Chemical Reactions and Ignition Initiation in Hydrocarbon-Air Mixtures by High-Voltage Nanosecond Gas Discharge


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Abstract

Numerical modeling of the process of ignition for H₂-air, CH₄-air, C₂H₆-air, C₃H₈-air, C₄H₁₀-air and C₅H₁₀-air mixtures at high temperatures under the action of fast ionization wave (FIW) was performed.

The ignition threshold shifts for different mixtures gas pressures, temperatures and equivalent ratios were obtained: the analysis of ignition efficiency, which enables to plan the experimental measurements of the initiation of ignition by FIW at high temperatures, was provided. Detailed investigation was provided of the dependence of ignition delay time from the energy release in the discharge, reduced electric field value, initial gas temperature, type of excitation and mixture composition.

Introduction

Different types of the electric discharge (spark, streamer, and barrier) are significantly subdivided by the type of energy release. Spark discharge creates almost equilibrium plasma. Electron temperature in this plasma practically equals to the ion temperature and the temperature of uncharged molecules. All degrees of freedom are equally excited.

In the non-equilibrium plasma of streamer discharge electron temperature is much higher than the temperature of heavy particles. Gas internal degrees of freedom are substantially overpopulated. Active particles density in the gas essentially exceeds its equilibrium value. Under the equal energy release per unit gas volume in the discharge, this leads to the substantial decrease of the translational temperature of the gas with compare to the equilibrium excitation case. A significant part of the energy in the case of non-equilibrium excitation of the gas is wasted irretrievable due to photons emission.

Energy of the translational degrees of freedom of molecules is used for reactions energy threshold overcoming. From the one hand, in the case of non-equilibrium excitation, the effective reaction chain length substantially reduces by the total translational temperature decrease. From the other, non-equilibrium excitation leads to the radicals production increase.
Low-Temperature Hydrogen Oxidation in Nanosecond Pulse Discharge

Influence of the electric discharge on the reaction dynamics and ignition delay time were investigated experimentally and numerically for different hydrogen-air and hydrocarbon-air mixtures.

The discharge cell consists of a quartz tube of length $l = 200$ mm and diameter of 47 mm with plate high-voltage electrode and ring low-voltage electrode at faces made of aluminum. Impulses of negative polarity voltage of amplitude $|V_{dcn}| = 13$ kV with duration at half maximum of the amplitude and 2 ns rise time were fed with repetition frequency of $f = 40$ Hz from pulse voltage generator to the high-voltage electrode of the discharge tube.

Transition $H_2(a^1\Sigma_g^+ \rightarrow b^1\Pi_g)$ results in the continuum in the discharge radiation spectrum which extends from 167 nm to the lowest infrared region of the spectrum. Temporal evolution of absolute concentration of the molecular hydrogen in the mixture was reconstructed on the basis of records of absolute radiation intensity for this transition at wavelength $\lambda = 239$ nm with spectral resolution of $\Delta \lambda = 0.24$ nm. Population of the upper level of transition ($H_2(a^1\Sigma_g^+)$) is generated by the electron impact directly from the ground electron state of the molecule:

$$H_2 + e \rightarrow H_2(a^1\Sigma_g^+) + e$$ (1)

The discharge gap current amplitude varies from $I = 300$ A at $p = 3$ Torr to $I = 155$ A at $p = 7$ Torr. The current impulse duration at half maximum in this range was constant with a good accuracy and made up $\tau_{imp} \approx 16$ ns.

The kinetic scheme that describes processes at the stage of electric current flow consists of $\sim 750$ chemical and $\sim 8700$ vibrational exchange processes with participation of 83 particles including electron-excited and charged atoms and molecules, electrons, radicals, non-excited components.

![Diagram](image)

Figure 1. Vibrational energy exchange diagram. $H_2$ air mixture. Calculation of the VT and VV processes rate constants was made within the frames of SSH-theory.

The following processes were taken into account: associative and Penning ionization, recombination of positive ions and electrons, attachment of electrons to atoms, detachment of electrons, interaction between neutral non-excited components, interaction between neutral excited and neutral non-excited components, conversion and recombination of ions.
Figure 2. Diagram of active particle flows within the time interval $10^{-10} - 10^{-6} \times 10^3$ s. Flow of active particles are shown for the most rapid channels of chemical conversions. The line thickness corresponds to the process rate, and number near it - its position in the hierarchy in the rate analysis of the kinetic scheme.

To calculate reaction rates with a participation of vibrationally-excited reagents we use an $\alpha$-model modification.

Computation was performed in the mode of "direct modeling" i.e. the discharge gap current impulses that follow each by other were directly calculated with consideration of the variation of the mixture composition between and during the impulses.

Influence of the reduced electric field value in the discharge on the ignition delay time was estimated for $\text{H}_2$-Air mixture at temperature $T = 1000$ K, pressure $P = 1$ atm, total energy release in the discharge $E = 4 \times 10^{-3}$ J/cm$^3$. Results of these calculations are shown on the Figure 4.

Region of the most-effective gas excitation from the point of view of ignition initiation in the gas system is in the range of reduced electric fields from 250 to 350 $\text{V/cm}$. This estimation coincides with the reduced electric field values in the region of the maximum energy release in the fast ionization wave.

