CHEMICAL REACTIONS AND IGNITION CONTROL BY NONEQUILIBRIUM LOW-TEMPERATURE PLASMA

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Abstract. Numerical modeling of the process of ignition for \(H_2\)-air and \(CH_4\)-air mixtures at high temperatures under the action of nanosecond high-voltage discharge has been performed. The analysis of ignition efficiency, which enables to plan the experimental measurements of the initiation of ignition by nanosecond discharge at high temperatures, was provided. Novel experimental scheme for investigation of threshold shift at high temperatures under the action of high-voltage nanosecond discharge has been developed. The ignition threshold shifts for different mixtures, gas pressures and temperatures were obtained experimentally.

Introduction

The problem of fast and homogeneous ignition of combustible mixture is extremely pressing. Presently various methods of ignition initiation in supersonic gas flows are regarded. The laser methods have severe disadvantages mainly related to the impossibility to provide the high uniformity of ignition initiation in large gas volumes. The spark ignition imposes the essentially restrictions on the system geometry. Ignition by direct injection of the arc discharge make it possible to operate in flow velocity range comparable or lower then the velocity of the injected plasma jet.

The homogeneous ignition method proposed in this paper which is fast in comparison with characteristic gas dynamic times is based on the usage of the nanosecond high-voltage discharge in the form of fast ionization wave (FIW) as a source of atoms, radicals, excited molecules. The fast ionization wave originates at very high – hundreds of percent – overvoltage on the electrode system, that is in the case when voltage at the time moment of the discharge initiation exceeds significantly threshold of initiation of stationary glow discharge. The most distinctive features of this type of discharge are high propagation velocity \((10^9-10^{10}\text{cm/s})\), good reproducibility of the parameters, and spatial homogeneity over a large gas volume. Brief review of our papers concerning kinetic approach to this discharge and detailed description of nanosecond technique of registration is given in [1].

Numerical Modeling

To determine region of parameters for experiment the numerical code for description of ignition kinetics under the action of high-voltage nanosecond discharge has been developed. Detailed kinetics in \(H-C-N-O\) mixtures tested on the shock tube experiments was taken into account; we considered processes important for the discharge as well as reactions in the afterglow at high (thousands degrees) temperatures typical for combustion.

Detailed experimental investigation of nanosecond discharge have proved that for first several nanoseconds the electric field burst is observed in the ionization wave front, therewith its value in maximum is close to the threshold of electron runaway or over it. For the following several tens nanoseconds the field decreases from values corresponding to active excitation of inner gas degrees of freedom to zero. It was shown that [2] the intensive production of electrons as well as population of electron states take place behind the ionization wave front in “residual ”fields (hundreds of \(\text{V/(cm-Torr)}\)).

Experimental and numerical analysis of the electron energy distribution function (EEDF) in the nanosecond discharge [1] allows to say that in spite of the fact that detailed description of gas excitation requires statistical modeling because of very high electric field in the discharge front and, as a consequence, influence of non-local and nonstationary processes on the EEDF formation, it is possible to estimate production of active particles in the discharge using solution of Boltzmann equation in two-term approximation for the EEDF description. So, the initial parameters of the task were gas composition, initial temperature and pressure. Discharge was given as a square pulse of electric field at given amplitude and duration of 40ns. As a first stage, we calculated EEDF and energy branching in the discharge. Mixture composition, temperature and active particles concentrations obtained in the solution on pulsed discharge action on the gas were taken as initial parameters for calculations on the ignition problem. The final results were kinetic curves for combustion products.

As a result of numerical modeling, region of parameters that is the most sensitive for the discharge action has been found. Figure 1 shows
results of numerical calculations of the ignition delay time in the H\textsubscript{2}-Air stoichiometric mixture at a total pressure of \(P=1\text{ atm}\). These calculations were performed for the non-equilibrium discharge conditions with different energy release in the discharge (as indicated in the Figure 1). Case with the excitation energy equals to zero corresponds to the thermal auto-ignition at given temperature. It is clearly seen that discharge energy variation allows to change the ignition threshold value and ignition delay time in H\textsubscript{2} -Air mixture in a wide range.

