

Adiabatic laminar burning velocities of CH₄ + H₂ + air flames at low pressures

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Abstract

Measurements of the adiabatic burning velocity of methane + hydrogen + air flames are presented. The hydrogen content in the fuel was varied from 0 to 20%. Non-stretched flames were stabilized on a perforated plate burner from 20 to 100 kPa. Equivalence ratio was varied from 0.8 to 1.4. The Heat Flux method was used to determine burning velocities under conditions when the net heat loss of the flame is zero. Adiabatic burning velocities of CH₄ + H₂ + air mixtures were found in good agreement with the literature results at atmospheric pressure. Also low-pressure measurements in CH₄ + air flames performed earlier were accurately reproduced. The effects of enrichment by hydrogen on laminar burning velocity at low pressures have been studied for the first time.

Introduction

The concept of hydrogen-enriched natural gas combustion is based on the extension of the flammability limits towards fuel-lean conditions where the emission of nitrogen oxides is significantly reduced. Enrichment by hydrogen also potentially leads to reduction of the emission of greenhouse gas, CO₂. The feasibility of this concept has been examined in a number of recent studies, including experiments in shock tubes, in well-stirred reactors, in premixed and diffusion flames. Typically these studies were accompanied by a comparison with modeling to validate kinetic mechanisms and to better understand the effects of enrichment by hydrogen.

Majority of the experiments with methane + hydrogen + air mixtures have been performed at atmospheric and higher pressures bearing in mind potential industrial applications. At lower pressures, combustion studies were usually limited to flame structure measurements [1, 2]. Laminar burning velocities of CH₄ + H₂ + air flames at low pressures have never been measured to the best of the authors' knowledge. The goal of the present study was, therefore, accurate determination of the burning velocities in these flames using the Heat Flux method, comparison with detailed kinetic modeling and analysis of their pressure dependence.

Most of the measurements using the Heat Flux method were performed at atmospheric pressure. Bosschaart and de Goey [3] extended this method to subatmospheric pressures and obtained laminar burning velocities of methane + air mixtures in the pressure range 80 – 1000 mbar, Fig. 1. They found that for the pressures below 150 mbar apparent burning velocities drop down as compared to calculations and expected pressure dependence. This effect was attributed to the diffusion of the unburned mixture into surroundings, which reduces the area where the flame is still one-dimensional and undistorted [3].

Also shown in Fig. 1 are stretch-corrected measurements in stoichiometric methane + air flames [4, 5]. Egolfopoulos et al. [4] used counterflow method

and linear stretch correction within the range 0.25 – 3 atm. Stone et al. [5] deduced burning velocities from pressure-time measurements made in near zero-gravity conditions in a spherical constant volume chamber. Original results have not been reported, instead correlation as a function of initial temperature and pressure within the range 0.5 – 10.4 bar was derived [5]. It is shown in Fig. 1 by dashed line. Other correlations evaluated by Bosschaart and de Goey [3] and earlier measurements summarized by Andrews and Bradley [6] show even larger scattering. Measurements performed in the present work and modeling results will be discussed in the following.

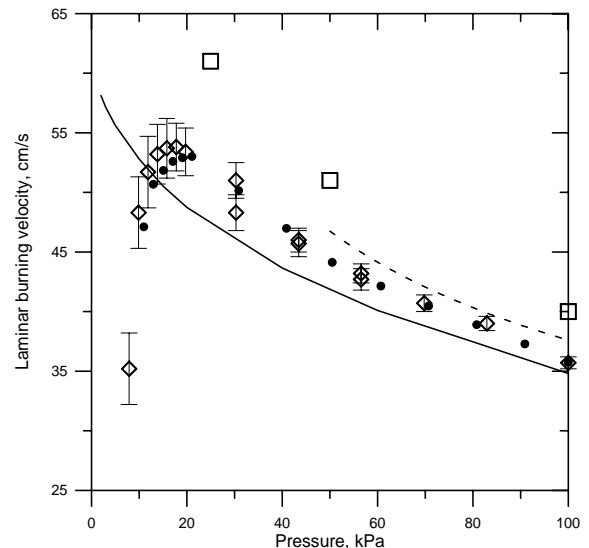


Fig. 1. Laminar burning velocities of stoichiometric methane + air flames at initial temperature of 298 K as a function of pressure. Diamonds: [3], squares: [4], dashed line: [5], solid line and dots: modeling and measurements of the present work.

