

Plasma Assisted Combustion Mechanism for Hydrogen and Small Hydrocarbons

Andrey Starikovskiy¹

¹*Princeton University, Mechanical and Aerospace Department, Princeton, 08544 NJ, USA*

The main mechanisms of nonequilibrium gas excitation and their influence on the ignition and combustion were briefly discussed. Rotational excitation, vibrational excitation, electronic excitation, dissociation by electron impact and ionization were all analyzed, as well as the ways in which the selectivity of the gas excitation in the discharge can be controlled. Despite of some lack of knowledge of mechanism details, a nonequilibrium plasma demonstrates great potential for controlling ultra-lean, ultra-fast, low-temperature flames and is an extremely promising technology for a very wide range of applications.

Introduction

Reviews of recent experimental studies of nonequilibrium plasma-assisted ignition and combustion can be found in the literature [1,2,5]. Over the last years, considerable progress has been made in understanding the mechanisms of plasma-assisted combustion in various mixtures, including hydrocarbon-containing mixtures [3]. The mechanisms of combustion were validated by performing experiments under controlled conditions and by comparing their results with numerical simulations of the discharge and combustion processes. In this work, we consider the possibility of generating a chemically active discharge plasma with desirable parameters and the mechanisms of the nonequilibrium plasma effect on ignition and combustion. The difficulties of these studies and some unsolved problems are discussed. The number of works devoted to plasma-assisted combustion is exceedingly large. Therefore, this survey tends not to cite all of the available papers. Instead, we have attempted to present only new results and to show the main obstacles to further progress in the use of nonequilibrium plasma in assisting and improving combustion processes.

A plasma chemical kinetic model has been developed. The model consists of two parts. The first part describes gas excitation by electron impact – rotational, vibrational and electronic states population by pulsed discharges. A local two-term expansion of Boltzmann equation is used for electron energy distribution function calculations. It limits the electrical fields in the discharge zone to 1000-1500 Td. The second part considers energy relaxation in the plasma (formation of Maxwell-Boltzmann equilibrium across translational, vibrational and electronic degrees of freedom of molecules), quenching and decomposition of excited states, their

reactions and recombination – with formation of thermally-equilibrium pool of radicals, which could be considered as initial conditions for any detailed combustion kinetic mechanism.

The mechanism includes excitation cross-sections for 25 components: N₂; O₂; Ar; He ; CO₂; H₂O; O₃; N₂O; H₂; CO; CH₄; methylal; C₂H₂; C₂H₄; C₂H₅OH; C₂H₆; C₃H₈; 2-propanol; propene; cyclopropane; C₄H₁₀; isoC₄H₁₀; C₅H₁₂; neoC₅H₁₂; DME. All cross-sections are available in BOLSIG+ format and ready to use. Cross-sections are optimized for two-term approximation of Boltzmann equation, which restricts the maximal reduced electric field value by 1000-1500 Td. For hydrocarbons above C₃ the cross-sections were tested only against swarm parameters and ionization frequency. The accuracy of excitation cross-sections is not very high for these hydrocarbons.

Energy branching in discharges

The major difference between common combustion and plasma-assisted combustion is the extremely nonequilibrium excitation of the gas in the discharge plasma. An external electric field accelerates electrons. Energy exchange between the electrons and the translational degrees of freedom of the molecules is very slow because of the large differences in mass. This means that electron impact can transfer energy to the internal degrees of freedom of the molecules only. If the rate of internal energy relaxation is not very high, the population distribution of the excited states of the molecules will be very far from the initial Boltzmann energy distribution. The overpopulation of excited states and the dissociation and ionization of the molecules, which can lead to UV generation and additional gas heating, cause an increase in the system reactivity and facilitate ignition and flame propagation. From

this point of view, the most important questions for plasma-stimulated chemistry concern how the discharge energy branches through the different degrees of freedom of the molecules, the rate of system relaxation (thermalization) and the chemically active system response to this nonequilibrium excitation.

The rate of the excited level population in the discharge depends on the electron energy. The excitation of rotational degrees of freedom requires the lowest energy of electrons. A typical rotational quantum is on the order of a few degrees Kelvin, and the electron energy at ~ 300 K (~ 0.03 eV) is enough for the efficient excitation of molecular rotations. A typical quantum of the vibrational degrees of freedom is in the range of 1-3 kK. This means that for the efficient excitation of vibrations, the average electron energy should be higher (in air, it should be in the range of 0.2-2 eV). The excitation of the electronic degrees of freedom and gas dissociation require energies of 3-10 eV. If the average electron energy exceeds 10 eV, the main process occurring in the plasma is gas ionization. Thus, the potential to control the energy of electrons suggests the potential to control the direction of energy deposition and to selectively excite the different degrees of freedom of the gas.

