

# Effects of pressure and carbon dioxide, hydrogen and nitrogen concentration on laminar burning velocities and NO formation of methane–air mixtures<sup>†</sup>

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## Abstract

We studied the effects of increasing pressure and adding carbon dioxide, hydrogen and nitrogen to Methane-air mixture on premixed laminar burning velocity and NO formation in experimentally and numerically methods. Equivalence ratio was considered within 0.7 to 1.3 for initial pressure between 0.1 to 0.5 MPa and initial temperature was separately considered 298 K. Mole fractions of carbon dioxide, hydrogen and nitrogen were regarded in mixture from 0 to 0.2. Heat flux method was used for measurement of burning velocities of Methane-air mixtures diluted with CO<sub>2</sub> and N<sub>2</sub>. Experimental results were compared to the calculations using a detailed chemical kinetic scheme (GRI-MECH 3.0). The results in atmosphere pressure for Methane-air mixture were calculated and compared with the results of literature. Results were in good agreement with published data in the literature. Then, by adding carbon dioxide and nitrogen to Methane-air mixture, we witnessed that laminar burning velocity was decreased, whereas by increasing hydrogen, the laminar burning velocity was increased. Finally, the results showed that by increasing the pressure, the premixed laminar burning velocity decreased for all mixtures, and NO formation indicates considerable increase, whereas the laminar flame thickness decreases.

*Keywords:* Burning velocity; Dilution; Heat flux; Laminar; Methane-air mixture; NO formation; Pressure

## 1. Introduction

With the depletion of crude oil reserves and the strengthening of automotive emission legislations, the use of natural gas (NG) as an alternative fuel has been promoted both in combustion engines and power generation. Natural gas contains mainly methane (typically 65-90 percent or more by volume) along with higher hydrocarbons, inert gaseous components like N<sub>2</sub>, CO<sub>2</sub>, water vapor and trace compounds. The composition of natural gas varies widely from one source to another in terms of the fractions of higher hydrocarbons summarized as “C2+” gases (at present vary from 7 to 16 percent) and inert gaseous components like N<sub>2</sub>, CO<sub>2</sub> (at present 20-25 percent maximum). This variation of both C2+ and inerts is expected to widen in the future [1]. Hence interest in fuel-flexible gas turbine engines has led to research on premixed combustion parameters like laminar burning velocity and ignition delay time. Fuel flexibility can impact several important premixed burner design issues such as flashback, blow off, auto ignition and stability.

Laminar burning velocities are important because they are related not only to flashback and blow off issues, but they also

play a role in the stability of the flame in the combustor [2]; of course, it will face some problems, such as low thermal efficiency or lean combustion capability [3]. The combustion of lean hydrocarbon-air mixtures offers the potential of reduced flame temperatures and NO<sub>x</sub> emissions according to the thermal mechanism. But there are two separated deficiencies in getting use of that; the first one is significant decrease of laminar burning velocity and the second one, increase of incomplete combustion. Many attempts have been made to solve these two problems and one of the most effective solutions has been fuel enrichment [4]. Laminar burning velocity is important, because not only is it related to feedback of the flame and combustion, but it plays an important role in stability of the flame in the combustion, and it is considered to be a criterion for providing the details of the reaction mechanism. Fast burning causes decrease in combustion duration, increase in thermal efficiency and decrease in fuel consumption [5].

There exist three effects of diluents on the laminar burning velocity (including dilution, thermal-diffusion, and chemical effects). The dilution effect is that, when diluent is added, the percentage of fuel and oxidant in the mixture is decreased, which decreases the laminar burning velocity. The thermal-diffusion effect is that, when diluent is added, the specific heat capacity and thermal diffusivity of the mixture vary and affect the laminar burning velocity. The chemical effect is that the

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diluent will participate in chemical reactions and affect the laminar burning velocity [6].

Two types of methods are used for determining laminar velocity: stationary flame methods and moving flame methods. In the former category, the flame front remains stationary in space, Bunsen burner method, heat flux method etc. In the latter, the flame moves with respect to some fixed point (i.e., the point of ignition): soap bubble method, constant volume method, constant pressure method etc. [7, 8]. The burning velocity directly affects the flame propagation speed and hence, the operation of the SI engine. Faster burning in SI engines leads to a more robust and repeatable combustion and permits engine operation with substantially larger amount of exhaust gas recirculation (EGR), bringing the reduction in  $\text{NO}_x$  emission [9]. Enrichment of methane fuel by hydrogen, nitrogen and carbon dioxide has been investigated by many researchers experimentally [10, 11], and the studies have indicated that laminar burning velocity of methane-hydrogen mixture will be increased, by increase of hydrogen fractional ratio [11, 12]. This paper is an experimental research indicating the effect of dilution of methane-air mixture with  $\text{N}_2$ ,  $\text{CO}_2$  and also numerically with  $\text{H}_2$  on flame burning velocity. Also the effect of pressure has been identified in these diluted mixtures. Moreover,  $\text{NO}$  formation under these different conditions has been investigated numerically.

