

Inert Gas Influence on Propagation Velocity of Methane-air Laminar Flames

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The flame propagation in methane-air mixtures diluted by inert additives (He, Ar, N₂, CO₂) was studied by means of pressure-time records of laminar deflagrations occurring in a spherical vessel with central ignition. Experiments were made using mixtures with various equivalence ratios between 0.610 and 1.310 and various inert concentrations between 5 and 25 vol%, at various initial pressures between 50 and 200 kPa. Examination of pressure-time records in the early stage of explosions delivered the normal burning velocities S_u via the coefficients of the cubic law of pressure rise, using a previously described procedure. The propagation velocities (or the flame speed) were calculated from the normal burning velocities using the expansion coefficients of the unburnt gas during the isobaric combustion. The propagation velocities of examined systems obtained from experimental data were examined against the propagation velocities obtained from kinetic modeling of methane-air-inert combustion by means of 1D COSILAB package using the GRI 3.0 mechanism.

Keywords: combustion, laminar deflagration, propagation velocity, methane, inert additive, closed vessel

Dilution of fuel-air mixtures by inert gases has a prominent influence on the explosion propagation in confined or unconfined conditions. Diluent addition at total constant pressure results in the decrease of volumetric concentrations of both fuel and oxidizer, as well as in changes of thermo-physical properties (heat capacity, thermal conductivity) of the flammable mixture and influences also the chemistry of the combustion process [1,2]. The primary effect of dilution is the decrease of flame temperature determined by a less amount of evolved heat, accompanied by the decrease of explosion pressure and of the maximum rate of pressure rise along with the increase of explosion time [2,3]. The dilution of fuel-air mixtures by inert additives determines the decrease of the overall reaction rate, resulting in the decrease of the normal burning velocity and of the propagation velocity, until the system reaches its flammability limits [4,5]. Indeed, the dilution of fuel-oxidizer mixtures by inert additives is one of most recommended methods to suppress fires and explosions: a progressive dilution of the explosive mixture removes eventually this mixture out of its flammability range. Dilution of flammable mixtures with exhaust (burnt) gases, by so-called EGR (Exhaust Gas Recirculation), is a procedure recommended for reduction of NOx emissions [6] of IC engines.

The normal burning velocity and the propagation velocity represent important properties, relevant for the rate of fuel conversion to oxidation products and for the rate of heat generation. The normal burning velocity, S_u , was defined as the speed of a planar one-dimensional flame relative to the unburnt gas mixture, along to the normal to its flame front [7,8]. It is an essential parameter for engine design, for modeling the laminar and the turbulent combustion, and for validation of kinetic models. The propagation velocity (or flame speed), S_g , was defined as the velocity of the flame front in respect to the vessel where combustion takes place [2,8] and depends on the normal velocity, S_u , and on the gas expansion velocity, S_g . The propagation

velocity of a flame is requested for assessing the risk factors in operating chemical reactors or in enclosures like rooms or mine galleries where flammable mixtures may form and for predicting the flame flash-back and blow-off [2,3]. Both the normal burning velocity and propagation velocity depend on the same operational parameters: fuel type, fuel-oxidizer ratio, mixture composition, pressure and temperature of the unburned mixture [3-7]; the propagation velocity depends also on the flow pattern. The propagation velocity is the vector sum of normal burning velocity and expansion gas velocity. For spherically expanding flames, when the two components have the same direction, these properties are related by [2,3]:

$$S_g = S_u + S_g \quad (1)$$

where S_g , the gas velocity, is the velocity of the flame front determined by the expansion of the burnt gas behind the flame front and the compression of the unburnt gas ahead of it.

