Effect of Equivalence Ratio on Particle Variation of CH_4 /Air Mixture of Coaxial Dielectric Barrier Discharge

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Abstract. The effect of equivalence ratio on particle components of dielectric barrier discharge of CH_4/air mixture were carried out by employing a coaxial cylindrical electrode. The result shows that molar fraction of active particles such as H, O_3, CH_3 and NO decrease slightly with the equivalence ratio, however, enough active particles could be obtained even at the smallest equivalence ratio conditions; no obvious change in the electron density with the equivalence ratio has been obtained, which has a very beneficial effect on the methane-air combustion reaction under the conditions of low equivalence ratio.

Introduction

As the main component of natural gas, methane has a high bond energy in C-H key [1,2], which leads to high ignition energy and low flame propagation rate [3]. So the combustion reaction of methane is difficult to perform under low equivalence ratio conditions. In recent years, the non-equilibrium plasma enhanced combustion technology has received a wide range of attention in the recent years because it has high electron temperature ($>10^4$ K) and has ability to activate the molecules to cause a chemical reaction effectively [4,5]. In the ionization mode of non equilibrium plasma, dielectric barrier discharge (DBD) is a kind of non equilibrium, unstable and non uniform gas discharge, which is an effective method to generate non-equilibrium plasma.

In the current study, only little literature could be found in the aspect of the effect of equivalence ratio change on the evolution law of electron and free radical concentration of DBD. However, the equivalence ratio is the key parameter to determine the combustion process. In this article, one dimensional numerical simulation was carried out to study the effect of discharge parameters and reactor structure on the distribution of electron density and the distribution of the main reactive particles in the DBD discharge process of atmospheric pressure.

Establishment of plasma model

The kinetic model of non equilibrium plasma generated by dielectric barrier discharge includes ionization, elastic collision, excitation, electron adsorption and recombination. In order to establish the plasma kinetic model, the following assumptions have been made: 1) ignore the magnetic effect of the plasma; 2) particle distribution in the ionization space is uniform; 3) the electric field distribution in the ionization space is uniform.

Physical model

Figure 1 is the schematic diagram of coaxial cylinder electrode structure, where the inner electrode is the anode and the radius is 3.0 mm. The outer electrode is the earth electrode. The space between the outer electrode and the inner electrode is the ionization space, and its width S is 10 mm. The thickness of the dielectric layer is 0.5 mm, which is installed on the inner electrode, and the dielectric constant

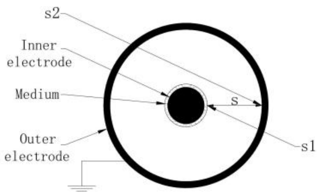

Fig. 1 Schematic diagram of coaxial cylinder electrode structure

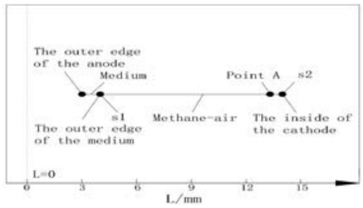

Fig. 2 One dimensional plasma model

is 10. The initial electron density is 1.0×10^{14} m^{-3}, the initial electron energy is 4 eV, the secondary electron emission coefficient is 0.15, and the secondary electron energy is 5 eV.

Mathematical model

Arrhenius formula is as shown formula 1

$$k_f=AT^n\exp(-E_a/RT) \quad (1)$$

The Surface reaction is shown as formula 2

$$A^+ + surface => e + A \quad (2)$$

The formula is shown as formula 3

$$-n\cdot\Gamma_e=(1-r)\cdot[(0.5v_{et}\cdot n_e)/(1+r)]-[\Sigma_i\,\gamma_i(\Gamma_i\cdot n)+\Gamma_t\cdot n] \quad (3)$$

where n represents the total particle number density; n_e represents the number density of electrons; Γ_e represents the diffusion term; r indicates the reflectivity of the particles bombarding; v_{et} is the velocity of electron thermal motion; Γ_i stands for the ith positive ion flux at the wall; γ_i represents the secondary electron emission coefficient of wall reaction of the ith positive ions; Γ_t is the gamma emission flux of wall heat.

In the computational model, the mixture of the gas composition is mainly considered as CH_4, N_2 and O_2 that carried out at atmospheric pressure and initial temperature of 298K.The reactions are shown in Table 1 and Table 2. For the surface reaction are as shown in table 3, heavy particles could excite secondary electron by wall-colliding. According to the physical model of figure 1, a one-dimensional plasma model as shown in figure 2 has been established. In the model, the horizontal axis represents the distance L from the center electrode to the outer electrode along the radius direction, and unit is mm.