## 2. Experimental setup

The heat flux method for the stabilization of adiabatic premixed laminar flames on a flat flame burner was proposed by Bosschaart et al. [13]. This method was extensively used for measuring laminar burning velocities of gaseous fuels [14–16] and has recently been extended towards liquid fuels [17]. The designed burner consists of three separate parts which are overlapped on each other and have formed one unique burner. These three parts are burner head, burner plate and plenum chamber as shown in Fig. 1. The brass burner plate (3 mm of thick) on which the flame is stabilized is a perforated disc with a hexagonal pattern of 0.5 mm diameter holes with 0.7 mm pitch as shown in Fig. 2. It has been shown that this kind of pattern stabilizes a flat flame on the burner [18].

An essential ingredient in the heat flux method is the attachment of thermocouples to the burner plate to determine the temperature distribution. Five K-type thermocouples of 0.4 mm wire were attached into selected holes using special glue on perforated plate on the upstream side. The thermocouples were positioned at different radii and different circumferential locations to measure the temperature profile on the burner plate. The upper half of the burner head has a heating jacket and a Teflon insulation ring that separates it from the lower half with cooling jacket. The burner head has a heating jacketed supplied with thermostatic water to keep the temperature of the burner plate constant. The heating jacket, water temperature was maintained at 358 K and the plenum chamber has a separate cooling system supplied with water at room tempera-

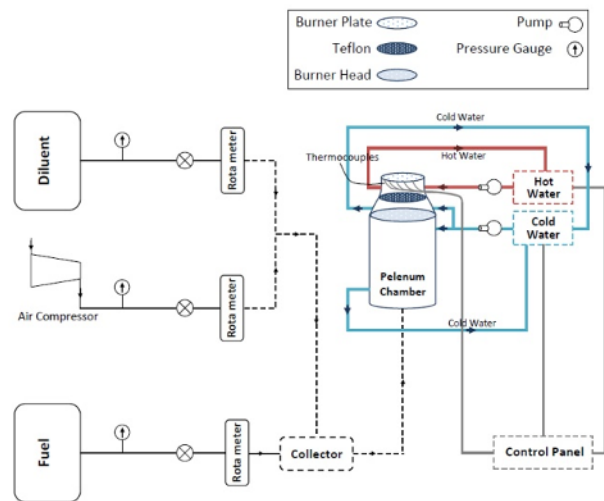


Fig. 1. Schematic of heat flux setup.

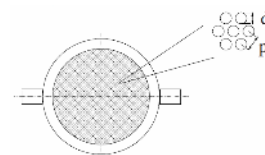


Fig. 2. Burner plate with a hexagonal pattern with  $d = 0.5$  mm and  $P = 0.7$  mm.

ture (around 307 K). This fixes the initial temperature of the fresh gas mixture. The heating jacket keeps the burner plate edges at a certain temperature higher than the initial gas temperature, thus warming up the (unburned) gases flowing through. Conductive heat transfer of the flame to the burner plate cools the gas flow on its turn. If the flame is stabilized under sub-adiabatic conditions, the gas velocity is lower than the adiabatic flame burning velocity, and the sum of the heat loss and heat gain is higher than zero. Then, the center of the burner plate is hotter than the heating jacket. If the unburned gas velocity is higher than the adiabatic burning velocity (super-adiabatic conditions), the net heat flux is lower than zero and the center of the burner plate is cooler than the heating jacket.

By varying the flow rate of the gas mixture, an appropriate value of gas velocity could be found where net heat flux is zero. This will manifest in the form of uniform radial distribution of temperature. The flow velocity at which the net heat flux is zero is shown to be adiabatic burning velocity. The temperature distribution of the burner plate is measured with the thermocouples attached to it and radial temperature profile of the plate obtained by solving the energy Eq. (1)

$$T_p(r) = T_{center} - \frac{q}{4\lambda x_p} r^2. \quad (1)$$

Here  $T_p$  is the temperature profile across the burner plate,  $T_{center}$  is the plate center temperature,  $q$  is the net heat flux into

the plate,  $\lambda$  is the thermal conductivity of burner plate,  $x_p$  is the plate thickness and  $r$  is the radial coordinate. Eq. (1) is expressed in the following general form:

$$T_p(r) = T_{center} + ar^2. \quad (2)$$

The coefficient  $a$  depends on the unburned gas velocity  $v$ . By plotting  $a$  against  $v$ , the adiabatic burning velocity  $S_L$  can be found by interpolation to  $a = 0$ , as described by Bosschaart [12].

### 3. Computational method

The PREMIX code [19] was used to calculate laminar flame velocities and to compare to our experimental results. PREMIX uses a hybrid time integrating/Newton iteration technique to solve the steady state mass, species and energy conservation equations and can simulate the propagating flame. Equations were solved by using the TWOPNT, a boundary value problem solver in the CHEMKIN package [20].

