Numerical study of the effects of non-equilibrium plasma on the ignition delay of a methane–air mixture using detailed ion chemical kinetics

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ABSTRACT

Researches on non-equilibrium plasmas in ignition and combustion processes have drawn attention of many scientists, because a non-equilibrium plasma-assisted approach provides a useful method to ignite a combustible mixture and stabilize the combustion process. The ignition delay times of methane–air mixtures have been investigated experimentally and numerically; however, the influence of non-equilibrium plasma on the ignition of argon-free methane–air mixtures has seen relatively little discussion. Here, we investigate the ignition delay time of methane–air mixtures via numerical analysis using detailed chemical kinetics. Discharge process and following ignition process are simulated separately, because of significant differences in their time scales and mechanisms. Data on the concentration of atoms and radicals produced in the discharge processes were used as the initial input data to determine the subsequent ignition process because they play an important role in the subsequent ignition process. We focus on the effects of the strength of the reduced electric field, the discharge duration, and the initial temperature on the ignition delay time for zero-dimensional and axisymmetric one-dimensional models. The simulation results showed that the reduced electric field was important in promoting chemical reactions for both the one-dimensional model and the zero-dimensional model; for a constant reduced electric field, longer discharge durations provided more energy to excite the nitrogen, leading to a larger mole fraction of excited nitrogen species during discharge; the gaps between ignition delay times for $E/N = 0$ and $E/N \geqslant 50$ Td were very small at high initial temperatures; however they became very large at low initial temperatures.

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1. Introduction

In recent decades, there has been growing research interest in non-equilibrium plasmas in ignition and combustion processes, as a non-equilibrium plasma-assisted approach provides a useful method to ignite a combustable mixture and stabilize the combustion process. A significant body of experimental and computational research into non-equilibrium plasma ignition and combustion of a wide variety of fuels has been reported [1–6]. Different mechanisms have been investigated, including the chemistry of ions and excited species. Comparisons between experimental results and simulated data under controlled conditions have generally shown good agreement [7–10]. Significant progress has been made in understanding the mechanisms of non-equilibrium plasma-assisted ignition and combustion.

The principle difference between common combustion and plasma-assisted combustion is the initial mechanism. In the discharge process, a large nanosecond-duration voltage is applied to the electrodes, and the resulting electric field attracts free electrons.

The energy from the electric field is generally used to heat the electrons. Therefore, the electron temperature can be several orders of magnitude larger than the temperature of the neutral species, or indeed of the ions, because of the large difference in mass between the free electrons and ions. When these energetic electrons collide with gas-phase atoms or molecules, electron-impact dissociation, excitation, and ionization reactions occur, resulting in radicals, ions, and electronically excited species. The ions, electronically excited species, free electrons, and neutral molecules react with each other; consequently, a large quantity of free radicals is produced. These reactions are termed quenching, charge exchange, and electron–ion recombination reactions. The rate coefficients of these reactions are much greater than those of chain-initiation reactions in common combustion. The production of radicals resulting from the above processes is significant in the subsequent stage of combustion following discharge because they can dramatically accelerate the chemical processes and extend the extinction limits.

Experimental and numerical investigations of the ignition delay time of a stoichiometric methane–oxygen mixture diluted with Ar under the action of a high-voltage nanosecond discharge have been reported [7]; the electron-impact dissociation and excitation reactions led to an increase in the densities of O• and H• radicals at the

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onset of ignition. As a result, the mixtures were ignited with an order-of-magnitude decrease in the ignition delay time. The experimental measurements agreed well with calculated ignition delay times under controlled conditions [7].

Similar research into the ignition of a methane–air mixture using a high-voltage nanosecond discharge has been reported [10]. The simulated data showed that the effect of N_2 on the ignition of methane-containing mixtures was reduced to a change in the density of the active particles due to a decrease in the average electron energy and the formation of new channels for O· radical production during discharge, as well as in the discharge afterglow.

From a practical standpoint, it is more interesting to study argon-free ignition via a non-equilibrium plasma in a fuel–air mixture, but few studies have reported non-equilibrium plasma behavior for methane–air mixtures. The purpose of this paper is to investigate the mechanism of plasma-assisted ignition of methane–air mixtures. We used zero- and one-dimensional models to focus on the effects of the reduced electrical field, discharge duration, and initial temperature of the mixture on the ignition delay time for auto-ignition (without ignition energy) of a methane–air mixture.

2. Numerical method and chemical kinetics

2.1. Governing differential equations and simplifying assumptions

The series of governing differential equations used in this work are the same as those reported in Refs. [15,16], i.e.,

(1) equations of state,
(2) continuity equation,
(3) conservation of momentum equation,
(4) species mass conservation equations, and
(5) energy conservation equation.

To simplify the mathematical treatment and to reduce the computational demand, the following assumptions were made.

