



ADDITIVE EFFECTS ON EXPLOSION PRESSURE AND FLAME TEMPERATURE OF STOICHIOMETRIC ETHYLENE-AIR MIXTURE IN CLOSED VESSELS

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The pressure-time evolution during the laminar deflagration of gaseous stoichiometric ethylene-air mixture in the presence of various inert additives is experimentally investigated in a spherical and two cylindrical vessels with central ignition, at initial pressures within 0.3-1.2 bar and ambient temperature ($T_0 = 298$ K).

The peak explosion pressures measured in the three closed vessels of different geometries are examined in comparison with the adiabatic explosion pressures, computed by assuming chemical equilibrium within the combustion products. These computations deliver also the adiabatic flame temperatures of isochoric combustion at various initial pressures. The influence of nature and amount of diluents on explosion pressure and flame temperature is examined together with the influence of initial pressure.

INTRODUCTION

Explosions of gaseous mixtures in closed vessels are characterized by important damaging effects: peak explosion pressures 7-10 times larger than the initial pressure and high maximum rates of pressure rise (between 50-500 bar/s), reached in a very short time (lower than one second, for small volume laboratory vessels). The knowledge of characteristic parameters of these processes allows the assessment of explosion risks for flammable mixtures in various conditions and the design of equipment and industrial plants where flammable mixtures might be formed.

The characteristic parameters of explosion propagation in confined conditions such as the peak explosion pressure, the maximum rate of pressure rise, the explosion index and the explosion time (time necessary to reach the peak pressure) depend on the various parameters. Among these, the amount of produced heat and its release rate are most important.

Many publications report values of characteristic explosion parameters of fuel-oxidant gaseous systems at various initial pressures and temperatures, obtained in various experimental conditions. Among these data, values of explosion pressures and explosion times of gaseous mixtures measured in explosion vessels with various geometries and volumes and ignition made by local sources with various energies refer to hydrocarbon-air and hydrocarbon-air-diluent mixtures.¹⁻⁹

The study of the influence of inert or inhibitor additives on the gaseous explosions is required by the necessity to mitigate their effects and to characterize and model the explosive combustion processes. Their presence in the explosive mixtures favors a better control of combustion evolution: longer induction periods, lower laminar burning velocities, lower amounts of pollutants etc.

Ethylene, one of the very important compounds in chemical industry (key intermediate in the production of ethylene oxide, ethylene dichloride and polyethylene), presents a significant fire and explosion hazard. Early studies on ethylene-air

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systems report values of the explosion limits and the influence of the additives on these parameters^{10, 11} and on burning velocities, for various initial conditions.¹²⁻¹⁶ Adiabatic values of explosion pressures were obtained by using available programs for thermo-chemical equilibrium calculations¹⁹ or by detailed modeling of combustion coupled with heat and mass transfer processes.¹⁸⁻²²

The present study reports data referring to confined explosions of ethylene-air in the presence of various additives (Ar, N₂, CO₂): the peak (maximum) explosion pressures in a spherical vessel and two cylindrical vessels with different volumes and height to diameter ratios. Data obtained from measurements at various initial pressures within 0.3 and 1.2 bar and ambient initial temperature are completed by computed values of adiabatic explosion pressures and adiabatic flame temperatures of constant-volume combustion. The scope of this work is to examine the influence of nature and amount of added diluents on these parameters, together with the influence of volume and shape of the explosion vessels on experimental peak explosion pressures.

EXPERIMENTAL

The experimental set-up consists in a vacuum and gas-feed line, tight at pressures from 0.1 mbar to 1.5 bar, which interconnects the vacuum pump, the gas cylinders with fuel, air and additive, the metallic cylinder for mixture storage and the explosion vessel. Details on the experimental set-up and procedure were previously given.^{29, 30} Experiments were performed in a spherical vessel S with the radius $R = 5$ cm, a cylindrical vessel C1 with $h = 15$ cm and $\Phi = 10$ cm and a cylindrical vessel C2 with $h = \Phi = 6$ cm.

