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Structure of premixed fuel-rich CH₄/O₂/N₂/CO₂ and C₃H₈/O₂/N₂/CO₂ flames stabilized on a flat burner at atmospheric pressure

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Abstract

Species concentration profiles in the fuel-rich (φ=1.2) methane/air, propane/air and methane/air/CO₂, propane/air/CO₂ flames stabilized on a flat burner at 1 atm were studied using the molecular beam mass-spectrometry and numerical simulation. Mole fraction profiles of reactants, intermediates and final products were measured and simulated. The results of measurements indicate that the replacement of 15% of N₂ with CO₂ leads to decreasing maximum mole fraction of majority of intermediate species in the reaction zone. Analysis of the results of calculating the structure of the flame under study and of the literature data has shown the effect of reducing the concentration of intermediate combustion products with partial replacement of N₂ with CO₂ to be connected with the increase of the reaction rate CO₂→CO+OH, resulting in the growth of the ratio of OH/H in the zone of reactions in rich flames. The increase of OH concentration results in acceleration of the transformation of intermediate carbon-containing species into the final combustion products, thus reducing the probability of soot formation.

1. Introduction

The reduction of pollutant emissions from combustion of fossil fuels is the world’s largest problem. One of the alternative methods of solving this problem is using the technology of recirculation of flue gas, the main component of which is CO₂ [1]. Previous studies have shown that the replacement of N₂ with CO₂ influences significantly on combustion efficiency of hydrocarbons [2-11]. Some researchers have shown that the effect of CO₂ is to inhibit the oxidation of CH₄ [6-9]. However, opposite results to inhibiting effect of CO₂ on the CH₄ oxidation have been reported also [10,11]. The effects of CO₂ on combustion characteristics of hydrocarbon/air mixtures were extensively studied [2-11] but chemical structure of premixed hydrocarbon/air/CO₂ flames at atmospheric pressure was not investigated earlier. An important issue, in particular, is the influence of replacement of N₂ with CO₂ in the fresh combustion mixture on soot formation in the flame.

The goal of this work is to study the effect of replacement of part of N₂ with CO₂ in fuel-rich CH₄/air and C₃H₈/air mixtures on chemical kinetics in premixed flame stabilized on a flat burner at 1 atm by measurement and numerical simulation of its thermal and chemical structure.

2. Experimental and Modeling details

Fuel-rich (φ=1.2) methane/air (CH₄/O₂/N₂=0.111/0.186/0.703), propane/air (C₃H₈/O₂/N₂=0.048/0.2/0.752) and methane/air/CO₂ (CH₄/O₂/N₂/CO₂=0.111/0.186/0.553/0.15), propane/air/CO₂ (C₃H₈/O₂/N₂/CO₂=0.048/0.2/0.602/0.15) flames were stabilized on a flat burner 16 mm in diameter at 1 atm. The burner was kept at 95°C. The linear velocity of the fresh mixture on the burner surface was 16.0 cm/s for the CH₄/O₂/N₂ flame, 40.2
cm/s for the C₃H₈/O₂/N₂ flame and 7.25 cm/s for the CH₄/O₂/N₂/CO₂ flame, 20.1 cm/s for the C₃H₈/O₂/N₂/CO₂ flame.

The concentration profiles of species were measured using mass spectrometer coupled with molecular-beam sampling system [12]. Sampling was performed using a quartz probe with the orifice diameter of 0.08 mm and inner angle of 40 degrees. The mass spectrometer was equipped with improved ion source with a narrow spread of electron energies (±0.25 eV) [13].

The uncertainty of determination of mole fraction of the flame reactants and major products (CO, CO₂, H₂O, H₂) was estimated to be ±15% of the maximum mole fraction values. For other species, mole fractions were determined to within a factor of about 2. Temperature profiles were measured using Pt/Pt+10%Rh thermocouple made of wires 0.02 mm in diameter and coated with SiO₂. To take into account the thermal disturbances induced in flames by a sampling nozzle temperature profiles were measured by a thermocouple, the junction of which was placed at the distance 0.2 mm from the probe’s orifice. The temperature was measured with an accuracy of ±25 K, the radiative heat losses of the thermocouple were taken into account. The flame structure was simulated using Premix code from the Chemkin-II collection of codes and detailed reaction mechanism for combustion of small hydrocarbons [14]. Experimentally measured temperature profiles were used as input data for the modeling.

