

Kinetics of Plasma Assisted Combustion At Low Reduced Electric Fields

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1. Introduction

The mechanism of plasma assisted ignition has been intensively discussed in recent years. Several possible mechanisms have been proposed to enhance the ignition with electrical discharges [1]. Among them, the excitation of molecules to vibrational and electronic states by plasma seems to be quite interesting due to its higher efficiency than others. The purpose of this paper is to study numerically the ignition of a hydrogen-oxygen mixture under influence of single delta oxygen (SDO, $O_2(a^1\Delta_g)$). A kinetic mechanism of the effect of singlet oxygen molecules was determined by calculating numerically the ignition characteristics. The efficiency of various electric discharges for enhancement of combustion is also presented.

2. Numerical simulation

The ignition process was numerically simulated using the kinetic scheme given by [2], which include 12 particle species (H_2 , H , O_2 , O , O_3 , $O(1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, OH , HO_2 , H_2O_2 , H_2O) and 80 reactions. Calculations were carried out in the zero-dimensional approximation at a fixed gas pressure.

In calculations, we determined the ignition delay time as the interval between the instant at which singlet oxygen molecules were injected and the onset of abrupt increase of gas temperature. To validate the calculated results, the comparison has been made between the experiment from [3] and our simulations. In order to convert the induction zone length provided in that paper to ignition delay time, the gas velocity is required. Fortunately, based on the given parameters, one can easily calculate the velocity of the H_2 - O_2 gas mixture.

Gas parameters from original experiment of a $H_2:O_2=5:2$ mixture measured delay times for autoignition, and ignition with different mole fractions of single delta oxygen.

Mole fraction of SDO (%)	0	1.2	4	6
Induction Zone Length, L_{in} (cm)	51	27	18.6	16.8
Ignition delay time from [3], τ_e (ms) $=L_{in}/v_0$	12.86	6.81	4.69	4.24
Calculated ignition delay time τ_c (ms)	49.1	23.2	18.7	17.7

Based on our kinetic model, the ignition delay time of different mole fractions of SDO are compared as figure 1. Good agreement between experiment and calculation has been achieved.

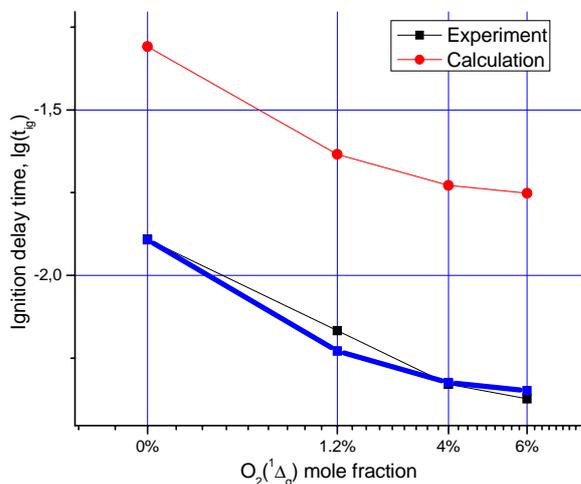


Figure 1. The ignition time in the H₂:O₂=5:2 mixture as a function of single delta oxygen mole fraction in oxygen. Comparison between experiment results (black square) and modeling calculations (red diamond) in double logarithmic chart.

To show the mechanism of the effect of the single delta oxygen on the ignition process, Fig. 2a and 2b compare the evolution in time of the calculated rates of the dominant chemical reactions for autoignition and plasma-assisted ignition. It follows from the calculation that an injection of sufficient single delta oxygen molecules leads to an efficient initiation. Indeed, in the induction phase of autoignition, the rates of the reactions keep a low rate at the start and jump by several orders of magnitude only immediately before ignition. In the case of plasma-

assisted ignition, the active single delta oxygen produces affluent OH radicals at the very beginning. Due to the high density of OH radicals, the rate of the reaction H₂+OH=H₂O+H is high. Consequently, the rates of chain branching reactions have been increased greatly. As a rule, in the induction period of SDO assisted ignition, the role of the radical reactions becomes more profound than that of the reactions with the main components.

Figs. 3a and 3b show the evolution in time of the mole fractions for the main components of the mixture during autoignition and plasma-assisted ignition, respectively. In the induction phase of autoignition, the density of atoms and radicals keep low until the instant right before ignition. With plasma-assisted ignition, the concentrations of H, O, and OH species jump very fast at 20 μs from the beginning and hence lead to decreasing of the ignition delay time.

In general, kinetics in the system can be explained in the following way. At the beginning of the ignition phase, OH radicals are efficiently produced through the reaction O₂(¹Δ_g)+H₂=OH+OH. This leads to an increase in the rate of the reaction H₂+OH=H₂O+H; in other words, the efficiency of production of H atom rises significantly. Consequently the rate of the reaction O₂(¹Δ_g)+H=OH+O boost up immediately, which can be clearly seen from fig. 2b. At about 80 μs from the start, the switch between the two SDO reactions rates occurs. As a result, these three reactions above create a new channel of chain initial reactions, which may be the key reactions at the induction phase of SDO-assisted ignition.

