Kinetic modeling and uncertainty analysis of hybrid repetitive nanosecond and DC discharge enhanced low temperature $H_2/O_2/He$ ignition

Xingqian Mao[1], Qi Chen[1,*], Aric Rousso[2], Timothy Chen[2], and Yiguang Ju[2]

[1] *School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, China*
[2] *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA*

Abstract: The present work reports on the kinetic study of a hybrid repetitive nanosecond (NSD) and DC discharge enhanced low temperature $H_2/O_2/He$ ignition at atmospheric pressure. Compared with NSD, the addition of a DC electric field further enhances ignition. Ignition enhancement by key excited species $H_2(v)$, $O_2(a^1\Delta_g)$ and $O(^1D)$ is investigated. Uncertainty analysis of reactions involving excited species and kinetic mechanisms on ignition delay time is demonstrated.

Keywords: Plasma assisted ignition, kinetic modelling, uncertainty analysis, hybrid nanosecond and DC discharge.

1. Introduction

Non-equilibrium plasma has shown a great potential in enhancing combustion and ignition in the past decades. Many researchers have studied plasma assisted combustion of small molecule fuels, such as H_2, CH_4, C_2H_4, as well as large hydrocarbons, like n-pentane and n-heptane, both numerically and experimentally [1, 2]. Specifically, researchers found that plasma played a dramatic role in enhancing combustion and ignition at low temperatures [3]. This is due to the significant kinetic enhancement caused by non-equilibrium excitation of excited species and radicals generated in the plasma. Previous studies mostly focused on a single discharge type to assist combustion, such as DC, AC, microwave, RF, gliding arc, or repetitively-pulsed nanosecond discharge (NSD). Few studies worked on the optimization or combination of discharge types to achieve increased enhancement on combustion. As the design of combustion systems trend towards fuel lean, the development of new discharge types with potential to augment real combustion systems becomes more applicable.

In our recent study [4], a hybrid repetitive nanosecond and DC discharge was used to enhance low temperature $CH_4/O_2/He$ ignition. We applied two characteristic electric field strengths to allow for the separation of the weak and strong electric field induced plasmas. The applied DC field was modulated to explore the kinetic effects on low temperature ignition, which showed that there existed an optimized condition of DC reduced electric field strength. For the excited species produced in hybrid plasma, vibrationally excited $CH_4(v)$ and $O_2(v)$ are quenched via fast relaxation. $O_2(a^1\Delta_g)$ and $O(^1D)$ enhances the low temperature CH_4 ignition effectively through kinetic pathways. Compared with $CH_4(v)$ and $O_2(v)$, $H_2(v)$ has a higher potential energy at the same vibrational level, and the relaxation rate constants of $H_2(v)$ in H_2/O_2 mixtures are several orders of magnitude lower than those of $CH_4(v)$, $O_2(v)$ and $N_2(v)$ in CH_4-containing mixtures [1]. This indicates $H_2(v)$ might have the potential to kinetically enhance ignition.

The present study therefore explores the ignition enhancement of $H_2/O_2/He$ mixtures by a hybrid repetitive nanosecond and DC discharge at low temperatures. Firstly, we develop a plasma-combustion kinetic model of $H_2/O_2/He$ mixtures and validate it by plasma assisted low temperature oxidation experiments. Secondly, ignition enhancement of $H_2/O_2/He$ mixtures by hybrid plasma is studied by numerical modeling. Kinetic effects of the key excited species $H_2(v)$ and $O_2(a^1\Delta_g)$ are demonstrated. Finally, the uncertanties of the reactions involving $H_2(v)$ and $O_2(a^1\Delta_g)$ on ignition delay time are studied.

2. Numerical method and experiment validation

A zero-dimensional solver incorporating the plasma kinetics solver ZDPlasKin [5] and the combustion chemical kinetics solver CHEMKIN [6] is used to model the plasma assisted ignition. The detailed description of the hybrid ZDPlasKin-CHEMKIN model is described in [4]. A plasma-combustion kinetic model of $H_2/O_2/He$ mixtures is developed. The species in the model consists of H_2(rot), O_2(rot); $H_2(v1)$, $H_2(v2)$, $H_2(v3)$, $O_2(v1)$, $O_2(v2)$, $O_2(v3)$, $O_2(v4)$; $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, O_2^*, $O(^1D)$, $O(^1S)$, He^*, He^{**}, He_2; O_3; H^+, H_2^+, H_3^+, O^+, O_2^+, O_4^+, OH^+, H_2O^+, H_3O^+, He^+, He_2^+, HeH^+, H^-, O^-, O_2^-, O_3^-, O_4^-, OH^-, and electrons. HP-mech [7] is used as the base combustion mechanism for $H_2/O_2/He$.

Experiments of NSD plasma enhanced low temperature H_2 oxidation are conducted to validate the $H_2/O_2/He$ plasma-combustion mechanism. The experiments are conducted in a $0.1667H_2/0.0833O_2/0.75He$ combustible mixture with an initial temperature of 298 K and a constant pressure of 60 Torr. Mole factions of major species are measured by GC sampling. A good agreement between experiment and modelling results validates the kinetic model and numerical methods.

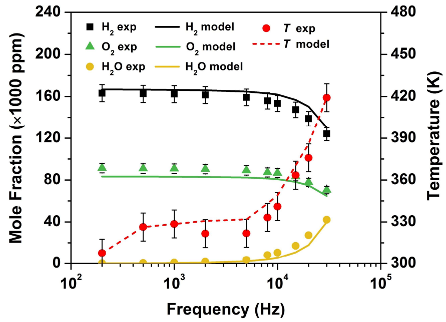

Fig. 1. Experiment validation.