In the present paper, the influence of inert gases on the propagation velocity of methane-air mixtures with various methane/oxygen ratios within the flammability range was examined. Methane was chosen as a test fuel because it is frequently encountered in domestic events and in coal mines, being also the main component of natural gas, widely used in IC engines and power generation systems. The flame propagation in methane-air mixture was intensively studied by various experimental techniques and flame configurations: stationary flames anchored on a burner [9-11]; stagnation flames [12-14] outwardly spherically propagating flames [8,15-19]. Numerous experimental and numerical studies examined the inert influence on normal burning velocity of methane in air [9-12,15,16,19-21] using nitrogen, carbon dioxide, argon, helium or water vapor as additives for CH₄-air mixtures with various equivalence ratios*. Less data are available about the inert influence on propagation velocity of CH₄-air mixtures, especially at concentrations different from

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* the equivalence ratio $\phi = \frac{[CH_4][O_2]}{([CH_4][O_2]_{stoich})}$ is the actual fuel to oxidizer ratio divided by the fuel to oxidizer ratio of the stoichiometric mixture, i.e. a composition where the fuel and the oxidizer are completely converted to CO₂ and H₂O (assuming no dissociation in the flame)

stoichiometric. The present study reports: (i) the propagation velocities of methane-air mixtures of various equivalence ratios within 0.61 to 1.31, at various initial pressures within 50 to 200 kPa, and (ii) the propagation velocities of methane-air-inert mixtures of various equivalence ratios within 0.61 to 1.31 and various inert concentrations within 5 - 25 vol%, at ambient initial pressure. For all systems of interest the propagation velocities obtained from experiments are compared to the propagation velocities obtained by the kinetic modeling of flames. These results supplement our previous data concerning the normal burning velocities of methane-air and methane-air-inert gaseous mixtures [22].

Experimental part

The experimental setup is formed from several main components: the combustion vessel, the vacuum and gas-feed line, the ignition controller and the data acquisition system, connected with a PC. The explosion vessel is a 10 cm diameter stainless steel sphere ($V = 0.52$ L) designed to withstand pressures up to 4 MPa under static tests. The vessel was fitted with several ports for the gas feed and evacuation valve, the pressure transducer, two electrodes and an ionization probe. The stainless-steel electrodes formed the spark gap of 2.5-3.0 mm width in the geometric center of the vessel. The ionization probe, formed by two thin steel rods, had its tip at 3 mm from vessel wall. Pressure-time records were performed by means of a Kistler 601A piezoelectric pressure transducer coupled with a Kistler 5001SN Charge Amplifier and a data acquisition system TestLab™ Tektronix 2505. The ignition was made by inductive-capacitive sparks generated by a standard automotive electronic ignition system. Other details were previously given [23-25].

CH₄-air mixtures were obtained in a 10 L storage cylinder using the partial pressure method, at a total pressure of 400 kPa. CH₄-air-inert mixtures were prepared directly in the combustion vessel by adding the inert gas to any CH₄-air mixture at appropriate partial pressures to reach the total initial pressure of 100 kPa. Before ignition the flammable mixtures were allowed 30 min. to mix and become quiescent.

Methane (99.99%), He (99.9995%), Ar (99.99%), N₂ (99.99%), and CO₂ (99.99%)

(SIAD Italy) were used without further purification.

Experiments using CH₄-air mixtures were made at initial pressures between 50 and 200 kPa, and variable initial concentration within 6-12 %. Experiments using CH₄-air-inert mixtures were made at ambient initial pressure, using inert concentrations within 0 - 40 % (He, Ar, N₂) and 0-30 % (CO₂).

Data evaluation

The propagation velocity of methane-air-inert flames at the initial moment of flame propagation, S_s , was calculated from S_u , the normal burning velocity and E_0 , the expansion coefficient of the unburnt fuel-air mixture in the isobaric combustion at pressure p_0 , as [2,3]:

$$S_s = S_u \cdot E_0 \quad (2)$$

where E_0 is defined as the ratio of the unburnt and burnt gas densities:

$$E_0 = \frac{\rho_u}{\rho_b} = \frac{T_{f,p}}{T_0} \cdot \frac{n_e}{n_0} \quad (3)$$

Here $T_{f,p}$ is the adiabatic flame temperature of isobaric combustion, n_0 - the initial mole number and n_e - the final (end) mole number.