Experimental details

The experimental setup for the adiabatic flame stabilization using the Heat Flux method is described

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elsewhere [3], however, the most relevant details are repeated here. Due to modification of some elements of the setup and of the mixture preparation procedure, validating experiments are also outlined.

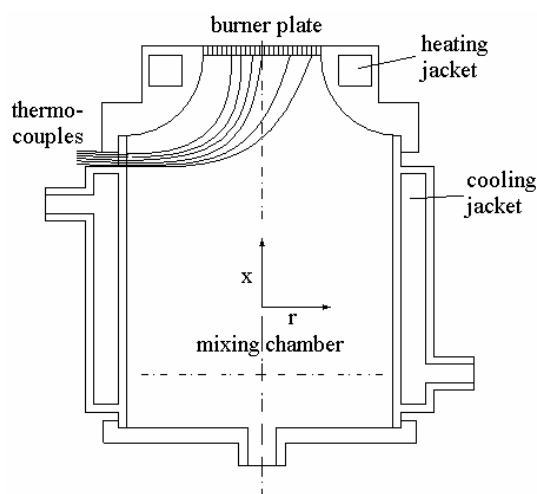


Fig. 2. The burner used in the Heat Flux method.

Cross-section of the burner used in the Heat Flux method is shown in Fig. 2. The burner plate perforated with small holes is attached to the burner outlet. Six thermocouples are soldered into the plate surface at the upstream side. The burner head has a heating jacket supplied with thermostatic water to keep the temperature of the burner plate constant. During the experiments this temperature was fixed at 353 K. The plenum chamber has a separate cooling system supplied with water at a temperature of 298 K. 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. 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 changing the flow rate of the gas mixture an appropriate value of the gas velocity can be found to nullify the net heat flux. In this case the radial temperature distribution in the burner plate is uniform and equal to the temperature of the heating jacket. Experimentally the series of thermocouples attached to the burner plate allow measuring the temperature distribution in it. The flow rate at which the net heat flux is zero is shown to be an adiabatic flame burning velocity [7]. A mixing panel was assembled for a gas supply from gas cylinders to the inlet of the burner's plenum chamber. It consists of two ducts for the fuel (mixture) and air. Each duct connected to its own gas cylinder has a buffer vessel and a mass flow controller (MFC). Two thermostats

provide the water supply to the heating and cooling jackets of the burner. Gas duct coils are immersed in the cold (298 K) thermostat to control the gas temperature before the MFCs.

The installation for the Heat Flux measurements at subatmospheric pressures was out of use for a long time. Due to replacement of some key elements, pump, thermocouples and MFCs, validating experiments were performed to ensure repeatability and accuracy of the measurements. Figure 3 shows laminar burning velocities of $\text{CH}_4 + \text{air}$ flames at atmospheric pressure and initial temperature of 298 K obtained on different Heat Flux installations [8, 9, 10] and in the present work.

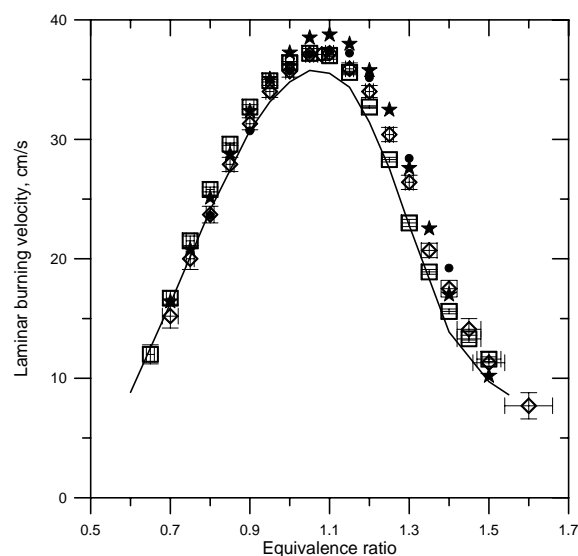


Fig. 3. Laminar burning velocity of methane + air flames at atmospheric pressure and initial temperature of 298 K. Diamonds: [8], squares: [9], stars: [10], solid line and dots: modeling and measurements of the present work.