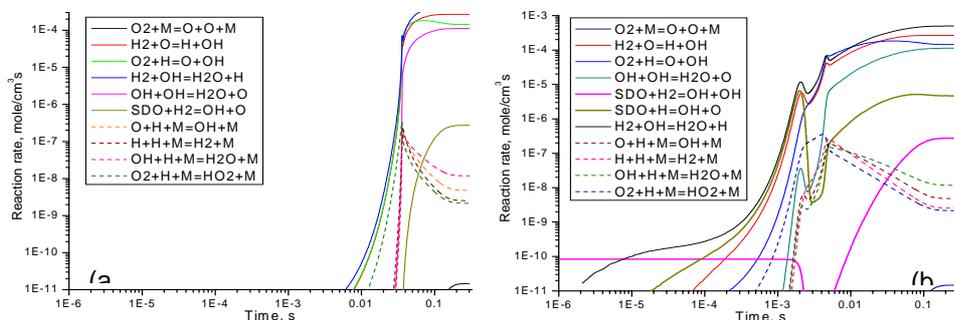


Figure 2. The evolution in time of the calculated rates of the main chemical reactions for autoignition (a) and ignition with 6% single delta oxygen (b).

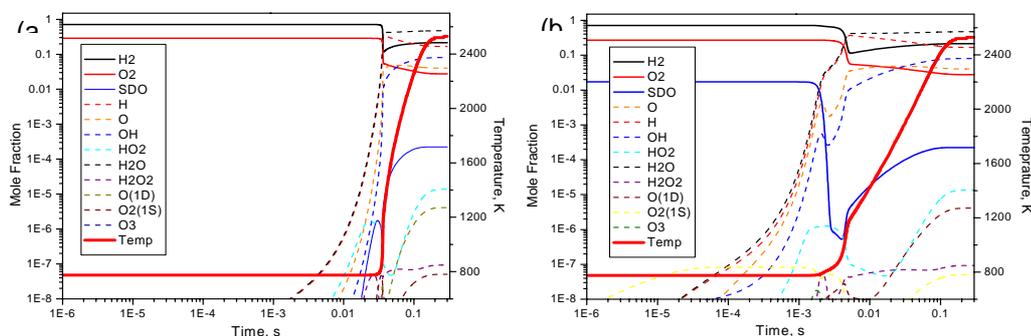


Figure. 3. The evolution in time of the mole fractions of the main component for autoignition (a) and ignition with 6% single delta oxygen. The gas temperature evolution is represented by the thick red line.

In addition, we made a sensitivity analysis of the kinetic scheme for autoignition, 1.2% and 6% single delta oxygen assisted ignition delay time. The analysis was made as follows: the rate constant of each reaction was in turn increased by 100% and the ignition delay time was calculated separately for each case. The sensitivity coefficients were calculated as $(\tau_i - \tau_0) / \tau_0$, where τ_0 is the ignition delay time calculated with unchanged rate constants and τ_i is the ignition delay time calculated with the increased rate constant of the i th reaction. The results of the calculations are given in Fig. 5. The delay time for SDO-assisted ignition is less sensitive to the variation in the rates of the reactions of chain initiation. Due to the high productivity of active species at the beginning of the ignition phase, the recombination reactions have higher sensitivities than those in autoignition. At the same time, the role of reactions of chain branching ($O_2 + H = OH + O$) decreases since the role of O_2 has been replaced by SDO especially at the beginning.