One of the critical elements for simulation is the proper reaction mechanism that can describe the essential fundamental reaction paths followed by the overall reaction. The chemical kinetic mechanism used is the GRI-MECH mechanism. GRI-MECH is an optimized detailed chemical reaction mechanism for the calculation of natural gas chemical reaction process and the latest version is GRI-MECH 3.0 [21]. GRI-MECH 3.0 consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermochemical parameters for 53 species. It includes the detailed combustion reaction mechanism for hydrogen. The ranges of GRI-MECH 3.0 are 1000-2500 K in temperature, 10 Torr to 10 atm in pressure and 0.1-5.0 in equivalence ratio. The initial flow rate of the unburned mixture was chosen equal to 0.04 g/cm<sup>2</sup>s, according to the measurement of stoichiometric methane/air flame speed by Egolfopoulos et al. [22]. To start the iteration the temperature profile estimation obtained by van Maaren et al. [14] for a stoichiometric methane/air flame was adopted, as suggested by Uykur et al. [23]. The temperature profile resulting from the first simulation step was used for the next step. At the inlet boundary temperature (298 K), pressure (0.1, 0.3 and 0.5 MPa) and composition of the unburned mixture were assigned. At the exit boundary it was specified that all gradients vanish. It is observed that by using adaptive grid parameters GRAD = 0.02 and CURV = 0.1, the burning velocity obtained is grid independent. Hydrogen mole fractions, nitrogen and carbon dioxide (from 0 to 20 percent) with other components existing in unburned mixtures of hydrogen-methane/air, nitrogen-methane/air and carbon dioxide-methane/air will be estimated. The length of calculations have been regarded 2 cm before the spot of reaction or generally equal to 12 cm. The conservation of mass is expressed by the general continuity equation [10]:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \quad (3)$$

where,  $\rho$  is the mixture mass density and  $u$  is the gas mixture velocity. The conservation of momentum, with no body forces other than gravity, is covered by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u u) = \nabla \cdot \Pi + \rho g \quad (4)$$

where  $\Pi$  is the stress-tensor and  $g$  is the acceleration due to gravity. The stress-tensor consists of a hydrodynamic and viscous part:  $\Pi = -pI + \tau$ , in which  $p$  is the pressure,  $I$  the unit tensor and  $\tau$  the viscous stress-tensor. The equation describing the conservation of energy is written in terms of specific enthalpy  $h$ ,

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho u h) = \frac{\partial p}{\partial t} + u \cdot \nabla p + \tau : (\nabla u) - \nabla \cdot q \quad (5)$$

where  $q$  is the total heat flux. The term  $\tau : (\nabla u)$  represents the enthalpy production due to viscous effects. When chemical reactions are to be considered, conservation equations for the species mass fractions  $Y_i$  are used. They are defined as  $Y_i = \rho_i / \rho$  with  $\rho_i$  the density of species  $i$ . The density of the mixture  $\rho$  is related to the density of the various species by

$$\rho = \sum_{i=1}^{N_s} \rho_i \quad (6)$$

with  $N_s$  the number of species. This leads to a conservation equation for every species mass fraction in the mixture [10]:

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho u Y_i) + \nabla \cdot (\rho U_i Y_i) = \dot{\omega}_i, \quad i \in [1, N_s]. \quad (7)$$

$U_i$  is the diffusion velocity of species  $i$ . The chemical source term  $\dot{\omega}_i$  in this equation, is characteristic for the reactive nature of the flow. Note that Eq. (7) together with the continuity Eq. (3) gives an over-complete system, so instead of  $N_s$  only  $N_s - 1$  equations in Eq. (7) have to be solved. The mass fraction of one of the species can be computed using the following constraint:

$$\sum_{i=1}^{N_s} Y_i = 1. \quad (8)$$

An abundant species, e.g. nitrogen, is commonly chosen for this species. By definition chemical reactions are mass conserving, so therefore the following relations hold:

$$\sum_{i=1}^{N_s} \rho Y_i U_i = 0, \quad (9)$$

$$\sum_{i=1}^{N_s} \dot{\omega}_i = 0. \quad (10)$$

Finally, state equations are needed to complete the set of differential Eqs. (4)-(7). The first state equation introduces the specific enthalpy  $h$  as a function of temperature  $T$ . This rela-

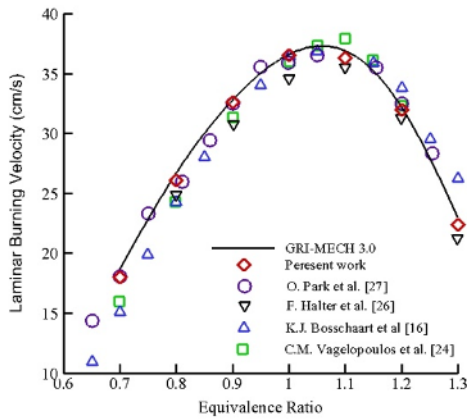


Fig. 3. Laminar burning velocities plotted versus equivalence ratio for CH4/air mixtures at  $P_{mi} = 0.1$  MPa and  $T_{mi} = 298$  K. Line represent calculations with CHEMKIN and Symbols represent experimental data.

tion is given by

$$h = \sum_{i=1}^{N_s} Y_i h_i \quad \text{with} \quad h_i = h_i^{ref} + \int_{T^{ref}}^T c_{p_i}(T) dT. \quad (11)$$

