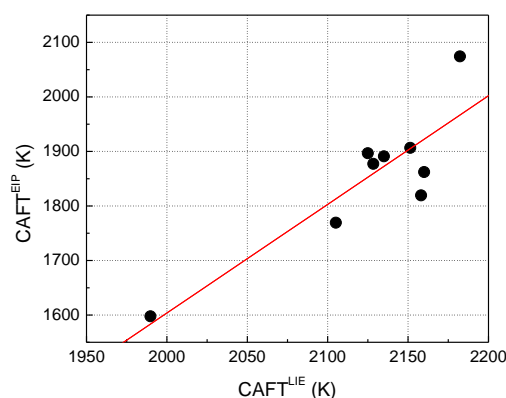


Fig. 2 – Variation of CAFT for fuel-N₂O–N₂ mixtures at the extreme point of flammability and fuel-N₂O at the lower flammability limit.

Here, additional calculations of adiabatic flame temperatures are necessary, since the composition of the mixture at its extreme inertization point is unknown. Assuming the variation range of [N₂] within 66 and 78 vol%, the composition of examined ternary mixtures is found by setting [N₂O] = 4·[CH₄], in accord with the stoichiometric composition. The results are given in Table 3 and in Fig. 3.

Table 3

Influence of added nitrogen on CAFT of ternary CH₄–N₂O–N₂ mixtures

[N ₂] (vol%)	([CH ₄] + [N ₂ O]) (vol%)	[CH ₄] (vol%)	[N ₂ O] (vol%)	CAFT (K)
66	34.0	6.8	27.2	2132.4
68	32.0	6.4	25.6	2065.3
70	30.0	6.0	24.0	1992.4
72	28.0	5.6	22.4	1913.9
74	26.0	5.2	20.8	1829.8
76	24.0	4.8	19.2	1740.7
78	22.0	4.4	17.6	1646.9

A plot of CAFT vs $[N_2]$ for ternary $CH_4-N_2O-N_2$ mixtures is given in Fig. 3. Their correlation is linear, characterized by the equation:

$$CAFT/K = (4819.4 \pm 75.1) - (40.51 \pm 1.047) \cdot [N_2]/(\text{vol}\%) \quad (3)$$

with the correlation coefficient $r_n = 0.998$ (7 points).

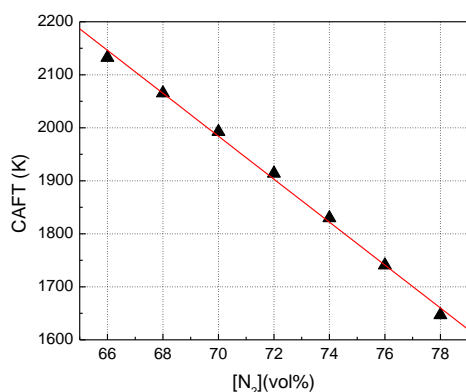


Fig. 3 – Nitrogen influence on Calculated Adiabatic Flame Temperature of $CH_4-N_2O-N_2$ mixtures, at ambient initial conditions.

The nitrogen concentration at the extreme inertization point of $CH_4 - N_2O - N_2$ mixtures, corresponding to $CAFT^{EIP} = 1753.2$ K is $[N_2]^{EIP} = 75.7$ vol%, according to this correlation. This predicted value of $[N_2]^{EIP}$ exceeds the measured $[N_2]^{EIP} = 71.3$ vol%.⁹ The deviation between the experimental and calculated $[N_2]^{EIP}$ is 6.2%, which can be accepted as common error in estimations of the Minimum Inert Concentration.