Previous measurements of the laminar burning velocities of methane + hydrogen + air flames using the Heat Flux method at atmospheric pressure have been performed by Coppens et al. [11, 12] and by Hermanns [9] and summarized by Hermanns et al. [13]. Coppens et al. [11, 12] used fuel mixtures delivered from the mixing plant, while Hermanns [9] produced fuel mixtures on the spot using separate MFCs for methane and hydrogen. Two approaches for the fuel mixture preparation may cause some discrepancies as was noted before in the case of oxidizer preparation [10]. In the present work methane and two mixtures containing 10 and 20 vol. % of hydrogen in the fuel delivered from the mixing plant have been used. These compositions correspond to those studied by Hermanns [9] and, for the sake of further validation, his data and present measurements at atmospheric pressure are confronted in Fig. 4. For the three fuels studied (Figs. 3 and 4) very good agreement with the literature results is found.

Finally low-pressure measurements of Bosschaart and de Goey [3] in stoichiometric methane + air flames have been repeated with excellent reproducibility, see Fig. 1. Apparent burning velocities drop down at pressures below about 20 kPa. Direct photographs of stoichiometric methane + air flames presented in Fig. 5 show that the central flat region of the flame rapidly shrinks with pressure hampering correct measurements at lower pressures on the burner of 30 mm in diameter. Therefore present experiments were confined to the range from 20 to 100 kPa.

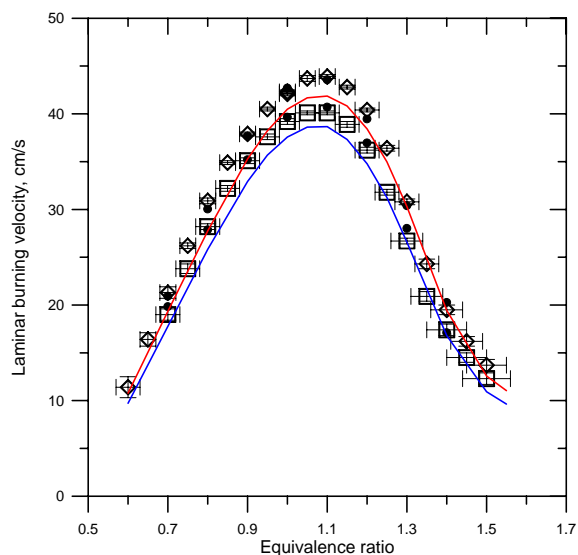


Fig. 4. Laminar burning velocity of methane + hydrogen + air flames at atmospheric pressure and initial temperature of 298 K. Squares: 10 % of H_2 in the fuel [9], diamonds: 20 % of H_2 in the fuel [9], solid lines and dots: modeling and measurements of the present work.

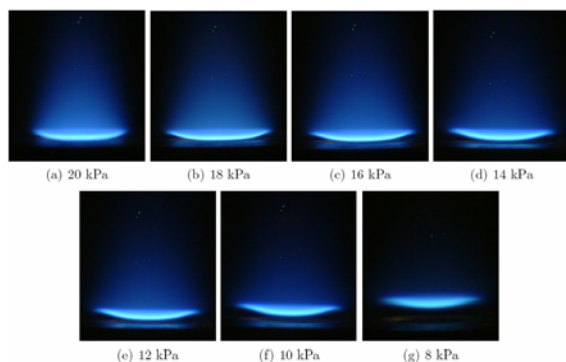


Fig. 5. Direct photographs of stoichiometric methane + air flames at low pressures.

An overall accuracy of the burning velocity measurements was estimated [3] to be better than ± 0.5 cm/s (double standard deviation with 95 % confidence level) at 100 kPa increasing to ± 5 cm/s at 10 kPa. A procedure for estimation of errors in equivalence ratio was extended to binary fuel mixtures by Coppens et al.

[12]. The relative accuracy of the equivalence ratio was found to be below 1.5%.

Modeling details

A detailed C/H/N/O reaction mechanism for the combustion of small hydrocarbons was used for the modeling [14]. The current version of the mechanism (Release 0.5) consists of 1200 reactions among 127 species. This mechanism has been validated with experimental data available for oxidation, ignition, and flame structure of hydrogen, carbon monoxide, formaldehyde, methanol, methane, ethane, propane, and some of their mixtures, e.g. [10, 11, 12, 14]. In the present work the modeling was used mostly to compare experimentally observed trends with those predicted by the calculations. No attempts to modify the mechanism in order to improve its performance and agreement with the experiments were made.