It holds for perfect gases. In this equation  $h_i$  represents the enthalpy of species  $i$  and  $h_i^{ref}$  the formation enthalpy of species  $i$  at a reference value for the temperature  $T^{ref}$  and  $c_{p_i}$  the specific heat capacity at constant pressure of species  $i$ . The mixture heat capacity is defined by

$$c_p = \sum_{i=1}^{N_s} Y_i c_{p_i}. \quad (12)$$

The species heat capacity  $c_{p_i}$  is commonly tabulated in polynomial form. In most combustion problems the mixture and its components are considered to behave as perfect gases. The ideal-gas law relates the density, temperature and pressure to each other by

$$\rho = \frac{p\bar{M}}{RT}. \quad (13)$$

$R$  is the universal gas constant and  $\bar{M}$  the mean molar mass. This  $\bar{M}$  can be determined from

$$\bar{M} = \left( \sum_{i=1}^{N_s} \frac{Y_i}{M_i} \right)^{-1} \quad (14)$$

where  $M_i$  is the molar mass of species  $i$ .

#### 4. Validation of experimental setup

In this section, initial experiments done on methane–air and to validate the experimental facility built are presented. There is abundant literature available on unstretched laminar burning

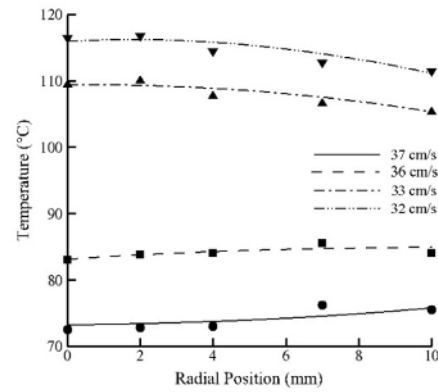


Fig. 4. Flame photo and temperature distribution of methane-air mixture.

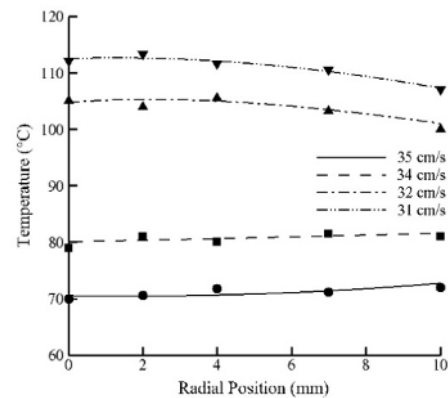


Fig. 5. Flame photo temperature distribution of diluted methane-air mixture with nitrogen.

velocity of methane for validation of the setup [24-27].

The present experimental and numerical results of adiabatic burning velocities of methane-air are plotted in Fig. 3; some experimental data of previous studies are mentioned in this figure which have been conducted in different methods.

Flame photos of methane-air mixture and diluted mixture with nitrogen at  $\phi = 1$  besides of their temperature distribution data in burner plate are shown in Figs. 4 and 5. As men-

tioned before, the velocities that are assumed lower than adiabatic velocities are defined as sub-adiabatic conditions, for instance 32 and 33 cm/s burning velocities in Fig. 4 and the velocities which are higher than adiabatic velocity are under super-adiabatic conditions, for example 37 cm/s burning velocity in Fig. 4.

## 5. The effects of dilution on burning velocity

Effects of dilution of Methane-air mixture with nitrogen and carbon dioxide experimentally and with hydrogen numerically on laminar burning velocity in terms of equivalence ratio have been studied. All the additions and dilutions in the present work are expressed as a fraction of fuel mixture. For example, 20 percent dilution with CO<sub>2</sub> means that the fuel is a gas mixture containing 80 percent methane and 20 percent CO<sub>2</sub> by volume. The air used is 21 percent O<sub>2</sub> and 79 percent N<sub>2</sub> and the relative proportion of air in the fuel–air mixture is defined by the equivalence ratio. Measured adiabatic burning velocities of methane-air with CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> dilution in fuel are plotted, respectively, in Figs. 6–8.

In Fig. 6, the effect of 10 and 20 percent dilution of methane-air mixture with carbon dioxide on laminar burning velocity in  $P_{ini} = 0.1$  MPa and  $T_{ini} = 298$  K has been shown in numerical and experimental methods. It is then compared with experimental data obtained from 20 percent dilution by Kishore et al. [28]. In Fig. 7, the effect of 10 and 20 percent dilution of methane-air mixture with nitrogen on laminar burning velocity in  $P_{ini} = 0.1$  MPa and  $T_{ini} = 298$  K has been shown in numerical and experimental methods. Also, Fig. 8 shows calculated velocities for diluted methane-air mixture with 10 and 20 percent hydrogen and Obtained results have been compared with experimental data of Halter et al. [29] and they show good agreement. When hydrogen is added to the mixture, burning velocity increases; the same behavior was found by Yu et al. [12]. However, their experimental burning velocities are higher than the present ones, even for pure methane–air mixtures. The results of Yu et al. [12] are probably too high due to the experimental configuration of their counter-flow burner.

