THERMAL AND KINETIC EFFECTS OF OZONE ADDTION ON THE COMBUSTION OF METHANE/AIR MIXTURES

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Summary The thermal and kinetic effects of ozone addition on the ignition and flame propagation of premixed methane/air mixtures are studied numerically. The thermal and kinetic effects are assessed separately and compared for different conditions. Chemical reaction pathway analysis is conducted and a mechanistic interpretation is provided for the combustion enhancement.

INTRODUCTION

In scramjet engines for hypersonic aircraft, the resistance time for combustion is a few mini-seconds. Therefore, ignition and combustion enhancement is of critical importance for the development of hypersonic propulsion system. Recently, non-equilibrium plasma assisted combustion (PAC) has been demonstrated to be promising in reducing the ignition delay time and enhancing the flame stabilization and propagation. There are plenty of experimental data on PAC reported in the literature. However, the underlying mechanisms for PAC are still not well understood. In this study, the thermal and kinetic effects of ozone (O_3, which is produced by plasma-discharge in air) addition on the combustion of methane/air mixtures are investigated and a mechanistic interpretation is provided for the combustion enhancement.

NUMERICAL METHODS AND SPECIFICATIONS

In order to assess the kinetic effects of ozone addition on the ignition of methane/air, the homogeneous ignition process is considered. Thus the governing equations for temperature T and mass fraction Y_k (k=1,2,⋯,n, n is the total kinds of species) can be simplified as follows:

$$dY_k \big/ dt = \omega_k W_k \big/ \rho \tag{1}$$

$$dT \big/ dt = -\Sigma_{k=1}^{n} (h_k \omega_k W_k) \big/ \rho C_P \tag{2}$$

where t, ρ, C_p, ω_k, and W_k correspond, respectively, to time, density, specific heat at constant pressure, production rate and molecular weight of the number k species. Thermal properties and chemical reaction rates at different conditions are calculated through CHEMKIN [1] package. The species and energy equations are integrated using VODE solver [2]. The ignition delay time is defined as the moment when the temperature gradient reaches the maximum value.

The laminar flame speed is another important parameter of a combustible mixture which affects the flame stabilization and combustion efficiency. In order to investigate the flame propagating enhancement due to O_3 addition, the laminar flame speeds of the CH_4/air/O_3 mixtures at different equivalence ratios and different O_3 concentrations are calculated by using CHEMKIN-PREMIX code [3].

Detailed chemical reaction mechanism for methane oxidation, GRI-Mech3.0 [4], is used and it has 53 species and 325 elementary reactions. There are twenty-four O_3 involved reactions [5] which are added to the GRI-Mech3.0. The collisions between O_3 and other molecules generate considerable amount of O atoms which can play an important role in the combustion initiation reactions. Moreover, ozone participates in some recombination with heat release and thereby enhances the combustion process thermally. As a result, the results based on this modified mechanism should contain both thermal and kinetic effects. In order to separately examine the contribution of the thermal and kinetic effects, the following reaction

$$O_3+O_3=O_2+ O_2+ O_2 \tag{R326}$$

is added into the GRI-Mech3.0 instead of the 24 reactions [5] mentioned before. Reaction R326 has a sufficiently fast rate to consume all O_3 to O_2 releasing considerable heat. Therefore, only the thermal effect is considered when reaction R326 is used in simulation.

RESULTS AND DISCUSSIONS

Homogeneous ignition

Figure.1 demonstrates the effects of ozone addition on the ignition delay time of stoichiometric methane/air mixtures at different initial temperatures and pressures. It is seen that at 0.5% vol. O_3 addition, the ignition delay can be reduced by one order of magnitude due to the kinetic effect, while the thermal effect is shown to be negligible. Therefore, the ignition enhancement by O_3 addition is mainly caused by the kinetic effect.