Gaseous fuel: ethylene (99.97% purity), oxygen (99.0%), Ar, N₂ and CO₂ (99.5%) were purchased from SIAD RG Italy and were used without further purification. Stoichiometric (6.54 vol%) ethylene-air mixtures diluted with Ar, N₂ or CO₂ (concentrations up to 48 vol%) were prepared at 4 bar total pressure, assuming all gaseous components were ideal gases.

Computing program

The calculations of adiabatic explosion pressures and adiabatic flame temperatures were made with the program ECHIMAD,¹⁷ based on a general algorithm meant to compute the equilibrium composition of products for any fuel-oxidizer-diluent gaseous mixture. The algorithm is based on the thermodynamic criterion of chemical equilibrium: the minimum of free Gibbs energy, at constant temperature and pressure or minimum of free Helmholtz energy, at constant temperature and volume. Fifteen compounds, among them one solid compound (C_{graphite}) were considered as products: the fuel (C_nH_m), C_{graphite}, CO₂, CO, H₂O, O₂, N₂, CH₄, C₂H₂, C₂H₄, H₂, NO, H, OH and O). Their heat capacities (expressed as

functions of temperature of the form: $C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2}$), the standard enthalpies of formation at 298 K and the standard entropies at 298 K were taken from literature.²³⁻²⁵

RESULTS AND DISCUSSION

The maximum explosion pressure is a characteristic parameter of confined gaseous explosions depending on initial pressure, temperature and composition of gaseous mixtures, size and shape of the explosion vessel, type, energy and position of the ignition source.

A comparison of pressure variation during the explosions of the stoichiometric C₂H₄-air mixture in spherical vessel S and in cylindrical vessel C1 is given in Fig. 1, for experiments performed at ambient initial pressure and temperature. As shown in Fig. 1, the volume and asymmetry of the vessel (vessel C1 is an elongated cylinder) influence both the maximum (peak) explosion pressure and the time to reach the peak pressure: $p_{max} = 9.6$ bar in vessel S and $p_{max} = 9.2$ bar in vessel C1; $\theta_{max} = 14$ ms in vessel S and $\theta_{max} = 24$ ms in vessel C1, for the stoichiometric ethylene-air mixture at ambient initial pressure and temperature. As expected, the highest value of the peak pressure is observed in vessel S. For this mixture, a close value of the peak pressure ($p_{max} = 9.7$ bar) was found by Brandes *et al.*, from measurements in a 20L spherical vessel with central ignition.²⁸ Compared to peak pressures obtained for methane (8.2 bar in a 20L, spherical vessel),^{6, 7} n-butane (8.5 bar in a 0.7L spherical vessel)²⁹ and propylene (8.6 bar in a 0.7L spherical vessel with central ignition),³⁰ the data for ethylene are slightly higher but of the same order.

For closed-vessel explosions in deflagration regime, the peak explosion pressure was found to depend on initial pressure according to a linear function.^{26,27, 29} The correlation is described by the equation:

$$p_{max} = a + b \cdot p_0 \quad (1)$$

The peak explosion pressure variation against the initial pressure in the examined closed vessels is presented in Fig. 2, for a stoichiometric C₂H₄-air-CO₂ mixture ([CO₂] = 15 vol.%). The differences of volume and geometric ratio (height/diameter) of the three explosion vessels account for the differences of maximum explosion pressures. In Fig. 3, plots of peak explosion

pressures measured in vessel S versus initial pressure, referring to the stoichiometric C_2H_4 -air mixture diluted with various amounts of CO_2 , are given. Such correlations were found for all examined ethylene-air and ethylene-air-diluent mixtures in the range of initial pressures between 0.3 and 1.2 bar, in all explosion vessels.

