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STRUCTURE OF CH₄/O₂/AR FLAMES AT ELEVATED PRESSURES STUDIED BY FLAME SAMPLING MOLECULAR BEAM MASS SPECTROMETRY AND NUMERICAL SIMULATION

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Abstract

The structures of lean, rich and stoichiometric premixed methane/oxygen/argon flames stabilized on the burner at 1, 3 and 5 atm are studied by the molecular-beam mass spectrometry (MBMS). The main products and intermediates (including H and OH radicals) in the flames are identified and their mole fraction profiles are measured. Experimental results are compared with the results of computer modeling using GRI 3.0 mechanism.

Introduction

Combustion of hydrocarbon and alternative fuels remains a key source of energy in the foreseeable future. In this regard, of particular importance is the knowledge of chemical kinetic mechanisms of combustion of the hydrocarbon fuels under conditions close to those in real processes in combustion devices, in which the operation pressure is significantly higher than atmospheric (usually ranges from 1 to 10 MPa). By now, extensive experimental data are available to test the chemical kinetic mechanisms for hydrocarbons' combustion. However, the majority of these data were obtained under low- or atmospheric-pressure conditions. Development of reliable chemical kinetic mechanisms for combustion of hydrocarbons is impossible without appropriate experimental studies carried out at elevated pressures.

Considerable recent attention has been focused on different combustion characteristics (laminar flame speed, concentration profiles of intermediates and final products of combustion, etc.) at elevated pressures in order to test chemical kinetic mechanisms. In particular, a number of studies have shown that the GRI 3.0 mechanism predicts well the laminar burning velocity of premixed CH₄-air flames at pressures of 1-5 atm. [1-2]. However, at pressures above 20 atm there is a significant discrepancy between the experimental data and the calculations using the GRI 3.0 of burning velocity of methane flame [3]

The most informative method to acquire data on the chemical kinetic combustion mechanism is a method of flame sampling molecular beam mass spectrometry with electron impact ionization or photoionization by synchrotron VUV radiation. This method allows one to detect not only stable species, but also short-living intermediates in the flame. MBMS is extensively used to investigate the structure of flames of hydrocarbon fuels, including oxygenates. However, these studies were carried out only at low pressures (20-30 torr) [4], and at 1 atm [5]. Only Paletskii et al [6] used this technique to measure the mole fraction profiles of the reactants and water in the hydrogen flame stabilized on a flat burner at a pressure of 10 atm.

In this work, the MBMS technique is applied for measuring species mole fraction profiles in premixed methane/oxygen/argon flames stabilized on a flat burner at pressures of 1, 3 and 5 atm. The goals are: (1) on the basis of these data to test the mechanism of methane combustion (GRI 3.0) under these conditions; (2) to find out how the pressure increase influences the mole fractions of the flame species (including H and OH radicals); (3) to address the effect of the equivalence ratio on the mole fractions of the species in the CH₄/O₂/Ar flame at elevated pressure.

Table 1. Molar composition and linear velocity at the burner surface (at 333 K) of fresh mixtures, and calculated (GRI 3.0) burning velocity of the flames studied in this work.

	Eq. ratio, ϕ	Pressure, atm	[CH ₄]	[O ₂]	[Ar]	Gas linear velocity, cm/s	Burning velocity, cm/s
Fuel-lean	0.8	5	0.071429	0.178571	0.75	17.8	35.8
Stoichiometric	1	1	0.083333	0.166667	0.75	27.5	68.69
	1	3	0.083333	0.166667	0.75	17.8	50.59
	1	5	0.083333	0.166667	0.75	17.8	42.28
Fuel-rich	1.2	5	0.09375	0.15625	0.75	17.8	34.55

Methane is the major component of natural gas, as well as an intermediate product of the combustion of higher hydrocarbons. Any detailed chemical kinetic mechanism for combustion of large hydrocarbons includes the reactions of methane oxidation. Therefore, understanding the chemistry of combustion of methane under conditions close to real, is of fundamental and practical interest.