Table 1 Chemical reactions of non electronic components

Reaction	Reaction equation	A	n	En
1	$N+O_2\rightarrow NO+O$	9×10^{9}	1	6500
2	$N+NO\rightarrow N_2+O$	2.7×10^{13}	0	355
3	$CH_4+O\rightarrow CH_3+OH$	4.7×10^{-10}	0	5.4×10^{4}
4	$CH_2O+O\rightarrow HCO+OH$	3×10^{-11}	0	1.2×10^{4}
5	$H+O_2\rightarrow OH+O$	1.6×10^{-10}	0	6.4×10^{4}
6	$CH_4+1.5O_2\rightarrow CO+2H_2O$	5×10^{11}	0	2×10^{5}
7	$CO+O\rightarrow CO_2$	2.24×10^{19}	0	1.7×10^{5}
8	$O_3+N_2\rightarrow O_2+O+N_2$	4×10^{14}	0	22667
9	$O_2+O+N_2\rightarrow O_3+N_2$	1.6×10^{14}	-0.4	-1391
10	$O_3+O_2\rightarrow O_2+O+O_2$	1.54×10^{14}	0	23064

Table 2 Electron impact reaction in methane air reaction

Reaction	Reaction equation	Reaction rate	$\Delta\varepsilon$/eV
1	$e+O_2\rightarrow e+O_2(ald)$	Collision cross section calculation	4.5
2	$e+O_2\rightarrow 2e+O_2^+$	Collision cross section calculation	12.06
3	$e+N_2\rightarrow e+N+N$	Collision cross section calculation	13
4	$e+CH_4\rightarrow e+CH_3+H$	Collision cross section calculation	10

Table 3 surface reaction

Reaction	Equation	Adhesion coefficient
1	$O_2^+ \rightarrow O_2$	1
2	$O \rightarrow 0.5O_2$	1
3	$N_2^+ \rightarrow N_2$	1

Results and discussion

The reactive particles produced by ionization have great influence on the reaction rate of CH_4. According to order of the influence of methane combustion reaction from strong to weak, four kinds of main active particles produced by ionization are: H, O_3, CH_3 and NO, where NO can enhance the generation rate of H, O and other particles. The initial molar concentrations of these four kinds of particles are all set to 1.0×10^{-8}, and the initial electron density is 1.0×10^{14}/m^{-3}.

