Monte Carlo simulation of the effect of “hot” atoms on active species production in high-voltage pulsed discharges

N.L. Aleksandrov\textsuperscript{1}, A.A. Ponomarev\textsuperscript{2} and A.Yu. Starikovskiy\textsuperscript{3}

\textsuperscript{1} Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, Russia
\textsuperscript{2} SSC Keldysh Research Center, Moscow, Russia
\textsuperscript{3} Princeton University, Princeton, NJ, U.S.A.

Abstract: Monte Carlo simulation is used to study energy degradation of high-energy H and O atoms in CH\textsubscript{4}:O\textsubscript{2} and CH\textsubscript{4}:air mixtures taking into account elastic collisions and chemical reactions. Based on the simulated results, the effect of high-energy atoms on the amount and composition of chemically active species produced in high-voltage pulsed discharges is estimated.

Keywords: Monte Carlo simulation, atom energy degradation, active species production, high-voltage pulsed discharge

1. Introduction
In the last two decades, the applications of non-equilibrium discharge plasma to ignition and combustion have been thoroughly studied \cite{1-3}. It was shown that plasma techniques can lead to ignition delay shortening, flame stabilization, combustion enhancement and emission reduction. These effects are due to active species production and rapid gas heating in discharge plasma and due to modifying transport processes in flames. In discharges, chemically active species (atoms, radicals and excited and charged particles) are created in collisions between molecules and electrons heated in a strong electric field.

Atoms and radicals produced in the discharge plasma possess excessive translational energy (a few electronvolts) that is lost after several elastic collisions with neutral particles. In \cite{4}, it was shown that, prior to the energy degradation of “hot” particles, they can be involved in chemical reactions with high energy threshold. This leads to an additional production of chemically active species. The purpose of this work was to simulate numerically this effect and to calculate the amount of active species produced in discharge plasmas taking into account chemical reactions with “hot” atoms and radicals. The simulation was carried out by a Monte Carlo method allowing competitive consideration of elastic and inelastic collisional processes leading to the translational energy relaxation of particles with excessive initial energy.

2. The method of simulation
We simulated the energy degradation of H and O atoms with excessive translational energy in stoichiometric CH\textsubscript{4}:O\textsubscript{2} and CH\textsubscript{4}:air mixtures at different initial gas temperatures. It was assumed that “hot” atoms were produced in a high-voltage pulsed discharge due to electron-impact CH\textsubscript{4} and O\textsubscript{2} dissociation and due to dissociative quenching of electronically excited N\textsubscript{2} molecules in collisions with O\textsubscript{2} and CH\textsubscript{4}. The motion of atoms and radicals was simulated one after another neglecting collisions between them. At the beginning, an atom was originated with a given translational energy in a given point. The free-flight time between the atom-molecule collisions was stochastically determined using the null collision technique described in detail, for instance, in \cite{5}. The molecule velocity before collisions was stochastically generated on the basis of the Maxwellian velocity distribution with the gas temperature $T$. The type of the collision was determined in a stochastic way using the cross sections for the corresponding processes. A new atom velocity after the collision was calculated taking into account the energy released and assuming that the center-of-mass velocity of the colliding particles is unaffected by any binary collision and that the angle distribution of the ion velocities in the center-of-mass frame is isotropic. We simulated the energy degradation of a given atom and new atoms and radicals formed during this process until these particles were thermalized.

Energy degradation was simulated for H and O atoms. The processes taken into account during the energy degradation were elastic collisions with CH\textsubscript{4}, O\textsubscript{2} and N\textsubscript{2} and chemical reactions

\begin{equation}
H + O_2 \rightarrow OH + O,
\end{equation}

\begin{equation}
O + CH_4 \rightarrow CH_3 + OH
\end{equation}

and

\begin{equation}
H + CH_4 \rightarrow CH_3 + H_2.
\end{equation}

The cross-sections for elastic collisions were taken from \cite{6} assuming the 12-6 Lennard-Jones intermolecular potential. The cross-sections for reactions (1) – (3) were determined on the basis of the hard-sphere model with energy threshold; the parameters for these cross sections were adjusted to obtain agreement between the calculated rates and available data in the literature.

---

P-I-13-1 1
3. Calculated results

Fig. 1 shows the mean amount of particles produced by one “hot” atom during its energy degradation as a function of its initial energy, $E_0$. “Hot” H atoms react with methane when their initial energy exceeds 0.54 eV. For higher values of $E_0$, the amount of H atoms decreases with $E_0$ due to reaction (3) in which CH$_3$ and H$_2$ are generated. When $E_0$ increases up to 1.4 eV, reaction (1) becomes important and leads to an increase in the amount of O atoms and OH radicals.

Calculations show that the effect of “hot” H atoms on the additional production of active species in the CH$_4$:air mixture is close to that in the CH$_4$:O$_2$ mixture because the addition of N$_2$ does not influence strongly the energy degradation of H atoms due to a large difference in masses for H and N$_2$.

The estimated energy of “hot” H and O atoms produced in a high-voltage pulsed discharge in air due to direct electron-impact dissociation and quenching of electronically excited states of N$_2$ by CH$_4$ molecules is in the range 0.7 – 3.3 eV [4]. Then, it follows from figure 1 that “hot” H and O atoms, during their energy degradation, are partially lost in chemical reactions to form CH$_3$, OH and H$_2$. As a result, the amount of active species increases and the composition of active species changes.

4. Conclusions

Using a Monte Carlo technique, energy degradation of “hot” H and O atoms was simulated in CH$_4$:O$_2$ and CH$_4$:air mixtures. It was shown that the degradation of H and O atoms leads to the additional generation of CH$_3$, OH and H$_2$. This affects the total amount and composition of active species produced in high-voltage pulsed discharges.

5. Acknowledgements

This work was partially supported by the Russian Ministry of Education and Science under the program “5Top100”, by the Russian Foundation of Basic Research under the projects No. 14-03-31449 and No. 14-08-00400 and by the AFOSR MURI program “Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma-Assisted Combustion”.

6. References