Approach

The flames studied in this work were stabilized at pressures of 3 and 5 atm on a flat home-made burner. The burner surface is a porous matrix made by pressing aluminum particles (~0.08 mm in diameter). The matrix thickness is 4 mm. The matrix was pressed into a copper tube with an inner diameter of 6 mm. This diameter determines the size of the matrix, i.e. the diameter of the burner. The tube is wrapped with a tube of smaller diameter, through which thermostated water is supplied. Water temperature was maintained at 333K. The burner is placed in a pressure chamber, and was equipped with a mechanism to move the burner in vertical direction. The high-pressure chamber is connected to the sampling probe flange of the molecular beam mass spectrometric setup. MBMS setup has been described in detail in our previous studies, in which we described our experimental data obtained at atmospheric pressure in a variety of flames [5]. In contrast to the experiments at atmospheric pressure, in which we have used a quartz probe with an orifice at the tip of 80 microns in diameter and the opening angle 40 °C, in this work (a pressure of 3 and 5 atm) we made a sampling probe (with the same opening angle) with the orifice of 40 microns. The mass flowrate through this probe at a pressure of 5 atm is only 20 % more than through that with 80 micron orifice at a pressure of 1 atm (in our previous 1 atm experiments).

Methane flame at 1 atm was stabilized on a flat burner, which has been used in our previous studies [5]. The burner surface represents a perforated brass disc (diameter of holes 0.5 mm, hole separation 0.7 mm) placed in a brass housing with a cooling jacket. The burner was

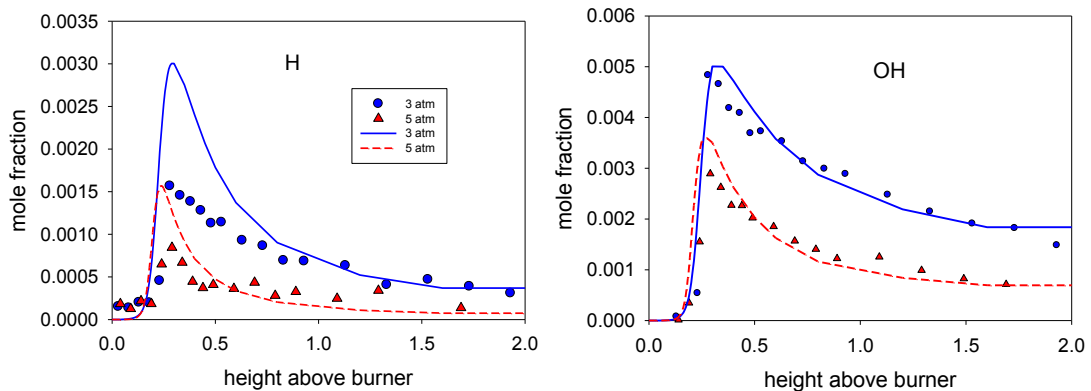


Fig. 1. H and OH mole fraction profiles in stoichiometric flames at 3 (blue) and 5 (red) atm. Symbols: modeling; curves: modeling.

filled with 3 mm diameter stainless steel balls to uniform flow speed at the burner surface and to thoroughly heat the flow. The cooling jacket was thermostated by water at 333 K. The composition of fresh gas mixtures investigated in this work is given in Table 1. This table also lists the linear velocities of the fresh mixtures at the burner surface and flame burning velocities calculated using the GRI 3.0 mechanism.

To account for the cooling effect of the probe on the flame temperature profiles in all flames were measured using a Pt-Pt +10% Rh thermocouple located at 0.05 mm from the tip of the sampling probe. The thermocouple was welded from wires 0.02 mm in diameter, covered with a thin layer of SiO₂ to prevent catalytic effects on its surface. The resulting thermocouple had a diameter of 0.03 mm.

Mole fraction profiles of the flame species were simulated using CHEMKIN II collection of codes with the measured temperature profiles as input data using TGIV keyword. GRI 3.0 mechanism [7] was used for the modeling.

Results and discussion

Figure 1 shows measured and calculated mole fraction profiles of H and OH radicals in the stoichiometric flames at 3 and 5 atm. One can see that pressure increase results in reduction of peak mole fractions of H and OH radicals. This is in an agreement with the observations of Matynia et al [8], who reported that OH concentration reduces in counterflow CH₄/air flame. Matynia and coworkers [8] explained this effect to be associated with the competition between the reactions of production and consumption of OH radicals depending on the pressure. However, as seen from Fig. 1, GRI 3.0 mechanism predicts well our experimental data, and reproduces adequately the effect of pressure on the mole fractions of H and OH radicals in the flame.