Table 1 enlists the slopes and intercepts of the linear correlations between p_{max} and p_0 , together with the determination coefficients of these correlations for some of the examined mixtures. Such equations are useful for evaluation of maximum explosion pressures at any initial pressure, p_0 , as long as the deflagration regime is maintained.²⁶

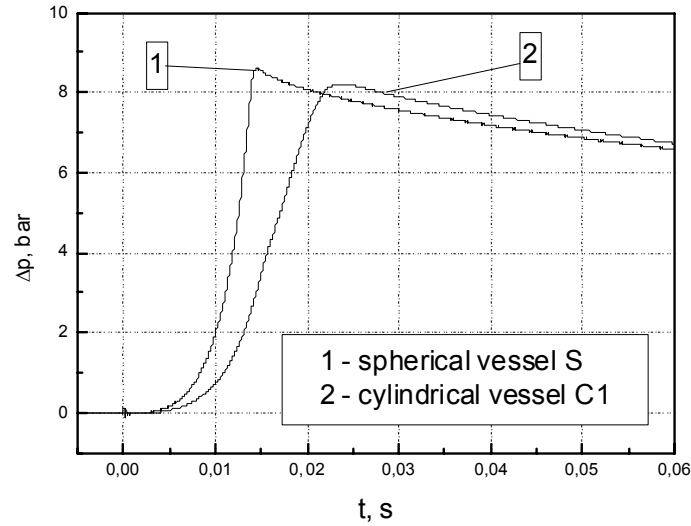


Fig. 1 – Pressure-time records for the stoichiometric C_2H_4 -air mixture in two closed vessels, at $p_0 = 1$ bar.

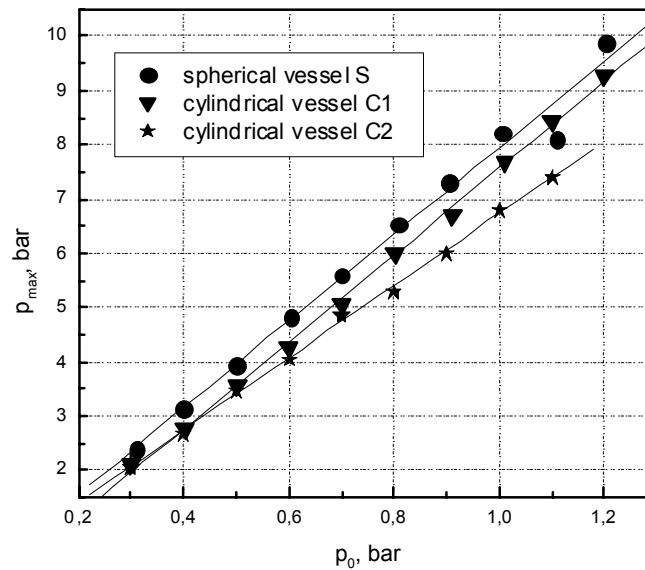


Fig. 2 – Maximum explosion pressures of a stoichiometric C_2H_4 -air mixture diluted by 15 vol. % CO_2 in three closed vessels with central ignition.

Table 1

Slope and intercept of p_{max} vs. p_0 linear regressions; spherical vessel S

$[CO_2]$	-a (bar)	b	r_n
0	0.181 ± 0.026	9.812 ± 0.035	0.999
5	0.226 ± 0.034	9.399 ± 0.040	0.999
10	0.201 ± 0.059	8.937 ± 0.073	0.999
15	0.254 ± 0.027	8.409 ± 0.032	0.999
20	0.263 ± 0.032	7.834 ± 0.036	0.999

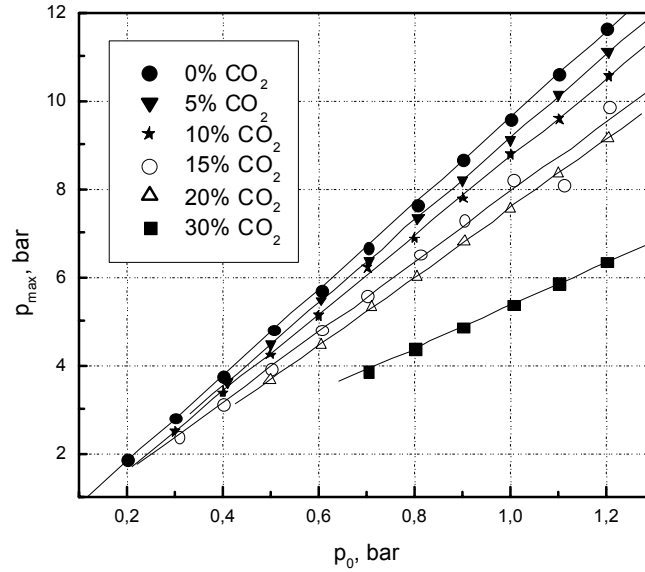


Fig. 3 – Linear correlations $p_{max}=f(p_0)$ for ethylene-air-CO₂ mixtures, spherical vessel with central ignition.