The normal burning velocity of gaseous flammable mixtures at initial pressure p_0 is related to the coefficient k of the cubic law of pressure rise by eq. (4), derived by assuming the isothermal compression of the unburned gas ahead of flame front, in the early stage of flame propagation [26]:

$$S_u = R \cdot \left(\frac{k}{\Delta p_{\max}} \right)^{1/3} \cdot \left(\frac{p_0}{p_{\max}} \right)^{2/3} \quad (4)$$

where R is vessel's radius, k is the coefficient of the cubic law of pressure rise, Δp_{\max} is the maximum (peak) pressure rise of the explosion and $p_{\max} = p_0 + \Delta p_{\max}$. As input values for eq. (4) we used the experimental values of Δp_{\max} and p_{\max} . The cubic law coefficient, given by equation: $\Delta p = kt^3$ was determined for each experiment by a nonlinear regression method using a relationship of the form [23-26]:

$$\Delta p = a + k \cdot (t-b)^3 \quad (5)$$

where a and b are pressure and time corrections respectively, meant to eliminate the signal shift of pressure transducer and any possible delay in signal recording. The computation was restricted to a pressure range $p_0 \leq p \leq 2p_0$ for all experiments.

Computing programs

The adiabatic flame temperatures and the ratio n_e/n_0 in isobaric combustion of CH₄-air and CH₄-air-inert mixtures were calculated with the 0D COSILAB package based on a general algorithm meant to compute the equilibrium composition of products for fuel-oxidant gaseous mixtures using the thermodynamic criteria of chemical equilibrium. Fifty-three compounds were considered as combustion products [27].

The kinetic modelling of methane-air/inerts laminar adiabatic premixed flames in various conditions was made by means of 1D COSILAB package. COSILAB was run using the GRI 3.0 mechanism (53 chemical species and 325 elementary reactions) [27]. The runs were performed for isobaric combustion of methane-air mixtures at various initial pressures within 50 and 200 kPa and at initial temperatures 300 K and for methane-air-inert mixtures at initial pressure 100 kPa and temperature 300 K. The input data were taken from thermodynamic and molecular databases of Sandia National Laboratories, USA, according to the international standard (format for CHEMKIN). More details were given in [22-24, 28,29].

Results and discussions

Methane-air

The experimental initial propagation velocities of methane-air versus methane concentration, at ambient initial temperature and various initial pressures are plotted in figure 1 (fig. 1(a) - experimental data; fig. 1(b) - computed data), where the fit curves as 2nd order polynomials are also given. For all examined pressures, peak values of the propagation velocities are observed at methane concentration 10.0 vol% ($\phi = 1.06$).

In comparison with propagation velocities reported by Agrawal [30] from optical records of flame front position during explosions in a closed spherical vessel (150 cm/s for a lean mixture with $\phi = 0.8$, 210 cm/s for the stoichiometric mixture and 195 cm/s for a rich mixture with $\phi = 1.2$) the present results are higher: $S_s = 241$ cm/s (for a lean mixture with $\phi = 0.83$); $S_s = 281$ cm/s (for stoichiometric mixture, $\phi = 1.0$) and $S_s = 185$ cm/s (for a rich mixture with $\phi = 1.3$). Our data match better the propagation velocities determined by Taylor [8] and Gu [31] for the stoichiometric CH₄-air mixture: $S_s = 270$ cm/s,

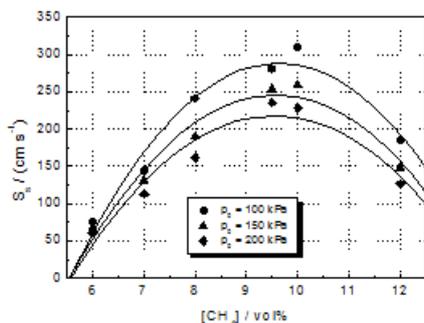


Fig. 1(a). Propagation velocities of CH₄-air at various initial pressures; experimental data

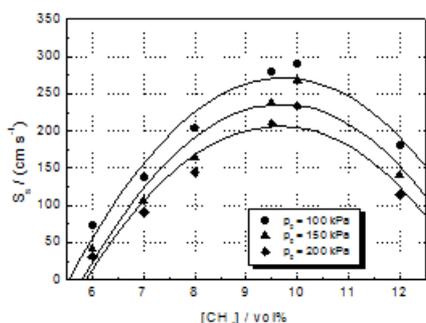


Fig. 1(b). Propagation velocities of CH₄-air at various initial pressures; calculated data

as propagation velocities of spherically expanding flames, extrapolated to the initial moment of the process, under no flame stretch.