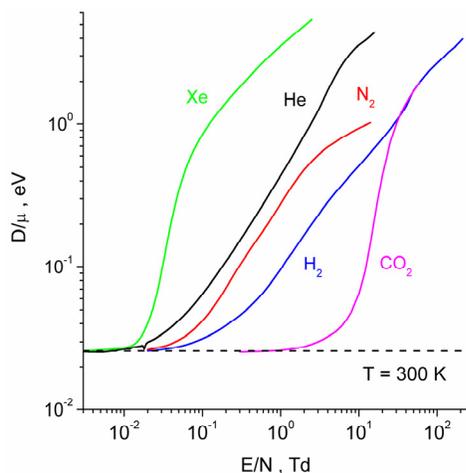


Figure 1. Characteristic electron energy.

He and Ar – [7]; H₂, N₂ and CO₂ – [8].

The average electron energy in a gas discharge is determined by a reduced electric field, E/n , where E is the electric field and n is the gas density [6]. Figure 1 illustrates the deviation of the characteristic electron energy, D/μ , from the temperature of the molecules, T , for different gases. Here, D is the diffusion coefficient of electrons and μ is their

mobility. The critical E/n that results in a noticeable difference between D/μ and T and, consequently, a nonequilibrium electron energy distribution function formation is close to $E/n \sim 0.1$ Td for atomic gases and $E/n \sim 1$ Td for molecular gases ($1 \text{ Td} = 10^{-17} \text{ V} \times \text{cm}^2$). A nonequilibrium electron energy distribution function (EEDF) can be found as a solution of the Boltzmann equation. In the simplest case, one can approximate the solution by a local, steady-state function that only depends on the local electrical field. Further simplification is possible using the so-called two-term approximation (the electron distribution function is presented in the form $f(\mathbf{v}) = f_0(v) + f_1(v)\cos\theta$ [6] (\mathbf{v} is the electron velocity, and θ is the angle between \mathbf{v} and \mathbf{E}), using a full set of cross sections for electron-molecule collisions. Table 1 shows self-consistent sets of electron cross sections for gases included into the mechanism. The electron transport and rate coefficients that are calculated using these data agree well in the pure gases with available measurements. Cross section database is compatible with Boltzmann solver BOLSIG+.

The EEDF that is obtained allows calculation of the energy branching through the different degrees of freedom. Figure 2 demonstrates the energy branching through the internal degrees of freedom of selected gases for different E/n values in a discharge. Rotational excitation dominates at a very low E/n , ~ 0.1 Td. Fast energy exchange between the rotational and translational degrees of freedom causes thermally-equilibrium gas heating in this type of discharge. An increase in the E/n value up to 0.4 Td changes the energetic priorities.

Above this point, the main mechanism of electron energy loss becomes the vibrational excitation of oxygen. For a reduced electric field, on the interval $4 \text{ Td} < E/n < 110 \text{ Td}$ in air, the most efficient mechanism of electron energy loss is the excitation of the vibrational levels of nitrogen (Figure 2a).

Table 1. Electron-molecules collisions database

Atmospheric	Saturated	Unsaturated	Oxygenated	Isomers
N ₂	CH ₄	C ₂ H ₂	CO	iso-butane
O ₂	C ₂ H ₆	C ₂ H ₄	CH ₃ OH	iso-propane
CO ₂	C ₃ H ₈	C ₃ H ₆	C ₂ H ₅ OH	neo-pentane
H ₂ O	C ₄ H ₁₀		CH ₃ OCH ₃ (DME)	
O ₃	C ₅ H ₁₂			
Ar	H ₂			
N ₂ O				

Under low-temperature conditions, VT relaxation is a rather slow process, and the vibrational temperature in the discharge can be higher than the translational temperature of molecules. In the same region of E/n values, the excitation of the lowest electronic level of oxygen, the $O(a^1\Delta)$ state, occurs. The efficiency of this electronic excitation in the presence of nitrogen is very small ($\sim 2\%$), but the low rate of singlet oxygen quenching under some conditions can lead to an increase in its concentration.