3. Results and Discussion

3.1. CH₄/O₂/N₂ and CH₄/O₂/N₂/CO₂ flames structure.

Figure 1a shows the mole fraction profiles of the total content of C₂H₆+CH₂O in the CH₄/O₂/N₂ and CH₄/O₂/N₂/CO₂ flames. In the experiment with the CH₄/O₂/N₂/CO₂ flame, the peak mole fraction of C₂H₆+CH₂O was about 3 times lower compared to that in the pure CH₄/O₂/N₂ flame, whereas the model predicts that it slightly decreases at CO₂ addition. The model does not quantitatively predict mole fraction profiles of C₂H₆+CH₂O and reproduces poorly the effect of CO₂ addition to the initial mixture on the C₂H₆+CH₂O concentration in the flame.

Figure 1b shows measured and calculated mole fraction profiles of C₂H₆ in both CH₄/O₂/N₂ and CH₄/O₂/N₂/CO₂ flames. For the maximum concentration of C₂H₆ in the CH₄/O₂/N₂ flame, the calculation provides a satisfactory agreement with the experiment, whereas in the flame with addition of 15% of CO₂.
the model overpredicts the measured peak concentration of ethylene by 3 times. The experimental data show that addition of 15% of CO₂ results in decreasing the peak concentration of C₂H₄ by approximately 3 times, while modeling results do not demonstrate any changes in peak concentration of C₂H₄ with addition of CO₂. Thus, the chemical kinetic mechanism used for modeling does not reproduce the effect of addition of 15% of CO₂ to the unburnt mixture on peak concentration of C₂H₄ in the reaction zone of the flame.

One of the key intermediate C2 hydrocarbons in the flames studied is acetylene. According to experimental data (see Fig. 1c), its maximum mole fraction reaches 0.09% at a distance 1 mm from the burner in CH₄/O₂/N₂ flame. In the CH₄/O₂/N₂/CO₂ flame, it is also reached at a height 2 mm, but it is smaller in magnitude and comprises approximately 0.02%. With further increase in the height above the burner, the acetylene concentration in both flames decreases monotonically down to zero level. The kinetic mechanism used in the calculations satisfactorily reproduces the experimental profiles of acetylene in the CH₄/O₂/N₂ flame. However, in the CH₄/O₂/N₂/CO₂ flame, modeling yields values of concentration of acetylene five times higher than those measured in experiment.

3.2. CₓHᵧO₂/N₂ and CₓHᵧO₂/N₂/CO₂ flames structure

Figure 2 shows the mole fraction profiles of the total content of methyl (CH₃), methane (CH₄), acetylene (C₂H₂), C₂H₄, vinyl (C₂H₃), C₂H₆+CH₂O, propargyl (C₃H₅), allen and propyne (C₃H₄) in the CₓHᵧ/O₂/N₂ and CₓHᵧ/O₂/N₂/CO₂ flames. In the experiment with the CₓHᵧ/O₂/N₂/CO₂ flame, the peak mole fraction of CH₃ was about 2 times lower compared to that in the pure CₓHᵧ/O₂/N₂ flame, whereas the model predicts that its 1.6 times decreasing with CO₂ addition.

Similar changes are observed for CH₄ – its maximum concentration in the experiment was 3 times lower in the CₓHᵧ/O₂/N₂/CO₂ flame than in the pure CₓHᵧ/O₂/N₂ flame, however, the calculation predicts reduction of CH₄ only 1.2 times. Slight decrease of the peak concentration of C₂H₄ when CO₂ is added to the flame is observed both in the experiment (1.34 times) and in the calculation (1.24 times). Besides, a slight effect of reduction of the maximum concentration of C₂H₃ as CO₂ is introduced in the flame is observed in experiment (1.3 times), whereas in the calculation this reduction is much greater to be equal to 2.4 times. Even slighter changes in the peak concentrations as CO₂ was added were recorded for C₂H₃ and C₃H₄, their concentrations get reduced 1.2 and 1.1 times, accordingly, although the model predicts greater changes - 1.9 and 2.1 times, accordingly. Unlike the methane flames, where addition of CO₂ led to significant reduction of C₂H₂ concentration and C₂H₆+CH₂O concentration, in propane flames the situation is reverse for these compounds: the peak concentrations of C₂H₂ and C₂H₆+CH₂O increased 1.4 and 2.8 times, respectively. This change does not agree with the calculation results – the model predicts reduction of the maximum concentrations of these species 1.3 and 1.2 times, respectively.
Ethylene, vinyl, propargyl, allene, propyne and other unsaturated hydrocarbon species are considered as the species, which under certain conditions are potentially capable of producing PAH and soot in fuel-rich hydrocarbon flames through the reactions with other C\textsubscript{3}H\textsubscript{2} intermediates. Therefore, the reduction in concentration of the above mentioned species in the reaction zone of the flames indicates indirectly the tendency towards reduction of soot formation when CO\textsubscript{2} is added to the fresh hydrocarbon/air mixture. To elucidate the observed phenomena, additional analysis was performed.