A comparison between the experimental and calculated propagation velocities is given in figure 2. The computed propagation velocities are systematically slightly lower than the measured ones, but the variation trend is the same for both data sets. The improvement of reaction mechanism would result in a better match between experimental and computed data.

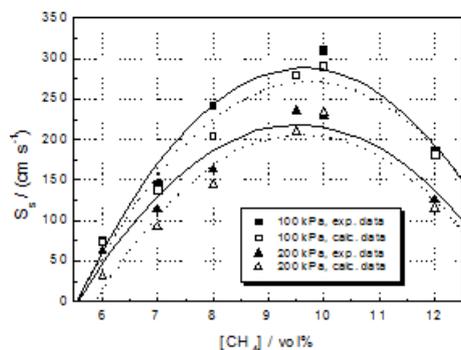


Fig. 2. Propagation velocities of CH₄-air at various initial pressures; experimental and calculated data

At constant composition and initial temperature, the propagation velocities decrease with increase of the initial pressure. For several lean- and for the stoichiometric CH₄-air mixture, relevant data obtained from experiments are plotted in figure 3(a). Similar diagrams of propagation velocities obtained from kinetic modeling of flames are plotted in figure 3(b).

The pressure dependence of propagation velocities for methane-air mixtures was rationalized by means of the empirical power law [23,32,33]:

[CH ₄] / vol.%	$S_{s,ref} / (\text{cm s}^{-1})$	$-\beta$	r_n^2
6.0	75.4 ± 0.1	0.296 ± 0.002	0.999
7.0	142.9 ± 2.9	0.353 ± 0.042	0.930
8.0	240.6 ± 0.1	0.575 ± 0.001	0.999
9.5	281.0 ± 0.1	0.254 ± 0.001	0.999
10.0	310.4 ± 0.4	0.442 ± 0.002	0.999
12.0	184.8 ± 0.3	0.549 ± 0.004	0.999

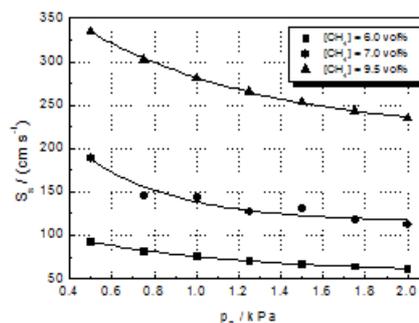


Fig. 3(a). Pressure influence on propagation velocities of CH₄-air; experimental data

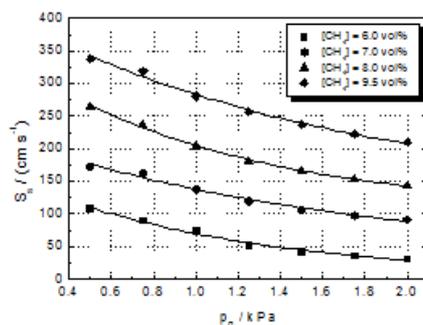


Fig. 3(b). Pressure influence on propagation velocities of CH₄-air; calculated data

$$S_s = S_{s,ref} \left(\frac{p}{p_{ref}} \right)^\beta \quad (7)$$

where $S_{s,ref}$ is the propagation velocity at reference conditions ($p_{ref} = 100 \text{ kPa}$) and β is the baric coefficient. The baric coefficients of experimental and calculated propagation velocities, determined by a non-linear regression analysis of S_s versus p data, are given in Table 1 and table 2. The baric coefficients reach peak values close to -0.25 (experimental propagation velocities, stoichiometric mixture) and -0.26 (computed propagation velocities, slightly rich mixture, $\phi = 1.06$) close to those determined for lean- and stoichiometric ethane-air mixtures at ambient initial temperature [23]. The baric coefficients β of propagation velocities for CH₄-air mixtures with a variable methane concentration are close to the baric coefficients of normal burning velocities previously reported [22], a fact determined by the weak dependence of expansion coefficients E_0 on initial pressure. No correlation was found between the baric coefficients β and the concentration (or the equivalence ratio) of CH₄-air mixtures.