From the analysis of the heat balance during the explosion propagation in a closed vessel a correlation between the end (final) explosion

pressure p_e and the initial pressure p_0 was derived:²⁶

$$p_e = p_0 \left(\xi + \frac{r_l}{\nu_l} \cdot \frac{\Delta_c U'}{C_{e,V} \cdot T_0} \right) - q_{tr} \frac{\gamma_e - 1}{V_0} = k_{a,V} \cdot p_0 - q_{tr} \frac{\gamma_e - 1}{V_0}, \quad (2)$$

where $\xi = n_e/n_0$ is the molar ratio of combustion (n_0 is the initial number of moles, n_e is the number of moles at the end of combustion); $r_l = n_l/n_0$ is the mole fraction of the limiting component of the mixture; ν_l is the stoichiometric coefficient of the limiting component in the mixture (since for a stoichiometric mixture the limiting component can be taken either the fuel or the oxygen, the first choice was adopted for the discussion, when $r_l = r_f$ and $\nu_l = \nu_f = 1$); $\Delta_c U'$ is the molar heat of combustion (at constant volume and T_0); $C_{e,V}$ is the molar heat capacity of the end gaseous mixture, averaged for the end components and for the temperature range T_0 to $\bar{T}_{e,V}$; q_{tr} is heat transferred to the vessel before the end of combustion, γ_e is the adiabatic compression coefficient of the end products and V_0 is the volume of explosion vessel. Equation (2) was further expressed as a simpler correlation with the slope $k_{a,V}$ (the coefficient of pressure rise in ideal, adiabatic explosions, taking place without heat losses from burning gas to the vessel).

It can be assumed, without a great error, that $p_{max} = p_e$ especially in the spherical vessel with central ignition; therefore, equation (2) can be used for an interpretation of linear correlations given in Figs. 2 and 3. In the examined flammable mixtures, ξ , ν_l and $\Delta_c U'$ are constant; addition of various amounts of inert gas results in a variation of the average heat capacity of burned gas $C_{e,V}$ and of the volume fraction r_l of limiting components (both ethylene and oxygen). Thus, the increase of inert gas concentration determines the increase of $C_{e,V}$ and the decrease of r_l resulting in the decrease of the slope $k_{a,V}$, as seen in data from Fig. 3 and Table 1. At constant composition and initial pressure of flammable mixture, the peak pressures obtained in various vessels depend on the amount of heat transferred by the burned gas to the vessel q_{tr} and on volume of flammable mixture, *i. e.* on the available energy of the system. These terms, grouped in the intercept of eqn. (2), reveal the extent of heat losses affecting the peak explosion pressures. At constant volume V_0 of the explosion vessel (of the flammable mixture), a higher amount of diluent results in a lower burning

velocity, therefore in a longer contact time of flame and vessel's wall, entailing the transfer of a higher amount of heat (q_{tr}) before the end of combustion.

A typical graph used to examine the influence of various additives on maximum explosion pressure is given in Fig. 4, where data referring to

$$\frac{p_e}{p_0} = \xi - q_{tr} \cdot \frac{\gamma_e - 1}{p_0 V_0} + \frac{\kappa}{1 + \kappa} \cdot \frac{\Delta_c U'}{C_{e,V} T_0} \left(1 - \frac{n_i}{100}\right) = \alpha + \beta \cdot \left(1 - \frac{n_i}{100}\right), \quad (3)$$