The same procedure can be applied now to data on $H_2-N_2O-N_2$ reported by Pfahl *et al.*⁵ The authors used a 11.25 L spherical vessel, with central ignition by high voltage electric sparks; the schlieren imaging of the flame kernel afforded the determination of the limit (critical) concentrations of components, as the composition where the flame propagates autonomously from the ignition source. Both the $LIE = 5.0$ vol% H_2 (in H_2-N_2O mixture) and $MIC = 73.2$ vol% N_2 (in $H_2-N_2O-N_2$ mixtures) differ from those reported by Meye,⁹ who used different measuring conditions: 5 L spherical vessel with central ignition and used as explosivity criterion the 5% increase of pressure above its initial value. Another significant difference is found in the H_2 / N_2O ratio at the extreme inertization point. While Meye *et al.*⁹ consider all fuel- N_2O-N_2 mixtures have a stoichiometric ratio at the extreme composition, Pfahl *et al.*⁵ reported for $H_2-N_2O-N_2$ mixtures a much smaller equivalence ratio ($\phi = 0.444$). These data are summarized in Table 4, which includes also results concerning the mixtures of C_3-C_5 alkanes with N_2O and N_2 .^{7,8} Based on these measured compositions, the predicted N_2 concentrations at the extreme inertization point are listed in Table 5. It is important to mention that separate correlations of $CAFT^{EIP}$ versus $[N_2]$ were determined for each listed fuel. Additional data on these correlations are given in the Supplementary information to this paper.

Table 4

The composition of limit mixtures at LIE and at the extreme inertization point (EIP)

Fuel	Measured values				Reference
	[Fuel] at LIE (vol%)	[Fuel] at EIP (vol%)	$[N_2O]$ at EIP (vol%)	$[N_2]$ at EIP (vol%)	
H_2	5.0	8.0	18.0	74.0	Pfahl <i>et al.</i> ⁵
C_3H_8	2.0	3.0	25.2	71.8	Shebeko <i>et al.</i> ⁷
n- C_4H_{10}	1.7	2.5	27.5	70.0	Shebeko <i>et al.</i> ⁷
n- C_5H_{12}	0.8	1.2	42.0	56.8	Koshiba <i>et al.</i> ⁸

Table 5

The calculated adiabatic flame temperatures of limit mixtures at LIE and at the extreme inertization point (EIP)

Fuel	[Fuel] at LIE (vol%)	$CAFT^{LIE}$ (K)	Predicted $CAFT^{EIP}$, by means of eq. (2) (K)	Predicted $[N_2]$ (vol%)	Measured $[N_2]$ (vol%)	Reference
H_2	5.0	2073.2	1749.8	59.3	74.0	Pfahl <i>et al.</i> ⁵
C_3H_8	2.0	2412.2	2425.1	59.2	71.8	Shebeko <i>et al.</i> ⁷
n- C_4H_{10}	1.7	2450.0	2500.4	55.6	70.0	Shebeko <i>et al.</i> ⁷
n- C_5H_{12}	0.8	2256.1	2114.2	70.8	56.8	Koshiba <i>et al.</i> ⁸

The comparison of measured and computed (predicted) nitrogen concentrations at the extreme inertization point is not satisfactory for any of the cases listed in Table 5. It is obvious that only coherent data sets, *i.e.* data reporting LIE and MIC measured with the same equipment, using the same experimental protocol and the same criterion for detecting these extreme concentrations, can be used for predicting the composition of inert-diluted fuel-nitrous oxide gaseous mixtures.

CONCLUSION

In the field of safety against damaging explosions of fuel-oxidizer gaseous mixtures, the flammability limits are major properties, used to delimitate dangerous conditions (composition, pressure, temperature) from non-dangerous ones. Available scientific information consists from measured LIEs and MICs of various single or blended fuels, using single or blended oxidizers. Such measurements are widely performed, but necessitate a specific equipment as required by international standards and are time- and material consuming. A short-cut for this endeavor is provided by the present method, which correlates the calculated adiabatic flame temperatures of mixtures at LIE and EIP. The predicting ability of the method, at this moment, is limited by the restricted number of available data. However, further tests can be included in the present task and could provide an improved correlation of adiabatic flame temperatures at the extreme inertization points.

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