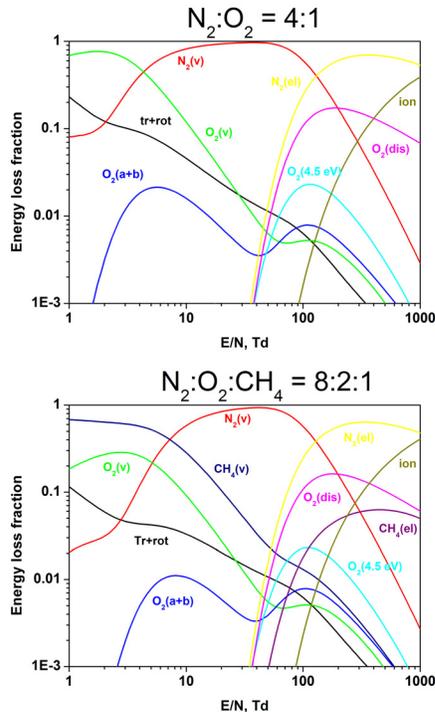


Figure 2. Fractional power dissipated by electrons into the different molecular degrees of freedom as a function of E/n . (a) Air; (b) Methane-Air stoichiometric mixtures.

It should be noted that the electric field value of $E/n \sim 120$ Td is a very important threshold in air. Above this point, the electric field is strong enough to ionize the gases in air, and the discharge can propagate in a self-sustained manner. Below this value, a discharge can exist only in the presence of an external source of ionization. At E/n values from 140 to 500 Td, the main mechanism of energy loss is the excitation of the electronic triplet states of nitrogen. Because of the high electron energy in this range of E/n (from 3 to 10 eV, respectively), the ionization of the gas in the discharge gap is very fast. Between 500 and 1000 Td, the excitation of nitrogen singlet states becomes most significant, and above

E/n of 1000 Td, the main portion of the electron energy goes to the ionization of the gas.

The presence of fuel additives (Figures 2b) does not change this picture dramatically. The main reason is the relatively small concentration of fuel molecules in the mixture under typical combustion conditions. Figure 2b demonstrates the effect of methane on the electron energy branching. A stoichiometric mixture of H_2 -air ($CH_4:O_2:N_2 = 1:2:8$) contains approximately 9.1% of methane. It is clear from the calculations that these additives only change the energy branching slightly at moderate and high E/n values, > 20 Td. The excitation of molecular nitrogen remains the main process. The vibrational and electronic excitation and ionization of methane only change the energy branching slightly (Figure 2b). At a low E/n , < 10 Td, the influence of methane addition becomes more significant. The vibrational excitation of methane is the main mechanism of energy losses for an $E/n = 5-10$ Td. The role of the rotational excitation of methane is also important and increases the energy flux into the rotational and translational degrees of freedom under low E/n conditions (Figure 2b).

Processes included into the model

The mechanism is designed to describe the plasma-chemical processes in discharges with reduced electric field value E/n up to 1500 Td, and energy density in the discharge up to ~ 1 eV/mol. At higher E/n the local electrical field approach cannot be used for quantitative description of the process; at very high energy density the e-e and electron-ion interactions become important.

The electrons multiplication process is most important for discharge development kinetics. Ionization, processes of charge transfer and recombination reactions were included into the kinetic model.

As a result of gas ionization and electron-ion recombination we have a fast gas heating; hot atoms formation; electronically-excited radicals; and ionic chains development. These processes are not very important at high temperature conditions but a play a key role at low temperatures. At very low temperatures this channel becomes important - because competing reactions with uncharged reagents cannot propagate at $T \sim 300$ K. For example, process $O_2^- + H \rightarrow OH^- + O$ is 11 orders of magnitude faster at 300K than process $O_2 + H \rightarrow OH + O$. The processes with ions are limited by ion-ion and electron-ion recombination and formation of

negative ions by electron's attachment: $O_2 + e + M \rightarrow O_2^- + M$. Electron's attachment to oxygen changes the recombination mechanism from electron-ion to ion-ion - and decreases the rate of recombination several orders of magnitude - because of low mobility of heavy ions with compare to electrons. Thus, the overall effect becomes pressure dependent - because it depends on the rate of three-body attachment process. The difference between atomic oxygen in ground state $O(^3P)$ and electronically-excited state $O(^1D)$ becomes critical at low-T. $O(^3P)$ mostly recombine at $T = 300K$, while $O(^1D)$ allows reactions of chain branching (most important is $O(^1D) + RH \rightarrow R^* + OH$). Both major channels of atomic oxygen production ($O_2 + e \rightarrow O + O + e$ and $N_2(C^3) + O_2 \rightarrow N_2 + O(^3P) + O(^1D)$) give almost equal amount of O in ground (3P) and excited (1D) state. Thus, at low T we need to analyze all reactions with $O(^1D)$. At high-T $O(^3P)$ has almost the same reactivity as $O(^1D)$ and we can consider both radicals as "atomic oxygen".