(1) The gases forming the mixture (including the electrons) are ideal gases.
(2) The Soret, Dufour, and pressure effects can be neglected because diffusion by these effects is much smaller than that due to temperature and concentration gradients.
(3) The influence of the magnetic field is negligible.
(4) Viscous dissipation and work done by pressure can be neglected in the energy conservation equation.
(5) Natural convection and heat transfer by radiation can be ignored.

2.2. Chemical kinetics of the discharge and ignition processes

The discharge process takes place on a nanosecond timescale; however, the ignition process evolves on a microsecond time scale. Therefore, the chemical mechanisms are completely different for the two processes, and may be separated in the simulation. Note that the effect of non-equilibrium plasma during the discharge process is significant because of the production and accumulation of active atoms and radicals, which are produced in both the strong electric fields during the discharge and in the zero electric field during the discharge afterglow. Data on the concentration of atoms and radicals produced in the discharge process were used as the initial input data to determine the subsequent ignition process because they play an important role in the subsequent ignition process.

The kinetic model in this paper is similar to that reported in Ref. [10] for simulating plasma-assisted ignition of methane–Ar mixtures with the addition of nitrogen, which takes into account the electronically excited states of N_2 because they are strongly involved in the production of O· radicals via quenching reactions with O_2. The major difference is that in this study, the authors did not consider the effects of Ar on the discharge process because of the extremely small content in air. Electronically excited O_2 and N_2 molecules, O·, H·, N·, and hydrocarbon radicals, as well as electrons and positive ions in the ground state, are all involved in the kinetics as active particles. The vibrationally and electronically excited states of O_2 can be neglected because they cannot compare to the momentum transfer in elastic collisions on the cross section and energy area according to Fig. 8(b) in Ref. [7]. The cross section can directly determine the rate of reactions. The excitation of metastable Herzberg $O_2(c^1\sum_u^-)$, $O_2(c^3\Delta_u)$, and $O_2\left(A^1\sum_u^+\right)$ states are substituted by the excitation of one effective metastable state (referred to as O_2^*) [7].

The electronically excited states of N_2 are considered in more detail because they can be efficiently quenched by O_2 molecules, resulting in the production of O· radicals, and they may also be quenched by CH_4 molecules [10]. When calculating the mole fractions of active particles, the $N_2\left(A^3\sum_u^+\right)$, $N_2\left(B^3\prod_g\right)$, $N_2\left(a'^1\sum_u^-\right)$ and $N_2\left(C^3\prod_u\right)$ states are regarded as different chemical species. The excitation of one effective state denoted as $N_2(B)$ substitutes the excitation triplet states of $N_2(B^3\prod_g)$, $N_2\left(B'^3\sum_u^-\right)$, and $N_2(W^3\Delta_u)$. The excitation rate coefficient of $N_2(B)$ is assumed to be the sum of the excitation rate coefficients of the three triplet states, whereas the quenching rate coefficient is taken as equal to that of the $N_2(B^3\prod_g)$ state. This approximation is based on the assumption of fast kinetic energy exchange between these states resulting from collisions. The excitation of the effective state of $N_2(a)$ is substituted for the excitation of the $N_2(a^1\prod_g)$, $N_2(a'^1\sum_u^-)$, and $N_2(w^1\Delta_u)$ singlet states. The excitation rate coefficient of the $N_2(a)$ state is assumed to be equal to the sum of the three singlet states, whereas the quenching rate coefficient is taken as equal to that of the $N_2\left(a'^1\sum_u^-\right)$ state [10,11].

Negative ionic species were ignored at temperatures above 1000 K because their densities are generally lower than the electron density [12,13]. Complex positive ionic species, such as Ar_2^+, O_4^+, and N_4^+, were not considered because their dissociation energy is small and so they decay rapidly at such gas temperatures. It is assumed that by the end of the discharge afterglow, the active particles produced in the discharge process are only atoms and radicals [10].

Table 1 shows the reactions of the kinetic model and the rate coefficients in discharge process used in this study. Electron impact dissociation, excitation, and ionization reactions of neutral particles, quenching reactions of electronically excited particles, and charge exchange reactions are accounted for. The rate coefficients for these reactions were taken from Refs. [7,10,14]. The rate coefficients of electron-impact dissociation reactions (R1–R3), excitation reactions (R4–R8), and ionization reactions (R9–R11) were determined as a function of the reduced electric field, E/N, from kinetic calculations by solving Boltzmann's equation for the electron energy distribution function, where E is the electric field and N is the gas number density. When solving Boltzmann's equation, the input parameters were the reduced electric field E/N, the initial gas temperature T_0, and the gas mixture composition; however, the electron distribution was not affected by the temperature of the gas, and only collisions between electrons and atoms or molecules of the dominant species in the mixture were considered. The effect of electron–electron collisions and collisions between elec-