3. Result and discussion

For modelling the effects of non-equilibrium excitation on $H_2/O_2/He$ low temperature ignition, a repetitive nanosecond and DC discharge with different DC *E*/*N* values is applied. The ignition delay times are calculated for auto-ignition, thermal ignition, NSD and hybrid discharge assisted ignition, respectively. All the calculations are conducted in a $0.1667H_2/0.0833O_2/0.75He$ mixture between 400 and 800 K in an adiabatic system at atmospheric pressure. The *E*/*N* of the NSD is 100 Td with a repetition rate of 30 kHz, when the dissociation of H_2 and O_2, electronic excitation, ionization and electron waves both occur efficiently. The deposited energy density used is 0.1 mJ/cm^3. In the hybrid discharge, DC discharge *E*/*N* values of 2, 10, 15 and 20 Td are studied, where most of the electron energy will go to the excitation of $O_2(v)$, $H_2(v)$ and $O_2(a^1\Delta_g)$. Fig. 2 shows the comparison of the ignition delay times at these different conditions. The effective enhancement of plasma in $H_2/O_2/He$ ignition is clearly seen, especially at low temperatures. Compared with the NSD, the DC application further enhances ignition. This is due to the efficient production of vibrationally excited $H_2(v)$, $O_2(a^1\Delta_g)$, O and $O(^1D)$ via electron impact reactions (1) - (4) in the hybrid plasma.

$$e + H_2 \rightarrow e + H_2(v) \quad (1)$$

$$e + O_2 \rightarrow e + O_2(a^1\Delta_g) \quad (2)$$

$$e + O_2 \rightarrow e + O + O \quad (3)$$

$$e + O_2 \rightarrow e + O + O(^1D) \quad (4)$$

These excited species and radicals further promote the production of O, H and OH through the kinetic pathways listed below (5) - (8).

$$O + H_2(v) \rightarrow H + OH \quad (5)$$

$$H_2(v) + OH \rightarrow H_2O + H \quad (6)$$

$$H + O_2(a^1\Delta_g) \rightarrow O + OH \quad (7)$$

$$O(^1D) + H_2 \rightarrow OH + H \quad (8)$$

For the key reactions (5) - (7) involving $H_2(v)$ and $O_2(a^1\Delta_g)$, there exist large uncertainties in the rate constants studied in previous stuides [8, 9]. Therefore, uncertainty analysis of these reactions is conducted for several cases with different rate constants, as shown in Fig. 3. Case 0 is calculated using the experimental coefficient α of $H_2(v)$ and the most recently updated rate constants of $O_2(a^1\Delta_g)$ for comparison. The results shows that the uncertainties of these key reactions lead to a 10%-30% difference in ignition delay time when a considerable amount of $H_2(v)$ and $O_2(a^1\Delta_g)$ is produced in the hybrid plasma. Therefore, the excited species and selection of accurate rate constants are important for plasma model development and plasma assisted ignition modeling.

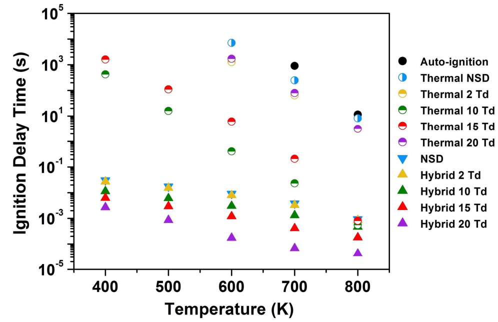

Fig. 2: Ignition delay time of auto-ignition, thermal ignition, NSD and hybrid discharge assisted ignition with different temperatures.

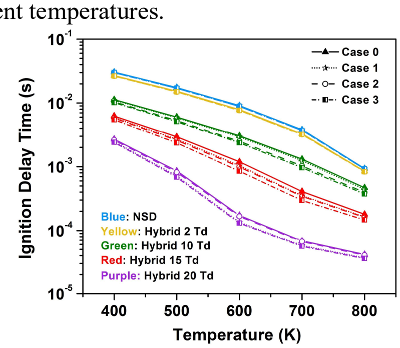

Fig. 3. Uncertainty analysis of key reactions involving $H_2(v)$ and $O_2(a^1\Delta_g)$ on ignition delay time in different cases.

Acknowledgment

We would like to thank the grant support from Exxon Mobil, the National Natural Science Foundation of China (21676024) and Beijing Natural Science Foundation (3182029) for the kinetic study of this research.

References

[1] A. Starikovskiy, and N. Aleksandrov, Progress in Energy and Combustion Science, 39, 1, (2013).
[2] Y. Ju, and W. Sun, Progress in Energy and Combustion Science, 48, (2015).
[3] Y. Ju, J.K. Lefkowitz, C.B. Reuter, S.H. Won, X. Yang, S. Yang, W. Sun, Z. Jiang, and Q. Chen, Plasma Chemistry and Plasma Processing, 36, 1, (2016).

[4] X. Mao, A. Rousso, Q. Chen, and Y. Ju, Proceedings of the Combustion Institute, (2018).
[5] S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, and L.C. Pitchford, http://www.zdplaskin.laplace. univ-tlse.fr, (2008).
[6] A.E. Lutz, R.J. Kee, and J.A. Miller, SENKIN: A FOR- TRAN Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis, Sandia National Laboratories, Report No. SAND87-8248, (1988).
[7] X. Shen, X. Yang, J. Santner, J. Sun, and Y. Ju, Proceedings of the Combustion Institute, 35, 1, (2015).
[8] A.A. Chukalovsky, K.S. Klopovsky, A.P. Palov, Yu.A. Mankelevich, and T.V. Rakhimova, Journal of Physics D: Applied Physics, 49, (2016).
[9] A.S. Sharipov, and A.M. Starik, Physica Scripta, 88, (2013).