It is interesting to compare different ways of energy consumption at the same absolute value. Ignition delay time changes slightly in a case of equilibrium excitation, when all degrees of freedom are heated simultaneously. At the same energy release, \(W=4\times10^{-3}\text{ J/cm}^3\), gas excitation by the non-equilibrium discharge at reduced electric field \(E/N=300\text{ Td}\) leads to significant decrease of ignition threshold. In addition, we analyzed influence of the electric field value on the ignition threshold. We have concluded that the 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 350Td. This estimation coincides with the reduced electric field values in the region of the maximum energy release in the fast ionization wave.

For the CH\textsubscript{4} -Air mixture excitation under the action of the pulse discharge is substantially more weak than for H\textsubscript{2} -Air mixture (Figure 2). Methane molecule has a relatively small cross-section of dissociation by electron impact. Besides, methane density in the stoichiometric mixture with air is considerably lower, than H\textsubscript{2} density. Therefore, ignition threshold shift for CH\textsubscript{4} -air mixtures is relatively small at low values of discharge energies. On the other hand, at high energy of the discharge (\(W=0.4\text{ J/cm}^3\)), ignition threshold shift exceeds 400K in the all temperature range investigated. So, preliminary numerical modeling has predicted region of temperatures and electric fields which are suitable for experimental check of the ignition threshold shift.

**Experiment Description**

In the problem under consideration the shock wave serves to prepare the gas mixture at the specified temperature and pressure. Because the gas dynamic times (1-100ms) are significantly more than the characteristic time of gas excitation by the impulsd breakdown (1-00ns) the gas in the shock wave may be regarded as motionless from the view point of the discharge development. The installation to investigate fast homogeneous ignition of combustible mixtures (Figure 3) consists of the discharge cell (DC) connected to a shock tube (ShT), the gas evacuation and supply system, the system of discharge initiation, the instrumentation system.

The shock tube made of the stainless steel has a square cross section of 25×25 mm with the 1.6m working channel length, high pressure cell (HPC) length of 60 cm. There are 2 pairs of optical windows along the working channel. The channel is calibrated along the inner cross section, which provides a low level of gas dynamic perturbations in the flow. To evacuate the system rotary and diffusive pumps that provide evacuation of the shock tube working channel and its mating dielectric discharge section are used. The installation parameters make it possible to obtain the uniformly heated gas volume behind the reflected shock wave, which is moveless relative to
the shock tube walls, in pressure range of \( P=0.1-3 \text{atm} \), temperature range of \( T=500-3000 \text{K} \).

The system of shock wave parameters monitoring includes the system of incident shock wave velocity measurements by the schlieren technique and the system of the initial pressure control. Schlieren system consisted of 3 He-Ne lasers mounted along the shock tube channel at different points and 3 pairs of photodiodes with differential analysers (DA); time delay between points 2-1 and 1-3 along the tube was registered by time-delay analysers (TD). From measured initial gas mixture composition, initial pressure and velocity of the shock wave we determined parameters behind the reflected shock wave, that is pressure, gas density and temperature. The parameters were determined by solving the system of conservation equations, which is standard technique for shock tube experiments.

The combustion process dynamics was investigated using emission spectroscopy technique. Emission which originates due to combustion process was registered with the use of monochromator MDR-23, photomultiplier FEU-100 and oscilloscope Tektronix TDS 3054 in the direction perpendicular to shock tube axis at a distance of 55mm from the end plate. We measured \( \text{OH} \) emission (\( \lambda=306.4 \text{nm} \)) in a wide range of experimental conditions: mixtures of various compositions, temperature variation from 800 to 2100K with pressure variation from 0.1 to 2atm. The same experiments were repeated under discharge action, at high-voltage pulse amplitude variation from 120 to 160 kV on the electrode (positive polarity) and pulse duration 30-40 ns at a half-height.

Discharge was synchronized with the reflected shock wave coming to the cross-section of observation. We used microsecond pulse generator (PG) to synchronize output from the Shlieren system and power supply (PW) for the high voltage generator (HVG). Breakdown was organized in a quartz-glass cell 20 cm in length with optical windows for emission output; the end plate of the shock tube served as high-voltage electrode of the discharge system; the electric circuit was closed via grounded stainless steel working channel of the shock tube.