The CHEMKIN - II collection of codes [15-17], including transport properties [18] from Sandia National Laboratories, were used. Multi-component diffusion and thermal diffusion options were taken into account. Adaptive mesh parameters were $GRAD = 0.05$ and $CURV = 0.5$. Relative and absolute error criteria were $RTOL = 1.E-5$ and $ATOL = 1.E-9$ respectively; total number of grid points was typically 350 – 400.

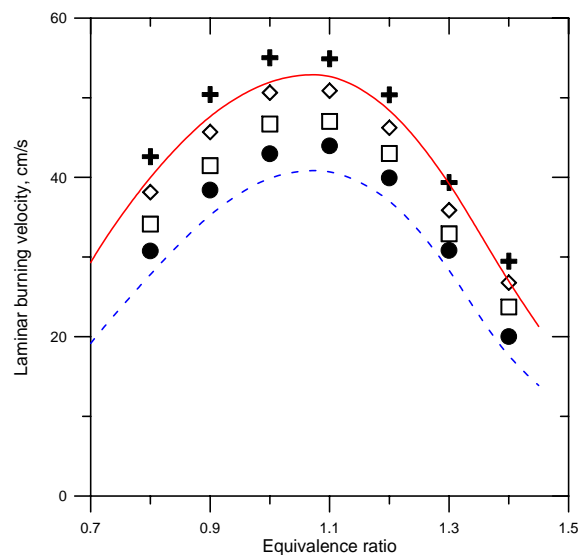


Fig. 6. Laminar burning velocity of methane + hydrogen + air flames (10 % of H_2 in the fuel) at different pressures and initial temperature of 298 K. Symbols: experiment, lines: modeling. Crosses and solid line: 20 kPa, diamonds: 40 kPa, squares: 60 kPa, solid circles and dashed line: 80 kPa.

Results and discussion

New measurements in methane + hydrogen + air flames at initial temperature of 298 K and low pressures are shown in Figs. 6 and 7 for 10 % and 20 % of H_2 in the fuel, respectively. Modeling results are shown for limiting series of 20 and 80 kPa to avoid too busy

graphs. The quality of agreement between the modeling and experiments is similar to the atmospheric data shown in Figs. 3 and 4 and demonstrated earlier in a wider range of hydrogen enrichment and dilution by nitrogen [11, 12]. Disagreement is most notable in around stoichiometric mixtures and slightly increases towards lower pressures, Fig. 1.

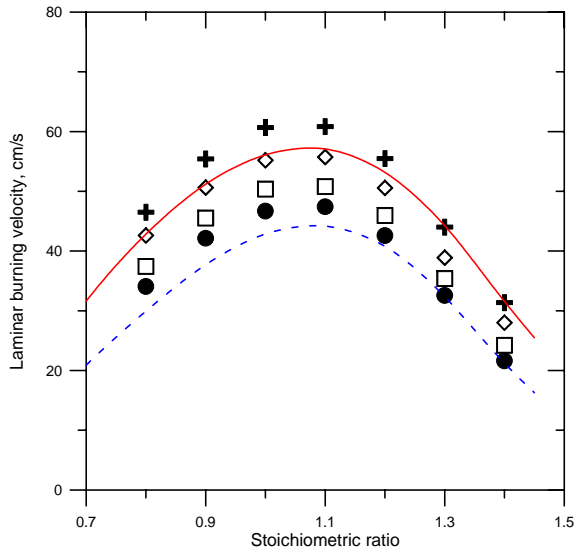


Fig. 7. Laminar burning velocity of methane + hydrogen + air flames (20 % of H_2 in the fuel) at different pressures and initial temperature of 298 K. Symbols: experiment, lines: modeling. Crosses and solid line: 20 kPa, diamonds: 40 kPa, squares: 60 kPa, solid circles and dashed line: 80 kPa.