Methane-air-inert mixtures

The propagation velocities of a lean- and stoichiometric methane-air mixtures diluted with different amounts of inert gases (He, Ar, N₂, CO₂) at ambient initial pressure and temperature follow the same trend as normal burning velocities: they decrease when the amount of inert gas increases. Representative data sets obtained from experiments are plotted in Figure 4(a) for CH₄-air-Ar and in

Table 1
REFERENCE PROPAGATION VELOCITIES AND THEIR BARIC COEFFICIENTS FOR CH₄-AIR MIXTURES AT 300 K (EXPERIMENTAL DATA), WITH r_n^2 -THE COEFFICIENT OF DETERMINATION

[CH ₄] / vol.%	$S_{S,ref\ calc} / (\text{cm s}^{-1})$	$-\beta$	r_r^2
6.0	64.0 ± 2.9	0.834 ± 0.087	0.952
7.0	131.7 ± 3.1	0.465 ± 0.049	0.948
8.0	199.8 ± 2.4	0.442 ± 0.025	0.984
9.5	275.0 ± 3.8	0.347 ± 0.029	0.966
10.0	291.0 ± 3.3	0.262 ± 0.024	0.959
12.0	175.5 ± 2.6	0.565 ± 0.040	0.980

Table 2
REFERENCE PROPAGATION VELOCITIES
AND THEIR BARIC COEFFICIENTS FOR
CH₄-AIR MIXTURES AT 300 K (CALCULATED
DATA)

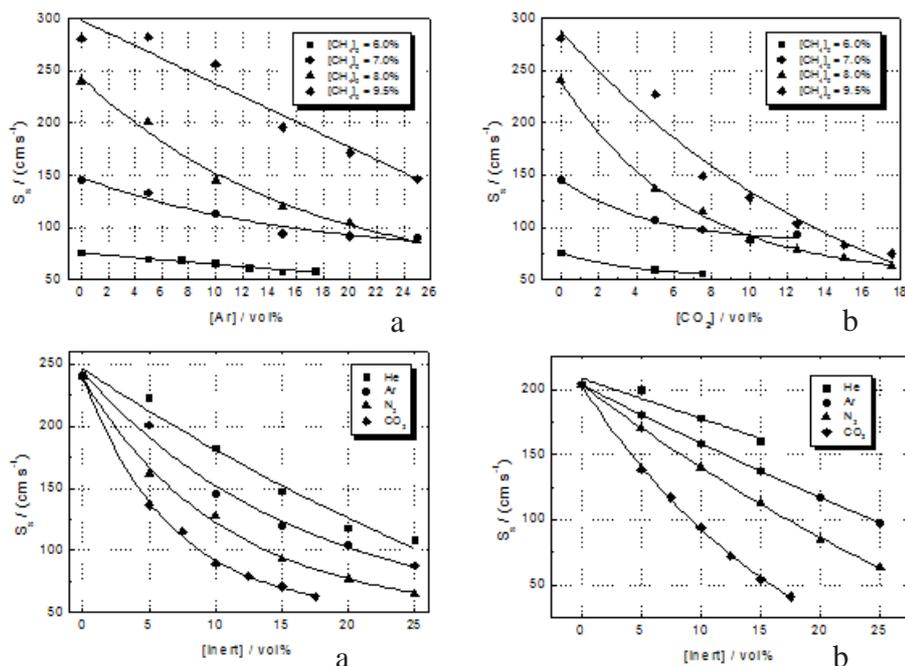


Fig. 4. Influence of inert gas addition on propagation velocities of lean- and stoichiometric CH₄-air mixtures: (a) Ar; (b) CO₂ at $p_0 = 100$ kPa; experimental data

Fig. 5. Influence of inert gas addition on propagation velocities of a lean CH₄-air mixture ($\phi = 0.832$) at $p_0 = 100$ kPa; (a) experimental data (b) calculated data

figure 4(b) for CH₄-air-CO₂ mixtures; similar plots were obtained for He- and N₂- diluted CH₄-air mixtures.