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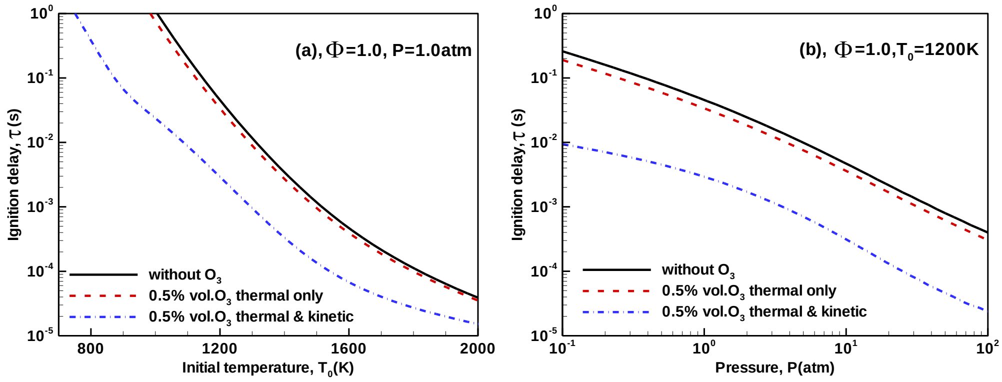

Fig.1 Ignition delay time of CH_4/air/O_3 mixture as a function of (a) initial temperature and (b) pressure.

Sensitivity analysis and reaction path analysis are conducted to interpret the kinetic enhance observed in Fig. 1. It is found that the oxidization rate of CH_3 is the most important factor controlling the ignition of CH_4/air mixture. Without the kinetic effect of O_3, the CH_3 is mainly oxidized by O_2 and the process is very slow. When the kinetic effect of O_3 is considered, the O atom generated through reaction R330 can oxidize CH_3 with a much larger reaction rate through reactions R10 and R284.

$$O_3+N_2 = O_2+O+N_2 \quad \text{(R330)}$$
$$O+CH_3 = H+CH_2O \quad \text{(R10)}$$
$$O+CH_3 = H+H_2+CO \quad \text{(R284)}$$

Therefore, the reduction in the ignition delay time by ozone addition is mainly caused by the above three reactions.

Flame propagation

Figure 2 demonstrate the thermal and kinetic effects of O_3 addition on the laminar flame speed of CH_4/air mixtures at different equivalence ratios. The volume fraction of O_3 changes from 0% to 1.0% while the laminar flame speed S_u can increase by 30% or more. It is seen that thermal effect dominates for the lean and stoichiometric mixture while kinetic effect dominates for the rich mixture. The kinetic and thermal effects are analyzed and the details are presented in the full paper.

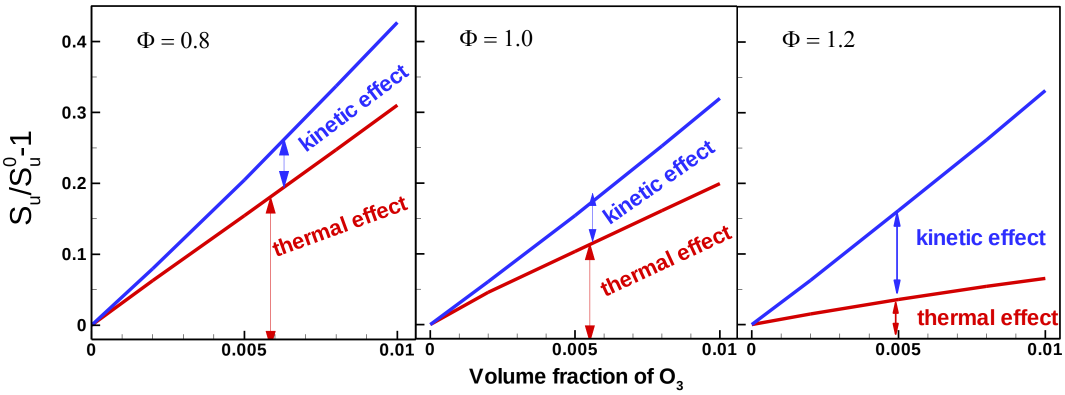

Fig.2 Thermal and kinetic effects of O_3 addition on the laminar flame speed of CH_4/air mixtures.

CONCLUSIONS

The kinetic and thermal effects of ozone addition on the combustion of methane/air mixtures are examined numerically. It is found that for the homogenous ignition, O_3 can accelerate the ignition of CH_4/air by increasing the oxidization rate of CH_3, while the thermal effect is almost negligible. For flame propagating, the thermal effect is shown to dominate over the kinetic effect for fuel lean and stoichiometric cases while the kinetic effect dominates for the fuel rich mixture.

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