Results show that diluting methane-air mixture with carbon dioxide and nitrogen decreases laminar burning velocity of premixed methane-air mixture, while diluting this mixture with hydrogen has a reverse result with these two conditions and increases laminar burning velocity of premixed methane-air mixture. In fact, hydrogen is one of the best options for natural gas, in order to increase the burning velocity, and we expect the mixture of natural gas and hydrogen to improve features of lean combustion and decrease polluting emissions of motors [30, 31] (particularly HC and CO). All calculated conditions are shown in Fig. 9 and it is noticeable that for the methane-air mixture, the maximum value of the laminar burning velocity is presented at near-stoichiometric mixture also. Reduction of burning velocity is less in lean side than at stoichiometric and rich side.

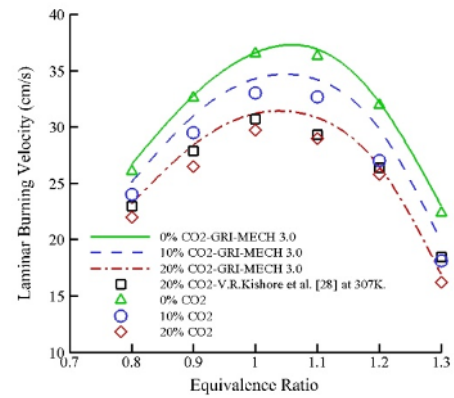


Fig. 6. Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>–CO<sub>2</sub>–air mixtures at  $P_{ini} = 0.1$  MPa and  $T_{ini} = 298$  K. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

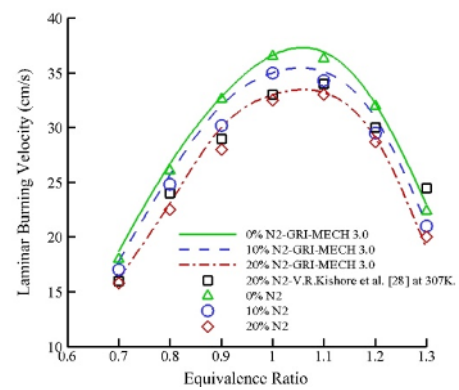


Fig. 7. Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>–N<sub>2</sub>–air mixtures at  $P_{ini} = 0.1$  MPa and  $T_{ini} = 298$  K. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

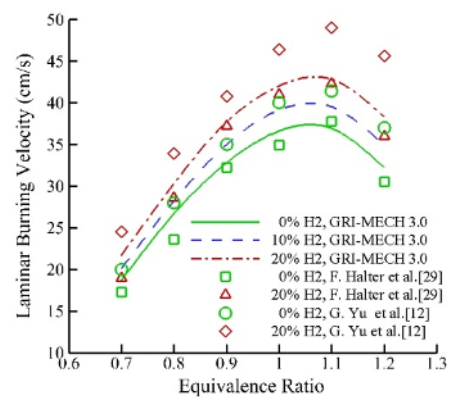


Fig. 8. Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>–H<sub>2</sub>–air mixtures at  $P_{ini} = 0.1$  MPa and  $T_{ini} = 298$  K. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

The laminar burning velocity decreases with the increase of the dilution ratio for both N<sub>2</sub> and CO<sub>2</sub> dilution. Dilution by CO<sub>2</sub> gives larger reduction in burning velocity compared to N<sub>2</sub>.

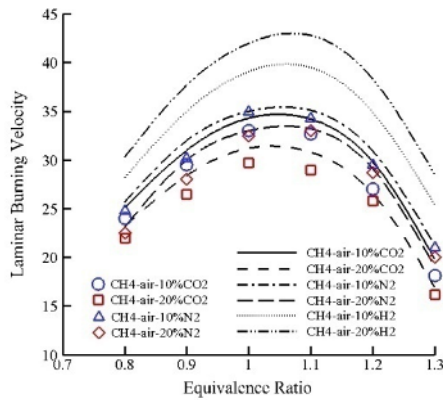


Fig. 9. Effect of 10% and 20% of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> dilution on laminar burning velocity of methane-air mixtures at P<sub>mi</sub> = 0.1 MPa and T<sub>mi</sub> = 298 K. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

This behavior of burning velocity reduction can be attributed to the higher specific heat of CO<sub>2</sub> in comparison to N<sub>2</sub>. Measurements and calculations of burning velocities were in reasonably good agreement for lean to moderately rich mixtures (i.e., up to  $\phi = 1.3$ ), for different concentrations of the diluents.

### 6. The effect of pressure on burning velocity

The effect of increasing pressure on laminar burning velocity of methane-air mixture with 10 and 20 percent dilutions with carbon dioxide, hydrogen and nitrogen in different equivalence ratios is shown in Figs. 10-12, respectively. The results of increasing pressure in three conditions of 0.1, 0.3 and 0.5 MPa are presented. Results show that in all conditions of experimented dilutions, increasing pressure decreases velocity. The variation of the unstretched laminar burning velocity with pressure can be expressed through the empirical expression [32]:

$$S_L = S_L^0 \left(\frac{T_u}{T_0}\right)^{a_p} \left(\frac{P_u}{P_0}\right)^{b_p}, \quad (15)$$

where  $S_L^0$  is the unstretched laminar burning velocity for a pressure  $P_0$  and a temperature  $T_0$ , the parameters  $a_p$  and  $b_p$  depend upon  $\phi$ .