This process is pressure dependent. At low-P we will have radiative depopulation of $N_2(C^3)$: $N_2(C^3) \rightarrow N_2(B^3) + h\nu$ and this changes the products of the quenching: $N_2(B^3) + O_2 \rightarrow N_2 + O(^3P) + O(^3P)$. At high-pressure radiative life-time of $N_2(C^3)$ (37 ns) becomes too long with compare to collisional quenching and products will be $O(^3P) + O(^1D)$.

It is well known that dissociation of molecules by electron impact and photons is going through repulsive energy surfaces - and an excessive energy is converted to translational motion of the products. Thus, the several very first collisions of these products with neighbors will take place with a huge energy (typically 1-5 eV). This energy is enough to overcome reaction thresholds for all possible channels - including direct dissociation in one collision. Thus, the reactivity of this "hot" radicals increases dramatically - almost non-reactive at $T = 300K$ $O(^3P)$ with additional kinetic energy will react with N_2 , H_2 , hydrocarbons - in chain-branching reactions. The influence of this effect decrease with the temperature increase - because at high-T atomic oxygen has significant reactivity even without additional energy. Thus, at low-T we have to take into account translational nonequilibrium effects - they increase the rate of radicals production from 2 to 4 times depending on conditions - but we can neglect their influence at high-T.

This process is concentration dependent. In diluted mixtures we can expect complete thermalization of the hot atoms before they will collide with possible

reagents. In undiluted mixtures, vice versa, the reaction channel will always prevail (probably it is a real reason why this channel was not discovered before - in strongly diluted mixtures its influence is negligible). Vibrational excitation leads to reactions acceleration. At high temperatures two factors decreases the role of nonequilibrium vibrational excitation: 1) increase of the reactivity of unexcited molecules and 2) increase of the VT relaxation rates. That is why at high T we can consider that the vibrational levels population is in equilibrium with translational degrees of freedom - corrections to "nonequilibrium" population are rather small.

At low T the channels with vibrationally-unexcited molecules are too slow. And two major "vibrational" pathways take place: 1) vibrational excitation of hydrogen by electron impact and reaction of $H_2(v)$ with oxygen (reaction $H_2(v=1) + O \rightarrow H + OH(v=1)$ is 3000 times faster than the same reaction with $H_2(v=0)$ at $T = 300K$); 2) vibrational excitation of nitrogen by electron impact and this vibrational energy participation in peroxides decomposition. This process has a limiting step of vibrational energy transfer from $N_2(v)$ to HO_2 : $N_2(v) + HO_2 \Rightarrow N_2 + HO_2^*$ which is followed by the fast decomposition of vibrationally-excited HO_2 and active radicals re-generation in the mixture. This mechanism can elongate the chemical chains below self-ignition threshold by 1-2 orders of magnitude - and dramatically change the chemical energy release during nonequilibrium stage of the ignition.

References

- [1] Starikovskii A.Yu., *Plasma supported combustion*, Proc. Comb. Inst. 30 (2005) 2405-2417.
- [2] Starikovskaia S.M., *Plasma assisted ignition and combustion*, J. Phys. D. Appl. Phys. 39 (2006) 265.
- [3] Starikovskaia S M, Starikovskii A Yu. *Plasma assisted ignition and combustion*. In: Handbook of Combustion, by M. Lackner (Ed.), Franz Winter (Ed.), A.K. Agarwal (Ed.), Wiley-VCH, (2010).
- [4] Starikovskiy A., Aleksandrov N. *Plasma-assisted ignition and combustion*. Progress in Energy and Combustion Science 39 (2013) 61-110
- [5] Popov N.A. *Effect of a Pulsed High-Current Discharge on Hydrogen-Air Mixtures*. Plasma Physics Reports, 2008, vol. 34, No. 5, pp. 376-391.
- [6] Raizer Y.P. *Gas Discharge Physics*. Springer.
- [7] Dutton J. J. Phys. Chem. Ref. Data 4 577 (1975)
- [8] Huxley L.G.H. and Crompton R.W. *The Diffusion and Drift of Electrons in Gases* (New York: Wiley-Interscience) 1974.