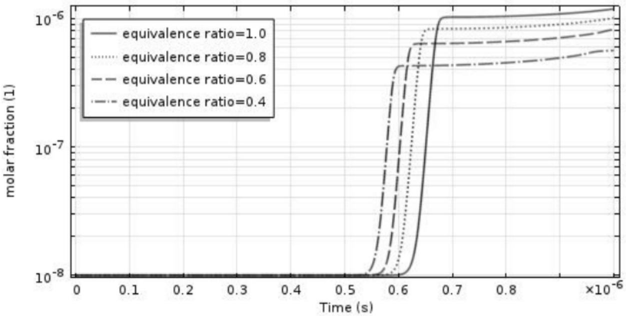

Fig.3 The change of mole fraction of H with time

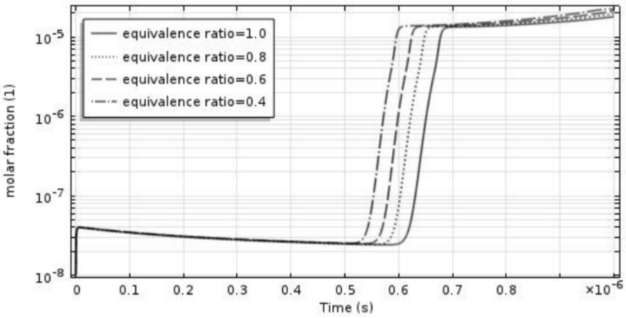

Fig.4 The change of mole fraction of O3 with time

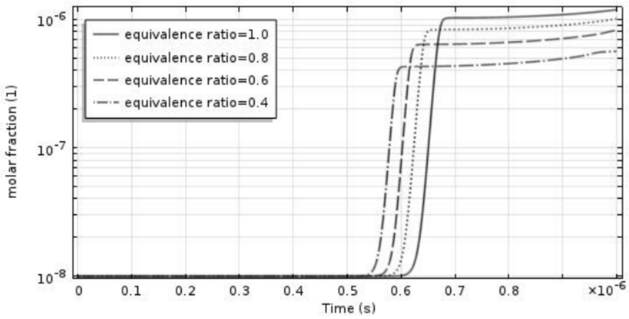

Fig.5 The change of mole fraction of CH3 with time

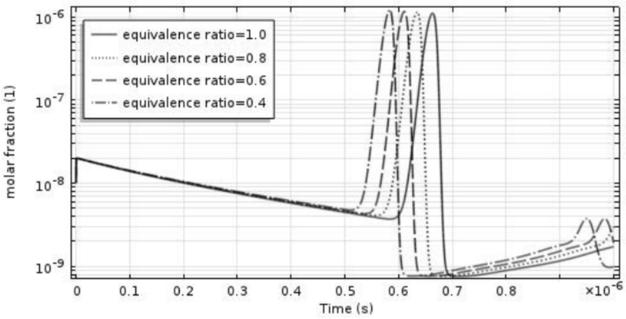

Fig.6 The change of mole fraction of NO with time

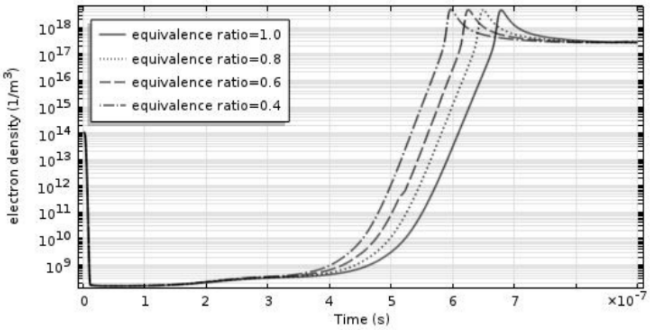

Fig.7 The change of electron density with time at different equivalence ratio conditions

Figures 3 to 6 show the variation of molar concentration of H、O_3、CH_3 and NO. As shown in figures 3 and 5, it can be seen that the evolving curve of the number density of H and CH_3 is completely consistent. This is due to the complete agreement (see Table 2) of the CH_3 and H reactions in the methane ionization model used in this paper. When the equivalence ratio is 0.4, the mole fraction of H and CH_3 begins to increase at 0.52 μs. With the increase of the equivalence ratio, there is a delay in the starting time when the molar fraction of H and CH_3 begins to increase significantly. When the equivalence ratio increases to 1.0, the molar fraction of H and CH_3 increases significantly at 0.60 μs.

Figure 4 shows the change of O_3 molar concentration. When $\Phi = 0.4$, O_3 begins to increase rapidly at 0.52 μs, and reaches the maximum value (1.4×10^{-5}) at 0.61μs. Then keeps increasing at less increase rate, and with the increase of the equivalence ratio it appears a postpone to reach the maximum value. Due to the time delay and the same changing tendency, more molar concentration of the particles have been obtained at low equivalence ratio condition at the same time.

Figure 6 shows the variation of NO molar fraction. As is shown in the figure, the molar fraction of NO begins to decline at the beginning, and then rises rapidly. After that, there is a rapid decline after reaching the peak value and followed by a slow rise process. Around 0.58 μs, the molar fraction of NO reaches the maximum 1.2×10^{-6} at $\Phi = 0.4$. With the increase in the equivalence ratio, the time of reaching to the maximum value of NO molar concentration has been delayed. After reaching to the maximum value, due to low energy of the secondary ionization, the amount of produced NO is relatively small. Therefore, the change tendency of NO molar concentration shows a rapid decline at first, and then followed by a slight increase.

Figure 7 shows the effect of equivalence ratio on the variation of electron density. As is shown in the figure, the variation trend of electron density at different equivalence ratio is basically the same, only that the electron density could reach to the maximum value faster at low equivalence ratio. The maximum electron density is about $5 \times 10^{18}/m^3$ under all equivalence ratio conditions, and the electron density is about $3 \times 10^{17}/m^3$ at the balance state. It could also be obtained that although the equivalence ratio has been reduced, it has no influence on the electron density which plays a key role in active particle production. It has a very beneficial effect on the methane-air combustion reaction under lean conditions.

Results and discussion

(1) The molar fraction of active particles decreases slightly with the equivalence ratio, however, enough active particles could be obtained even at the smallest equivalence ratio conditions.

(2) There is no obvious change in the electron density with the equivalence ratio, which has a very beneficial effect on the methane-air combustion reaction under lean conditions.

(3) Discharge has greatly improved the molar concentration of H, O_3, CH_3 and NO which lay a major role in the combustion reaction of methane. H and CH_3 have the same change tendency, and the molar fraction can reach to the maximum value and then maintain roughly balanced; NO molar fraction reaches to the maximum value firstly, then appears a sharply decrease, and finally has a slight increase.

Acknowledgements

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