In Figs. 10 and 11, the laminar burning velocities measured (symbols) and calculated (lines) for mixtures diluted with carbon dioxide and nitrogen are plotted. A similar pressure dependence to the one obtained for diluted mixtures is observed. When the pressure increases, the laminar burning velocity decreases both for diluted methane-air mixture with carbon dioxide and nitrogen. The agreement between measurements and calculations is good, especially for atmospheric pressure. A similar trend is seen for diluted methane-air mixture with hydrogen, which is calculated and plotted in Fig. 12. The pressure effect on the flame thickness calculated by nu-

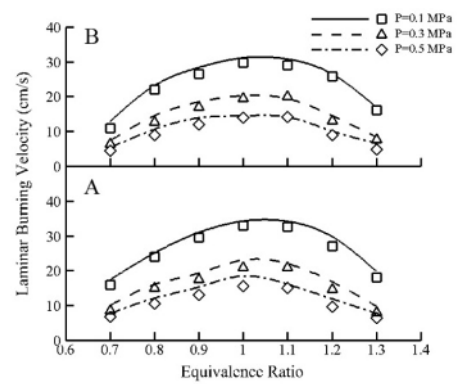


Fig. 10. Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>-CO<sub>2</sub>-air mixtures at T<sub>mi</sub> = 298 K: (a) 10% dilution; (b) 20% dilution. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

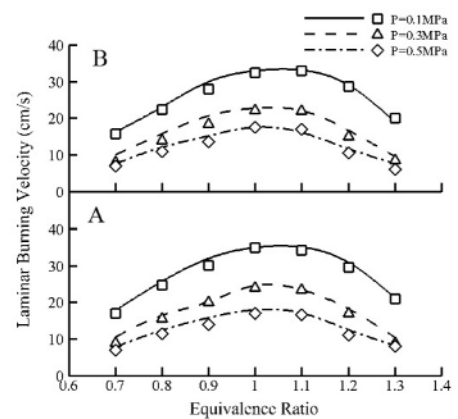


Fig. 11. Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>-N<sub>2</sub>-air mixtures at T<sub>mi</sub> = 298: (a) 10% dilution; (b) 20% dilution. Lines represent calculations with CHEMKIN and Symbols represent experimental data.

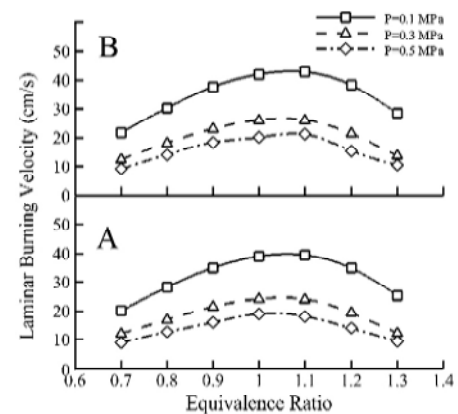


Fig. 12. Numerically calculated Laminar burning velocities plotted against the equivalence ratio for CH<sub>4</sub>-H<sub>2</sub>-air mixtures at T<sub>mi</sub> = 298: (a) 10% dilution; (b) 20% dilution.

merical method for methane-air mixtures is shown in Fig. 13. The laminar flame thickness decreases when the pressure in-

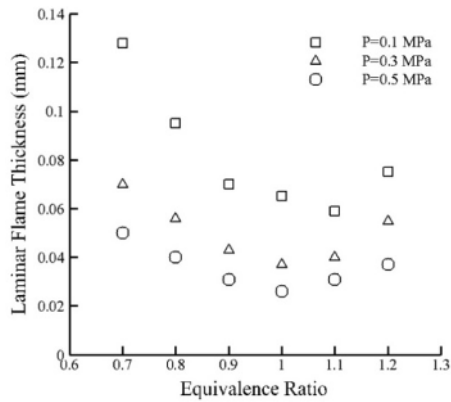


Fig. 13. Numerically calculated Laminar flame thickness plotted against the equivalence ratio for CH<sub>4</sub>-air mixtures at T<sub>ini</sub> = 298 K.

creases. The influence of the equivalence ratio is almost the same at atmospheric pressure and for 0.5 MPa (decrease of 33 percent between equivalence ratios of 0.8 and 1.0 both at 0.1 and 0.5 MPa).

### 7. The effects of pressure and dilution on NO formation

Study of combustion mechanism resulting from adding diluents such as carbon dioxide, nitrogen and hydrogen to methane and decreasing NO<sub>x</sub>, is one of the most important topics in combustion. Literature shows that concentration of NO<sub>x</sub> resulting from methane combustion, increases by adding hydrogen, especially in high ratios [33-35]. Also, in constant equivalence ratio, adding hydrogen to methane-air flame increases the flame temperature significantly [36]. In the combustion of fuels that contain no nitrogen, nitric oxide (NO) is formed by three chemical mechanisms or routes that involve nitrogen from the air. They are thermal or Zeldovich mechanism, prompt or Fenimore mechanism, and N<sub>2</sub>O-intermediate mechanism [37].