where $\kappa = \frac{r_f}{r_a} = \frac{n_f}{n_a}$ is a constant in the examined stoichiometric mixture; n_f , n_a and n_i are the mole numbers of fuel, air and inert in 100 moles of flammable mixture, and r_a is the mole fraction of air in the mixture. Explosion pressures obtained in each explosion vessel ($V_0 = \text{ct.}$) at constant initial pressure fit this correlation, as shown in Fig. 4. The plots reveal also that CO_2 is the most efficient additive for the stoichiometric ethylene-air mixture, followed by N_2 and Ar, according to their

the stoichiometric C_2H_4 -air mixture diluted by Ar, CO_2 and N_2 at $p_0 = 1$ bar are plotted. For all inert additives, a linear variation of maximum explosion pressure against inert concentration is observed, at least for the examined concentration ranges. The found correlation can be explained by examining eq. (3), derived by a rearrangement of eq. (2):

heat capacities. Similar diagrams were found for vessels S and C1.

For all studied mixtures the adiabatic explosion pressures reached from $p_0 = 1$ bar were also calculated. As expected, the adiabatic values of the explosion pressures were higher as compared to measured ones, as seen in Fig. 5, where data measured in cylindrical vessel C2 were also plotted. The computed explosion pressures $p_{e,ad}$ follow the same linear correlation when plotted against the concentration of added inert gas. In this case, the heat balance during the isochoric combustion is written as:

$$\frac{p_{e,ad}}{p_0} = \xi + \frac{\kappa}{1 + \kappa} \cdot \frac{\Delta_c U'}{C_{e,V} T_0} \left(1 - \frac{n_i}{100}\right) = \alpha' + \beta \cdot \left(1 - \frac{n_i}{100}\right), \quad (4)$$

which is the equation of a line with the same slope as eq. (3), but with a different intercept. The slight curvature observed at large concentrations of inert gas, especially for systems containing CO_2 , can be

assigned to the variation of $\Delta_c U'$ (the combustion heat corrected for the endothermic processes) over various ranges of inert concentration.

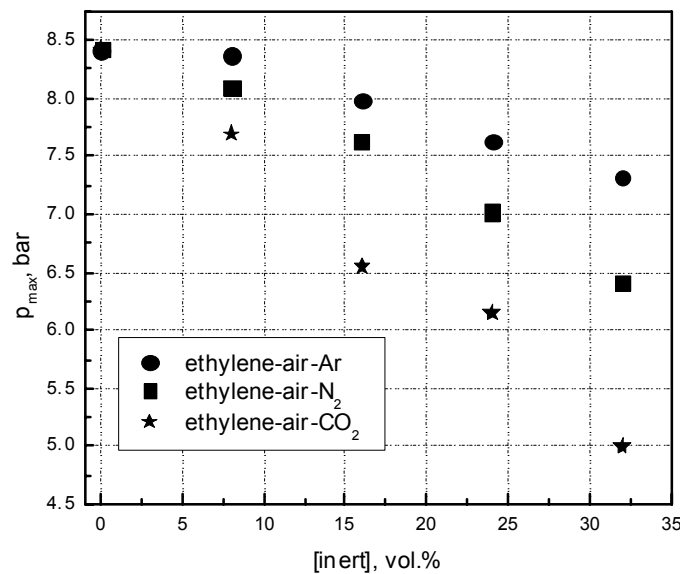


Fig. 4 – Diluent influence on maximum (peak) explosion pressure, in experiments at $p_0 = 1$ bar, in cylindrical vessel C2.