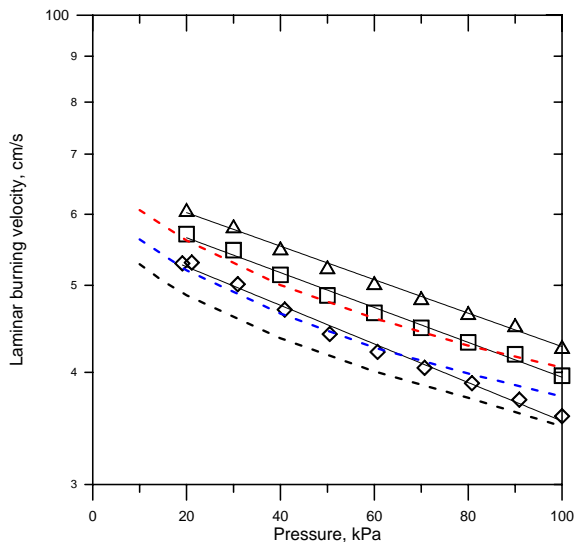


Fig. 8. Laminar burning velocity of stoichiometric $CH_4 + H_2 + air$ flames at initial temperature of 298 K as a function of pressure. Diamonds: pure methane; squares: 10 % of hydrogen in the fuel; triangles: 20 % of hydrogen in the fuel. Dashed bold lines: modeling, solid thin lines: exponential correlation (see text).

Figure 8 presents new measurements and modeling results in stoichiometric $CH_4 + H_2 + air$ flames. Calculated burning velocities shown as dashed bold lines in Fig. 8 are in satisfactory agreement with the experiments. Figure 8 reveals two remarkable features:

- Although diffusion properties of the fuel mixtures are different, the measured burning velocities show no signs of drop down when the pressure approaches 20 kPa (cf. Fig. 1);
 - Experimental data show almost linear pressure dependences (solid thin lines) on a semi-logarithmic plot, while the modeling does not.
- These two features are discussed in the following.

Diffusion at low pressures

Bosschaart and de Goeij [3] attributed the effect of drop down of the apparent burning velocity to diffusion of the unburned mixture (primarily fuel) into surroundings, which reduces the area where the flame is still one-dimensional and undistorted. At low pressures there are two possibilities, diffusion of the fuel to the surroundings, or diffusion of the burnt gases into the fresh mixture. Thus the composition of the gas present in the vacuum chamber may affect the laminar burning velocity. Therefore the laminar burning velocities were measured while air was added to the chamber through an additional nozzle at the bottom of the chamber keeping the pressure constant. During the measurement the pressure was set to 21 kPa. Lower pressures were not accessible, since the pump could not cope with the increased “leakage”, the extra flow. The equivalence ratios were set to 0.8, 1.0 and 1.2. Maximum additional air flow is comparable to the total flow of the fresh combustible mixture. The results of the measurements are presented in Fig. 9. It is clear that when the concentration of the air in the chamber is varied, there is no relevant effect on the laminar burning velocity.

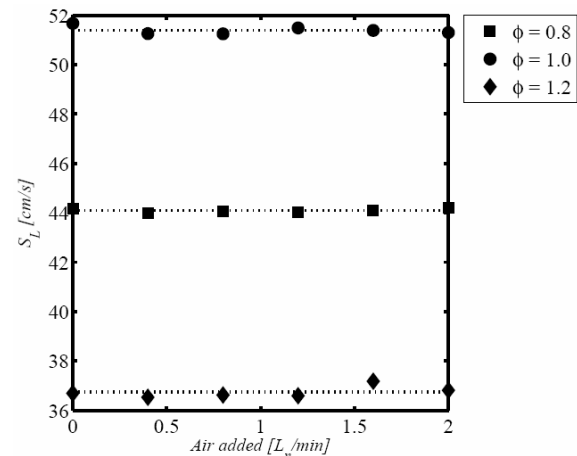


Fig. 9. The effect of the amount of the air added to the vacuum chamber on the apparent burning velocity.

As it was stressed above, diffusion properties of the fuel mixtures are different, yet the measured burning

velocities show no signs of drop down when the pressure approaches 20 kPa (Fig. 8). One can conclude that diffusion of the fuel and oxidizer in and out of the fresh mixture is of minor importance. Besides of the diffusion of the mixture components, diffusion of radicals should be considered. Modification of the concentration profiles of radicals related to the burner size at low pressures has been demonstrated in [19, 20]. Rapid loss of radicals and, most probably, highly diffusive H atoms may effectively reduce burning velocity in all flames, either lean or rich. One can also argue that if the reason of the considered effect was a change in the fresh mixture composition, then at some conditions local burning velocity close to the burner edge could be higher than in the center. Yet, pressure decrease always leads to concave flames, Fig. 5. It is thus possible to conclude that diffusion of radicals and atoms from the flame is the main reason of the dramatic drop down of the apparent burning velocities at the pressures below 20 kPa (Fig. 1).