In order to estimate the impact of two different factors – of the thermal and chemical ones, which arise when CO\textsubscript{2} is introduced into the fuel mixture, on the oxidation processes of a hydrocarbon fuel, the structure of the flames investigated in this study was modeled. The concentration profiles of stable species, as well as of intermediates and radicals for methane- and propane- air flames (without CO\textsubscript{2} addition) were calculated using the experimentally measured temperature profiles in flames, in which 15% nitrogen was replaced with CO\textsubscript{2}. Such approach allows the thermal effect from introducing CO\textsubscript{2} into the combustible mixture to be considered and at the same time the chemical effect of adding CO\textsubscript{2} to be eliminated. Comparison of the results of the calculation made using the approach described above with the concentration profiles of the species calculated for the flames with partial replacement of nitrogen with CO\textsubscript{2} (in such computations, transformation of introduced CO\textsubscript{2} into the fuel mixture is considered) allows the effect of adding CO\textsubscript{2} on the major intermediates in flame to be estimated. Shown in Fig. 3 are the concentration profiles of intermediates in the methane/air flame and in the methane/air+CO\textsubscript{2} flame, calculated by the same temperature profile measured in the methane/air + CO\textsubscript{2} flame. As seen from the above data, the presence of CO\textsubscript{2} in the fresh fuel mixture significantly reduces the maximum concentration of intermediates in the chemical reactions zone. Shown in Fig 3 are the concentration profiles of H and OH for the same conditions. As seen from the above data, the maximum concentration of H changes only slightly, while the maximum concentration of OH in the flame with CO\textsubscript{2} increases 1.7 times. The results of calculating the profile of the rate of reaction CO\textsubscript{2}+H→CO+OH in the combustion zone in flames with addition of CO\textsubscript{2} and without it (by the temperature profile measured in the flame with CO\textsubscript{2}) have shown that replacement of 15%
nitrogen with CO$_2$ increases the maximum value of the rate of this reaction 1.8 times (Fig.4). Similar conclusions can be made also for the propane/air flame, in which the maximum value of the reaction rate of reaction CO$_2$+H→CO+OH due to replacement of nitrogen with CO$_2$ increases 1.5 times. Thus, partial replacement of nitrogen with CO$_2$ in rich hydrocarbon/air fuel mixtures leads to the change in the H and OH concentrations in the zone of chemical reactions, resulting in the increase in the oxidation rate of the intermediate products of fuel transformation and in the lower probability of soot precursors formation.

4. Conclusions

The results of measurements indicate that the replacement of 15% of N$_2$ with CO$_2$ in CH$_4$/O$_2$/N$_2$ and C$_3$H$_6$/O$_2$/N$_2$ flames leads to reducing the post-flame temperature and decreasing maximum mole fraction of ethylene, vinyl, propargyl, allene, propyne and other intermediate hydrocarbon species in the reaction zone. Addition of CO$_2$ to fuel-rich methane and propane flames is shown to result in considerable reduction of mole fraction of soot precursors. Konnov’s chemical kinetic mechanism, in general, adequately reproduces the experimental profiles for major flame species, however, noticeable discrepancies take place between measured and calculated mole fraction profiles for some combustion intermediates. Analysis of the results of calculating the structure of the flame under study and of the literature data has shown the effect of reducing the concentration of intermediate combustion products with partial replacement of N$_2$ with CO$_2$ to be connected with the increase of the reaction rate CO$_2$+H→CO+OH, resulting in the growth of the ratio of OH/H in the zone of reactions in rich flames. The increase of OH concentration results in acceleration of the transformation of intermediate carbon-containing species into the final products of combustion, thus reducing the probability of soot formation.

Acknowledgements

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