The propagation velocities of a lean CH₄-air mixture in the presence of several inert gases at $p_0 = 100$ kPa and 300 K are plotted in figures 5(a) (experimental data) and 5(b) (calculated data) as function of added inert concentration. Similar plots were obtained for all examined CH₄-air mixtures. The effect of dilution by inert gases on propagation velocities varies in the order of CO₂ > N₂ > Ar > He for the same dilution. For all data sets, dilution by carbon dioxide determined the highest decrease of the propagation velocity whereas helium had the smallest influence. The decrease of propagation velocities determined by dilution with an inert gas can be linked with the decrease of adiabatic flame temperatures of CH₄-air-inert mixtures. The plots of adiabatic flame temperatures $T_{f,p}$ in the isobaric combustion of CH₄-air-inert mixtures at constant initial concentration of CH₄ against the inert content, shown in figure 6, follow the same variation trend as the propagation velocities. A similar variation was found for the normal burning velocities of inert-diluted CH₄-air mixtures [9,11,12,15,16,19-22]. At constant pressure, the increase of the additive concentration determines the decrease of the initial fuel concentration, resulting in a decrease of the available amount of released heat and the reaction rate, followed by the decrease of flame temperature and of propagation velocity. Besides this effect, inert addition influences the thermal diffusivity of the reacting mixture, $D = \lambda / \rho \cdot c_p$ (λ is the thermal conductivity, ρ is the density and c_p is the specific heat capacity of the unburned gas). The differences in thermal diffusivities are

observed by examining the propagation velocities of CH₄-air flames diluted by He and Ar, gases with the same heat capacity. Argon, with a higher molecular weight than helium, has a lower thermal diffusivity, resulting in lower burning velocities for Ar-diluted mixtures compared with He-diluted mixtures. In the case of CO₂ dilution, the heat capacity effect seems to be dominant, and its ability to dissociate and to dissipate heat by radiation contribute to the inerting effect.

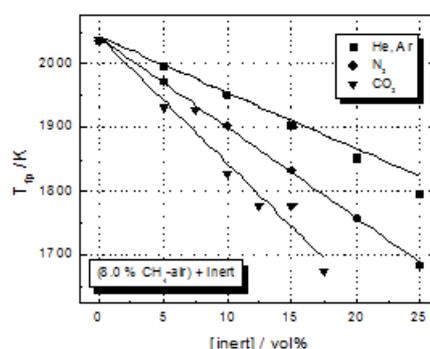


Fig. 6. Influence of inert gas addition on adiabatic flame temperatures of a lean CH₄-air mixture ($\phi = 0.832$)

Conclusions

The propagation velocities of methane-air flames were determined for a range of initial methane concentrations ([CH₄] = 6.0 to 12.0 vol%) and initial pressures ($p_0 = 50$ to 200 kPa) using pressure-time records obtained in a spherical closed vessel. For all initial conditions, the experimental propagation velocities were lower than computed propagation velocities obtained from the kinetic

modeling of methane-air flames, but the observed deviations were within 5 - 7%.

The pressure influence on propagation velocities of methane-air was examined by means of a power law and the baric coefficients of experimental and calculated propagation velocities were found to range between -0.60 and -0.25 but no dependence was found between the baric coefficients and the methane concentration of flammable mixtures. The data have a great practical interest for predicting the propagation velocity of methane-air at initial pressures different from ambient, with direct application to safety recommendations for reactors, and enclosures like rooms or mine galleries where flammable methane-air mixtures are formed.

The propagation velocities of methane-air-inert flames, with He, Ar, N₂ and CO₂ as inerts, were determined for a range of initial methane concentrations ([CH₄] = 6.0 to 12.0 vol%) and initial inert gas concentrations (0 to 25 vol%) at ambient initial pressure using the experiments in a spherical closed vessel and the kinetic modeling of flames. Dilution by increasing amount of inert additive determines the decrease of propagation velocity and of adiabatic flame temperature, for all examined compositions of the methane-air mixtures. Among inert gases, CO₂ has the highest inerting effect followed by N₂, Ar and He. The observed differences of propagation velocities and of adiabatic flame temperatures for the inert additives can be assigned to differences of their thermal diffusivities, determined by the differences of thermal conductivity, density and heat capacity. In addition, the inerting effect of CO₂ is enhanced by its endothermic dissociation under flame temperature.

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