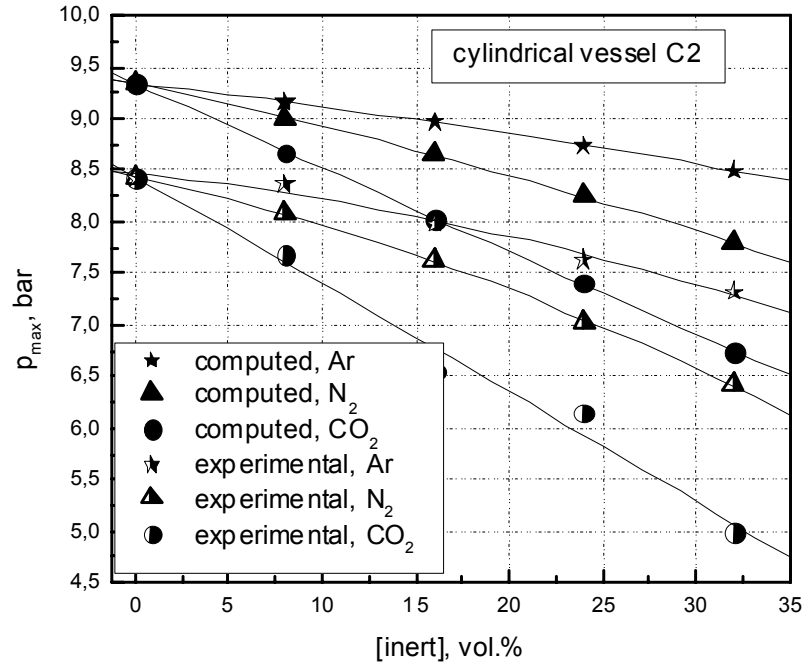


Fig. 5 – Calculated explosion pressures for ethylene-air-diluent mixtures at $p_0 = 1$ bar, compared to experimental explosion pressures measured in vessel C2.

Further re-arrangements of eq. (4) outline the dependency of flame temperature, T_f , on inert gas concentration, at constant initial pressure:

$$\frac{T_f}{T_0} = 1 + \frac{\kappa}{1 + \kappa} \cdot \frac{\Delta_c U'}{\xi \cdot C_{e,V} T_0} \left(1 - \frac{n_i}{100}\right), \quad (5)$$

$$T_f = T_0 + \frac{\kappa}{1 + \kappa} \cdot \frac{\Delta_c U'}{\xi \cdot C_{e,V}} \left(1 - \frac{n_i}{100}\right) = \alpha + \beta \cdot \left(1 - \frac{n_i}{100}\right) \quad (6)$$

Plots of adiabatic flame temperature of isochoric combustion (T_f) of ethylene-air-inert mixtures are similar to those given in Fig. 5, referring to adiabatic explosion pressures. The data confirm that CO_2 is the most efficient additive among the examined gases, due to its larger heat capacity.

The found correlations between the explosion pressures and the initial pressures are extremely useful for predicting the explosion pressures of ethylene-air-inert flammable mixtures at pressures higher than ambient, as long as the laminar deflagration regime is maintained. Their slopes and intercepts depend both on the concentration and on nature of added inert gas. The correlations between explosion pressures (measured or calculated) or the flame temperatures and the inert concentration are also useful tools for predicting the flammability envelope of ethylene-air mixtures in the presence of inert additives.

CONCLUSIONS

Measurements of pressure-time histories of several ethylene-air-inert mixtures, at various initial pressures, in closed vessels of different shapes and volumes show a similar behaviour of investigated diluents (Ar , N_2 and CO_2). Linear correlations were found between maximum explosion pressures and initial pressures; such correlations are extremely useful for predicting the explosion pressures of ethylene-air-inert flammable mixtures at pressures higher than ambient, when direct measurements are not available. The slopes and intercepts of found correlations depend both on the concentration and on nature of added inert gas.

The measured explosion pressures were compared with the adiabatic explosion pressures, computed assuming that chemical equilibrium is reached in the flame front. Experimental explosion pressures are lower than adiabatic values due to heat losses from burned gas to explosion vessel, during flame propagation. The effectiveness of the three examined inert gases vary in order $\text{Ar} < \text{N}_2 < \text{CO}_2$, according to the heat capacities of these compounds. Their effect is more pronounced with increasing the inert concentration.

Linear correlations were found between the measured explosion pressures and the inert concentration, when systems with the same initial pressure are examined, burning in the same closed

vessel. Similar dependencies, derived for the variation of calculated explosion pressures and flame temperatures versus inert gas concentration from the heat balance of closed-vessel combustion, were also found for all examined ethylene-air-inert mixtures.

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