Ignition of $\text{H}_2$-Air Mixtures

Figure 5 shows results of numerical calculations of the ignition delay time in the $\text{H}_2$-Air mixtures at total pressure $P = 1$ atm. These calculations were performed for the non-equilibrium discharge conditions. Case with the excitation energy equals to zero corresponds to the thermal auto-ignition at given temperature. Ignition delay time in the system is very sensitive to the additional non-equilibrium gas excitation.

Even an excitation with the energy $E = 4 \times 10^{-4}$ J/cm$^3$ causes a considerable decrease of the ignition delay time and ignition threshold. For the energy level of $E = 4 \times 10^{-1}$ J/cm$^3$ (near to the upper limit of homogeneous energy deposition in the fast ionization wave) ignition threshold shift reaches the value of 400 K.

Thus, discharge energy variation allows to change the ignition threshold value and
Figure 3: Profiles of absolute number density of the molecular hydrogen in \( \sigma^3 \Sigma^+ \) electron excited state in dependence on the pressure. Subfigures from 1 to 4 correspond to initial mixture pressure \( p = 4, 5, 6 \) and 7 Torr respectively. The solid lines - experiment, dashed lines - calculation.

Figure 4: Ignition delay time vs Reduced Electric Field Value. H\(_2\)-Air Stoichiometric Mixture. \( P = 1 \) atm \( T = 1000 \) K. Total Energy Release \( E = 4 \times 10^{-2} \) J/cm\(^2\).

Figure 5: Ignition delay time vs energy consumption. H\(_2\)-Air stoichiometric mixture. \( P = 1 \) atm. \( T = 1000 \) K. \( E/n = 300 \) J/cm\(^3\).
ignition delay time in H₂-Air mixture in the wide range.

Ignition of Hydrocarbon-Air Mixtures

![Graphs showing ignition delay time vs initial gas temperature for H₂-Air and CH₄-Air mixtures.](image)

Figure 6: Ignition delay time vs Initial Gas Temperature. H₂-Air Stoichiometric Mixture. $E/n = 300$ Td.

Figure 7: Ignition delay time vs Initial Gas Temperature. CH₄-Air Stoichiometric Mixture. $E/n = 3$ atm.

Non-equilibrium excitation $E/n = 300$ Td.

For the CH₄-Air mixtures excitation under the effect of the pulse discharge is substantially more weak than for H₂-Air mixtures. Molecule CH₄ has a relatively small cross-section of dissociation by electron impact. Besides, CH₄ molecules concentration in the stoichiometric mixture with air is considerably lower than H₂ concentration. Therefore, ignition threshold shift for CH₄-air mixtures is relatively small at low values of discharge energies (Fig.6,7). On the other hand, at high energy of the discharge ($E = 0.1$ J/cm³), ignition threshold shift exceeds 400 K in the all temperature range investigated.

Ignition threshold shift in the C₂H₆-Air system under the effect of the pulsed discharge is somewhat smaller than for the CH₄-Air and C₂H₄-Air mixtures (Figure 8,9). The value of the threshold shift is less than 300 K at the energy release $E = 0.4$ J/cm³. For the energy release $E = 0.1$ J/cm³ this shift becomes a negligible value under all investigated conditions. This behavior of the system perhaps is due to the characteristic features of the kinetics in C₂H₆-Air mixture. It is still a possibility of some defects in kinetic scheme. The additional investigations of this mixture are needed. From the other hand, influence of the pulsed electric discharge on the ignition is clearly seen in the wide range of initial parameters.

The system sensitivity on the non-equilibrium excitation increases with pressure increasing and decreasing of the equivalence ratio. Absolute value of the ignition threshold shift remains sufficiently high and exceeds 300 K for the discharge energy $E = 0.1$ J/cm³ and 200 K for $E = 0.1$ J/cm³.

Conclusions

The proposed mechanism of chemical kinetics description in essentially nonequilibrium conditions gives a possibility of the quantitative analysis of vibrationally nonequilibrium
processes and their influence of a whole chemical kinetics in the system. It was shown that in the conditions of a pulsed high-current nanosecond discharge the role of the processes with participation of vibrationally excited components is principal and significantly influences the kinetics in the system.

The results obtained in the present work show us a possibility of utilizing the non-equilibrium gas discharge for wide control of hydrocarbon-air mixtures ignition and combustion. This control may be effective in the wide range of gas parameters: pressures, temperatures and equivalence ratios. It was shown that sensitivity of the ignition delay time with respect to the non-equilibrium excitation increases with pressure. The more important conclusion is that the induction time sensitivity increases for lean fuel-air mixtures with compare to the stoichiometric ones.

The kinetics scheme that describes ignition of chemically active hydrocarbon-air mixtures under action of ionization wave was constructed. Basic factors that determine the combustion process in such systems were revealed. A possibility of utilizing the non-equilibrium gas discharge for wide control of the hydrocarbon-air mixtures ignition and combustion was shown. This control may be effective in the wide range of gas parameters: pressures, temperatures and equivalence ratios. It was shown that sensitivity of the ignition delay time with respect to the non-equilibrium excitation increases with pressure. The more important conclusion is that the induction time sensitivity increases for lean fuel-air mixtures with compare to the stoichiometric ones. It was shown that for H₂-Air mixtures ignition threshold shift reaches the value of 400 K. This value decreases slightly for hydrocarbon-air mixtures. The absolute value of the ignition threshold shift remains sufficiently high and exceeds 300 K for C₃H₇-air mixtures.

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