Thermal mechanism dominates in high-temperature combustion over a wide range of equivalence ratios, while a prompt mechanism is particularly important in fuel-rich combustion. It appears that the N<sub>2</sub>O intermediate mechanism plays an important role in the production of NO in the high lean and low-temperature combustion process. Figs. 14 and 15 show mole fraction of NO resulting from numerical solution of adding 10 and 20 percent carbon dioxide, hydrogen and nitrogen to methane-air fuel mixture, in initial pressure of 1 atmosphere, initial temperature of 298 K and in stoichiometric condition in terms of distance from the burner. In Fig. 16, all conditions of these two studies are presented.

In the case of  $\phi = 1$ , formation of NO is almost completed at the distance greater than 10 cm from the flame front due to the Zeldovich thermal-NO mechanism. Because of the high flame temperature near the stoichiometric mixtures, the NO formation results from the thermal NO mechanism. While in fuel-rich flames, there are many CH radicals in the flame front

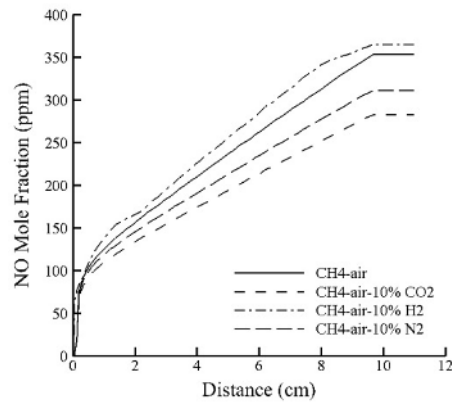


Fig. 14. Calculated NO mole fraction of methane-air flame diluted with 10% of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> versus distance at  $\phi = 1$ , P<sub>ini</sub> = 0.1 MPa and T<sub>ini</sub> = 298 K.

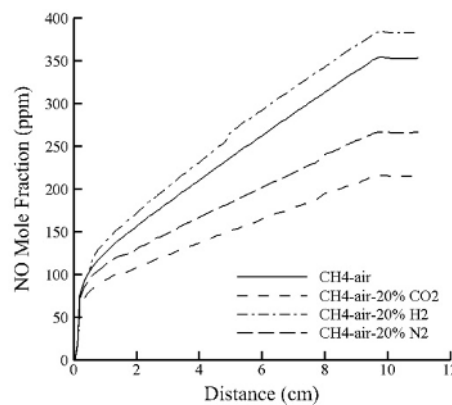


Fig. 15. Calculated NO mole fraction of methane-air flame diluted with 20% of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> versus distance at  $\phi = 1$ , P<sub>ini</sub> = 0.1 MPa and T<sub>ini</sub> = 298 K.

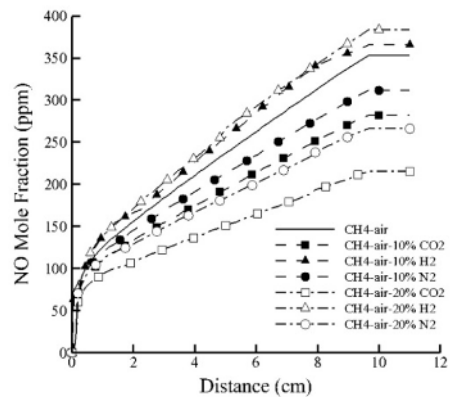


Fig. 16. Calculated NO mole fraction of methane-air flame diluted with 10% and 20% of CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub> versus distance at  $\phi = 1$ , P<sub>ini</sub> = 0.1 MPa and T<sub>ini</sub> = 298 K.

and the flame temperature is lower, so NO formation results from the Fenimore prompt-NO mechanism, which occurs within the flame front [38]. From Figs. 14-16, we can conclude that adding carbon dioxide and nitrogen to methane-air

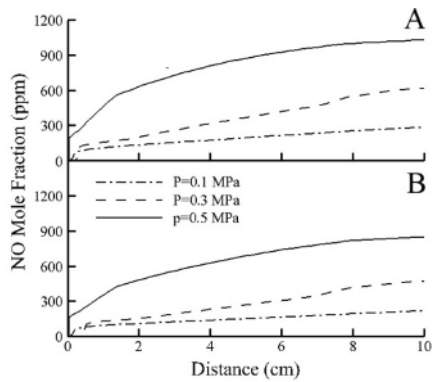


Fig. 17. Calculated NO mole fraction of methane-air flame diluted with CO<sub>2</sub> at P = 0.1, 0.3 and 0.5 MPa versus distance at  $\phi = 1$ ,  $T_{ini} = 298$  K: (a) 10% dilution; (b) 20% dilution.

fuel mixture, decreases NO formation; however, increasing in NO formation is seen by adding hydrogen to methane-air mixture. By adding 10, 20 percent carbon dioxide and nitrogen, the most decrease in NO formation is related to adding 20% carbon dioxide. This decrease is apparently due to flame temperature decrease. With the increase of hydrogen fraction, the adiabatic flame temperature is increased and it induces the mechanism to be active; as a result, it causes NO formation increase.