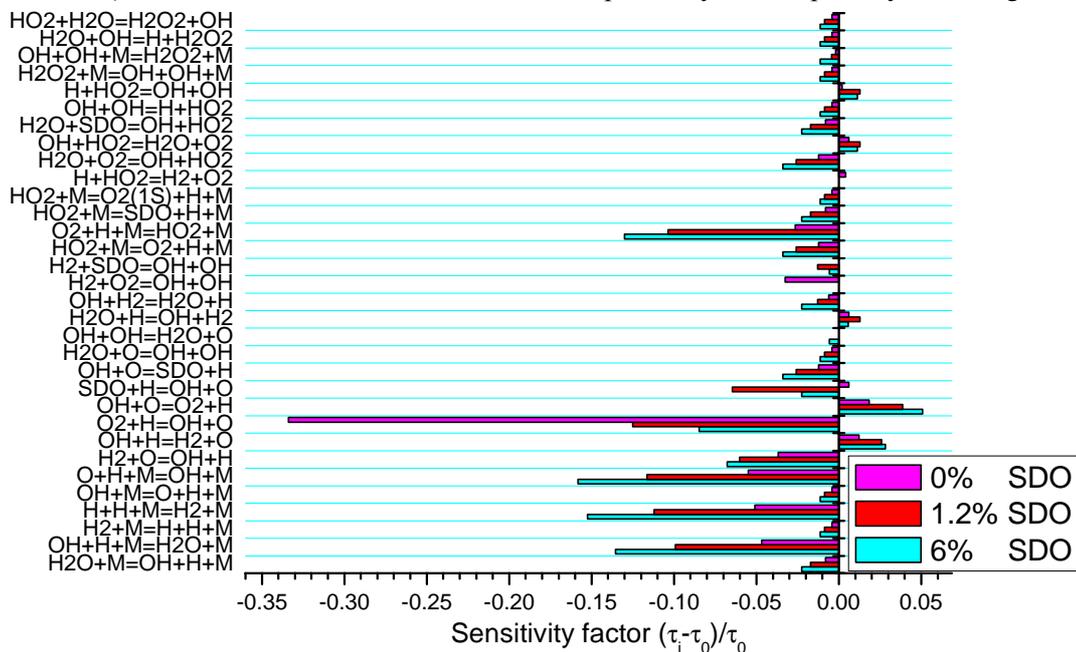


Figure. 4. The sensitivity factor analysis for ignition with 0%, 1.2% and 6% single delta oxygen mole fractions in oxygen respectively, at $T=775$ K and $P=10$ Torr in the $H_2:O_2=5:2$ mixture.

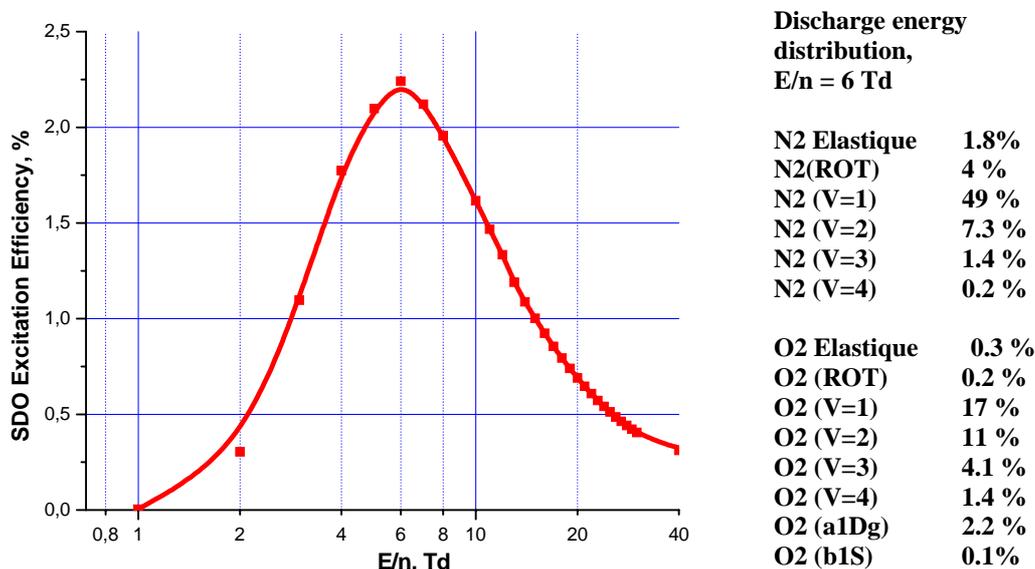


Figure 5. Efficiency of the SDO excitation in gas discharge.

We also simulated different yield of singlet oxygen molecules in various electric discharge conditions. As given in fig. 6, the highest amount of single delta oxygen molecules could be generated up to 70% in pure oxygen plasma at about 10 Td of reduced electric field. However, the maximal efficiency of single delta oxygen from atmosphere discharge is only 2.2% at 6 Td. Moreover, from our analysis of all reactions with SDO participation during the whole process, the radical generation efficiency starts at about 200% ($O_2(^1\Delta_g) + H_2 = OH + OH$), but reduces to 100% ($O_2(^1\Delta_g) + H = OH + O$) after about 80 μs . Meanwhile, we should also notice that, with reduced electric field at the value of 200 Td, air plasma can contain significant amount of oxygen atoms (60%), which lead to the decrease of importance of the role of singlet oxygen molecules at such circumstance.

3. Conclusion

We have made a numerical study of the ignition of hydrogen-oxygen mixtures with the participation of singlet oxygen molecules and showed that it agrees well with the measurements from experiment. It follows from the analysis of the calculated results that, with single delta oxygen molecules, the great amount of active species with fast reactions lead to the decrease of ignition delay time. Besides, in order to obtain best results at various conditions, relatively low E/n (~ 10 Td) is required in pure oxygen electric discharge, while larger value of E/n (~ 300 Td) is recommended for high efficiency in air plasma.

References

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- [2] A.M. Starik, N.S. Titova, Kinetics and Catalysis, **44** (1) (2003) 28–39
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