The GIN-9 high voltage Marks generator (HVG) consists of 10 stages and provides a starting voltage range from 100 to 300kV on the high voltage electrode of the discharge section. The system of monitoring of fast nanosecond breakdown electrical parameters includes magnetic calibrated current gauge (MCG) to control current pulse and capacitance gauge (CG) over the high-voltage electrode to monitor the high-voltage pulse shape and amplitude. We placed additional capacitive gauge near the low -voltage electrode (CG1) to estimate the velocity of discharge development. Signals from electrical gauges were monitored using Tektronix TDS 380 oscilloscope. All cables were additionally screened and oscilloscopes placed into the shielded room to diminish high-frequency electrical noise.

Experiments were performed in hydrogen and methane mixtures with air diluted with argon or helium at initial pressures in low pressure chamber rom 5 to 40 Torr. Helium, air or \( \text{CO}_2 \) were used as high-pressure chamber gases.

**Results of Experiment**

Experiments were performed in \( \text{H}_2 \) and \( \text{CH}_4 \) mixtures with air or \( \text{O}_2 \) diluted with \( \text{Ar} \) or \( \text{He} \) at initial pressures from 5 to 40Torr. \( \text{He} \), air or \( \text{CO}_2 \) were used as high-pressure chamber gases. This corresponds to pressures 0.5-1.5 atm behind the reflected shock wave. We used mixtures \( \text{H}_2: \text{O}_2: \text{N}_2: \text{Ar} = 6:3:11:80 \), \( \text{H}_2: \text{O}_2: \text{Ar} = 12:6:82 \), \( \text{CH}_4: \text{O}_2: \text{N}_2: \text{Ar} = 1:4:15:80 \); \( \text{H}_2: \text{O}_2: \text{He} = 12:6:82 \). Dilution by \( \text{Ar} \) or \( \text{He} \) increased specific heat ratio and molecular weight of the mixture and, so, allowed to reach high temperatures behind the reflected shock wave.

Figure 4 represents dependence of ignition delay time for \( \text{H}_2: \text{O}_2: \text{Ar} = 12:6:82 \) mixture. Voltage on high voltage electrode was 160kV, pulse duration was 40ns. Air or \( \text{CO}_2 \) (symbols are indicated in the Figure 4) was used as high-pressure chamber gas. As a result, parameters behind the reflected shock wave were varied. It is clear that in a range of 800-900 K the ignition initiation is possible under the action of discharge.
only (symbols are marked "with FIW"). In the same Figure results of numerical modeling are represented. To calculate density of $O$ and $H$ atoms we used experimental estimations of electric field value in the discharge and standard BOLSIG solver for the EEDF (W.L.Morgan. Kinema software and J.-P.Boeuf, L.C.Pitchford. BOLSIG Boltzmann solver http://www.kinema.com). To simulate kinetics in the afterglow at high temperatures GRI-Mech 3.0 mechanism was used (G.P.Smith, D.M. Golden, M.Frenklach, et al. http://www.me.berkeley.edu/gri_mec). It is obvious that correlation between measurements and calculation is good enough and this scheme can be used for estimation of nanosecond discharge efficiency for ignition of combustible mixtures.

The same tendency we observe for methane-air mixture (Figure 5). Ignition threshold changes dramatically under the action of the discharge. The figure demonstrates also difference in the delay time at different pressure behind the reflected shock wave. Curves at different pressure values were obtained using different gas in high pressure chamber of the shock tube. Regime 1 was obtained with He, which lead to the highest velocity of the shock wave, and, consequently, to the highest temperature behind the reflected shock wave; regime 2 was obtained with dry air, and regime 3 was obtained with $CO_2$. As for the discharge development, in our conditions it is much more efficient at a pressure below 1 atm. This lead to higher energy consumption, and, as a result, to significant increase in threshold shift. Typical energy release is indicated in the Figure. We were able to provide the ignition of methane-air-argon mixture at a pressure of 0.3 atm and a temperature of 1100K using 0.05 J/cm$^3$ energy release in the discharge.

Conclusions

The numerical code that describes ignition of $H_2$-air and $CH_4$-air mixtures under the action of high voltage nanosecond discharge has been developed. Basic factors that determine the combustion process in such systems were revealed. Experimental scheme for testing of ignition threshold shift under the sequential action of the shock wave and nanosecond discharge has been proposed. A possibility of utilizing the non-equilibrium gas discharge for wide control of the fuel-air mixtures ignition and combustion was shown both numerically and experimentally. This control may be effective in the wide range of gas parameters. Shift of the ignition time delay has been obtained experimentally; it was demonstrated that correlation with theoretical prediction is good enough.

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References