Finally, we study numerically the effect of increasing pressure from 1 to 5 atmospheres on NO formation of methane-air fuel mixture diluted with carbon dioxide, hydrogen and nitrogen in stoichiometry condition. Few experimental and numerical studies have been done about the NO formation in premixed flames in different pressure [39, 40]. In Fig. 17, the effect of increasing pressure on methane-air mixture diluted with 10 and 20 percent CO<sub>2</sub> is shown. Also, Figs. 18 and 19 show the study of increasing nitrogen and hydrogen, respectively. Results show that in high pressures, NO formation increases, and in 10% increase of diluents, NO formation is more than that in 20% increase of diluents. Temperature profiles are strongly dependent upon pressure, when the temperature changes, the rate of the reaction increases [41], which results in observed growth of the calculated NO mole fractions with pressure.

## 8. Conclusion

Our focus was on the effects of adding carbon dioxide, hydrogen and nitrogen as well as increasing pressure on laminar burning velocity of methane-air mixture and NO formation. Laminar burning velocity was studied experimentally through the heat flux method, also numerically with the use of PREMIX code in CHEMKIN package, which was used to simulate progression of laminar flame combustion which has the required efficiency in diluting and pressure increasing in premixed mixtures. Good agreement was observed between results of dilution by numerical and experimental solutions

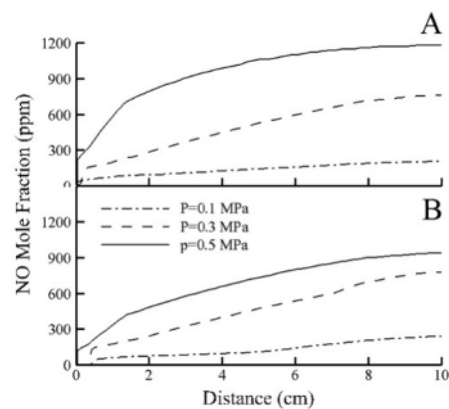


Fig. 18. Calculated NO mole fraction of methane-air flame diluted with N<sub>2</sub> at P = 0.1, 0.3 and 0.5 MPa versus distance at  $\phi = 1$ ,  $T_{ini} = 298$  K: (a) 10% dilution; (b) 20% dilution.

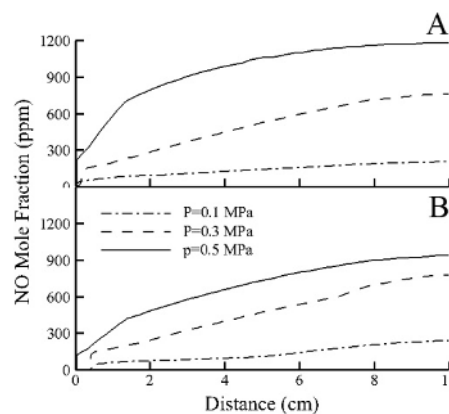


Fig. 19. NO calculated mole fraction of methane-air flame diluted with H<sub>2</sub> at P = 0.1, 0.3 and 0.5 MPa versus distance at  $\phi = 1$ ,  $T_{ini} = 298$  K: (a) 10% dilution; (b) 20% dilution.

and results of experimental studies in previous papers. Increasing hydrogen increases velocity of combustion, while increasing carbon dioxide and nitrogen indicates decrease of laminar burning velocity. Reduction of NO formation by adding N<sub>2</sub> or CO<sub>2</sub> to the methane-air mixture is seen to be caused by flame temperature decrease; by contrast, the addition of H<sub>2</sub> induces the mechanism to be active due to high temperature flame and it brings NO formation growing up.

When initial pressure increases, combustion velocity decreases for all mixtures and NO increases reactions. At higher pressures, flame temperature increases and as a result NO mole fraction grows up, moreover, increasing pressure decreases flame thickness for methane-air mixture. When the pressure increases, the fundamental burning velocity decreases for mixtures, as well as the laminar flame thickness. The version of the CHEMKIN package used succeeds to some extent in simulating the evolution of laminar burning velocity when hydrogen, nitrogen and carbon dioxide are added and when pressure is increased; however, it needs to be improved before it gives the correct values.



## Nomenclature

$c_{pi}$	: Specific heat capacity at constant pressure of species $i$
$g$	: Gravity acceleration
$h_i$	: Enthalpy of species $i$
$h_i^{ref}$	: Formation enthalpy of species $i$
$I$	: Unit tensor
$M_i$	: Molar mass of species $i$
$M$	: Mean molar mass
$N_s$	: Number of species
$p$	: Pressure
$q$	: Heat flux
$r$	: Radial coordinate
$R$	: Universal gas constant
$S_L$	: Adiabatic burning velocity
$S_L^0$	: Unstretched laminar burning velocity
$T$	: Temperature
$u$	: Gas mixture velocity
$U_i$	: Diffusion velocity of species $i$
$v$	: Gas velocity
$x_p$	: Plate thickness
$Y_i$	: Species mass fractions
$\rho_i$	: Density of species $i$
$\rho$	: Mixture mass density
$\lambda$	: Thermal conductivity
$\phi$	: Equivalence ratio
$\tau$	: Viscous stress-tensor
$\dot{\omega}_i$	: Chemical source term
$\Pi$	: Stress-tensor

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