Pressure dependence

Power-law pressure dependences were typically observed at pressures above atmospheric pressure:

$$S_L = S_{L,0} * (P/P_0)^a$$

where $S_{L,0}$ is the burning velocity at reference conditions (usually at 1 atm), and P_0 is the reference pressure. To analyze apparent pressure dependence at low pressures measured burning velocities of stoichiometric methane + air flames are shown in Fig. 10 on a log-log scale.

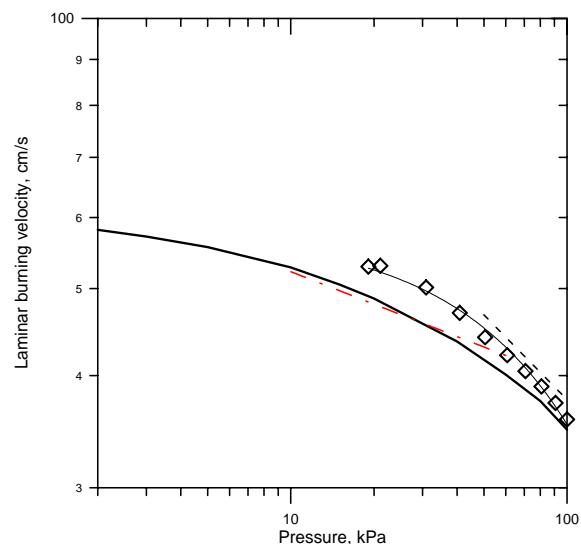


Fig. 10. Laminar burning velocities of stoichiometric methane + air flames at initial temperature of 298 K as a function of pressure. Bold line and diamonds: modeling and measurements of the present work. Thin line: exponential approximation (see Fig. 8), dashed line: correlation of Stone et al. [5]; dash-dot line: correlation of Tsatsaronis [21].

Andrews and Bradley [6] derived the correlation $S_L = 43 P^{-0.5}$ cm/s for pressures greater than 5 atm; Stone et

al. [5] proposed for stoichiometric methane + air flames from 50 to 1040 kPa an empirical correlation (dashed line in Fig. 10) with the power exponent of -0.314. Tsatsaronis [21] found that predicted burning velocities at pressures below 60 kPa show a much lower pressure exponent of -0.12 (dash-dot line in Fig. 10), which differs significantly from the calculated power exponent of -0.51 at pressures greater than 4 atm. At very low pressures all these power-law pressure dependences attain infinity, which has no physical sense. Neither experimental data nor detailed kinetic modelling shows this trend. Calculated burning velocities (bold line in Fig. 10) tend to a limiting value and qualitatively correspond to an empirical exponential approximation (like the thin line in Fig. 10). These approximations for stoichiometric mixtures (Fig. 8) are:

$$S_L = 57.9 \exp(-0.495 * P) \text{ cm/s for CH}_4 + \text{air,}$$

$$S_L = 61.8 \exp(-0.447 * P) \text{ cm/s for 10 \% of H}_2 \text{ in the fuel, and}$$

$$S_L = 65.6 \exp(-0.429 * P) \text{ cm/s for 20 \% of H}_2 \text{ in the fuel. Obvious trends in the limiting burning velocities at zero pressure and in the logarithmic sensitivities to the pressure call for further research, which is an objective of the authors.}$$

Conclusions

Experimental measurements of the adiabatic burning velocity in methane + hydrogen + air flames using the Heat Flux method are presented. The hydrogen content in the fuel was varied from 0 to 20%. Non-stretched flames were stabilized on a perforated plate burner from 20 to 100 kPa. Equivalence ratio was varied from 0.8 to 1.4. Adiabatic burning velocities of $\text{CH}_4 + \text{H}_2 + \text{air}$ mixtures were found in good agreement with the literature results at atmospheric pressure. Also low-pressure measurements in $\text{CH}_4 + \text{air}$ flames performed earlier were accurately reproduced. Calculated burning velocities using the Konnov mechanism are in satisfactory agreement with the experiments over entire range of conditions. Dramatic drop down of the apparent burning velocities at the pressures below 20 kPa could, most probably, be attributed to the diffusion of radicals and atoms from the flame. Pressure dependences of the burning velocities for the three fuels studied could be approximated by empirical exponential correlations. Implementation of power-law pressure dependences at lower pressures should be discouraged.

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