Figures 2 and 3 represent the mole fraction profiles of H, OH, CH₃ radicals, as well as

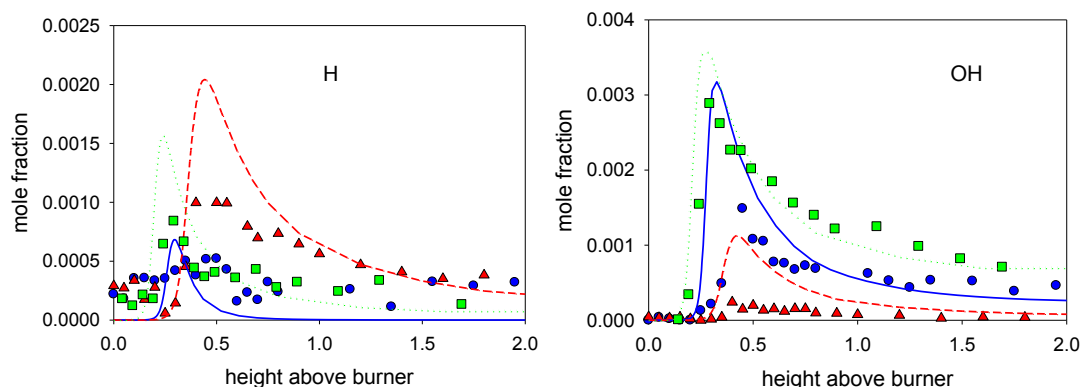


Fig. 2. H and OH mole fraction profiles in stoichiometric, fuel-lean and fuel-rich flames at 5 atm. Symbols: modeling; curves: modeling.

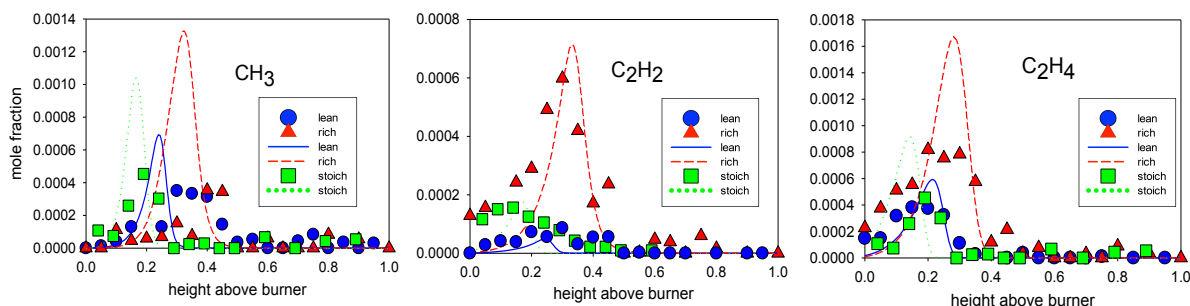


Fig. 3. Mole fraction profiles of methyl radical, acetylene and ethylene in stoichiometric, fuel-lean and fuel-rich flames at 5 atm. Symbols: modeling; curves: modeling.

acetylene and ethylene in stoichiometric, fuel-lean and fuel-rich methane flames. As can be seen from Fig.2 the experiment gives an obvious result: increasing equivalence ratio results in increasing mole fractions of H radicals and decreasing mole fraction of OH radicals. The GRI 3.0 mechanism provides a good qualitative and qualitative agreement with the measurement data. Mole fraction profiles of the intermediates of the methane flames, such as methyl, acetylene and ethylene, are also predicted well by the mechanism.

Conclusions

New experimental data on the structure of laminar premixed CH₄/O₂/Ar flames (at various equivalence ratios) stabilized on a flat burner at 1, 3, and 5 atm, acquired by the MBMS are represented in this work. Numerical modeling of the structure of the flames using GRI 3.0 chemical kinetic mechanism is performed. Comparison of the results of the experiment and the simulation showed in general a good agreement between them.

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