Plasma supported combustion

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Abstract

Oxidation of molecular hydrogen and different hydrocarbons in stoichiometric mixtures with air and oxygen in the pulsed nanosecond discharges was studied at room temperature, and the detailed kinetics of the process has been numerically investigated. In the discharge afterglow, the reactions including electron-excited particles play a dominant role for the time up to 100 ns, ion–molecular reactions—for the time of microsecond range, and reactions including radicals mostly contribute for the time interval of several milliseconds. The principal role of processes with formation of excited components that support the development of the chain mechanism of oxidation has been shown. The spatial uniformity of the gas-mixture combustion initiated by a high-voltage nanosecond volume discharge is investigated at gas pressures of 0.3–2.4 atm and temperatures of 1000–2250 K. The self-ignition time and the time of discharge-induced ignition are determined. It is found that the discharge significantly (by 600 K) decreases the ignition temperature with very low energy in the discharge ($\sim10^{-2}$ J/cm$^3$). The influence of gas excitation by a pulsed nanosecond discharge with a high-voltage pulse amplitude up to 25 kV on the properties of a premixed propane–air flame has been investigated over a wide range of the equivalence ratios (0.4–5). It was experimentally found that the flame's blow-off velocity increased more than twice at a discharge energy input less than 1% of the burner power. Efficient production of active radicals under the action of a barrier discharge has been observed. The increase in the flame's propagation velocity is explained by the production of atomic oxygen in a discharge by the quenching of electronically excited molecular nitrogen $N_2$ and the dissociation of molecular oxygen on electron-impact. A numerical model has been developed, which describes the influence of pulsed electric discharges on the ignition, combustion, and flame propagation. © 2004 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

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1. Introduction

The effect of an electric field on a flame was first observed in 1814 by Brande [1], who discovered that the flame's behavior substantially changed when the flame was placed between two electrodes. It was found that the influence of an electric field on heat and mass transfer was so strong that both the flame and soot began to move toward the negatively charged electrode. Thus, Brande was the first to affect the flame's propagation velocity by applying an electric field. A review of this field is available in the papers of Malinovsky [2]. Run on more recently, the interaction of electric fields and discharges with flames has been widely studied. The main idea is flame stabilization [3], the production of the atoms, ions, and...
active radicals neutralizing hazardous wastes from power plants and chemical factories (NOx, SO2, etc.) [4], extending flammability limits, and increasing a flame’s luminosity. A determination of the basic mechanisms responsible for combustion stability is also of great interest. It is known that unstable combustion of solid, liquid, or gaseous fuels in power plants manifests itself in a spontaneous onset of self-oscillating combustion regimes, which are accompanied by significant fluctuations of the thermal flux rate and pressure, as well as by mechanical vibrations (or even destruction) of the combustion chamber. Therefore, the control of combustion stability is very pressing.

A separate field of research is the use of electric fields and discharges to change the flame propagation velocity. By applying an electric field, one can decrease the flame propagation velocity along a channel and even extinguish the flame [5] or, on the contrary, accelerate the combustion rate by increasing the flame’s blow-off velocity [6]. This field of research holds great promise and is quite challenging for practical applications, such as aircraft engines, in which combustion should be as rapid and complete as possible. More rapid combustion makes it possible to use more lean mixtures, which results in a decrease in the temperature of the combustion products and a reduction in the amount of the NOx produced.

Discussion about the real mechanisms by which an electric field can affect the rate of combustion has been lasting for many years. The problem of determining such mechanisms is particularly important because of the rapidly growing interest in the possibility of also controlling a flame’s dynamics with the help of a non-equilibrium plasma.

The simplest means for affecting a combustible mixture with an electric discharge is a pulsed arc, which occurs, for instance, in the spark plug of an IC engine. In this case, the discharge current density is high enough, the plasma produced is close to thermal equilibrium, and the fuel is ignited due to the heating of the mixture in a small-volume arc channel and the adjacent regions. The energy input on such an ignition can be rather high, and the ratio of the discharge energy to the gas’s chemical energy in the spark channel is much larger than unity. For this reason, this type of discharge is inapplicable for volume ignition because of the high energy consumption. However, it is volume (or nearly volume) ignition, which is of greatest interest for applications with a high rate of energy release. The slow propagation of a flame front from the point of ignition limits this rate and does not allow one to use spark discharges in high-speed (including supersonic) gas flows.

Therefore, it is of especial interest to find such methods of flame control at which energy deposition in the gas is certainly insufficient to heat the mixture up to the temperature of spontaneous thermal ignition. That is why we consider below discharges in which Joule heating is negligibly small in comparison with the chemical heat release and is distributed over the gas’s volume.

A flame is a low-temperature plasma with a mean particle energy of ~0.2 eV. This plasma mainly consists of molecules and radicals, as well as electrons and positively charged ions produced by chemical or thermal ionization. Calculations of the equilibrium composition of the combustion products of a hydrocarbon–air mixture at atmospheric pressure and the temperature corresponding to the adiabatic equilibrium (higher than 2000 K) by Saha’s equation give an electron density lower than 10^8 cm^-3, whereas the total density of the molecules, radicals, and atoms is ~10^18 cm^-3. For this reason, the following two mechanisms (besides Joule heating) through which the electric field affects the flame characteristics are considered in the literature.

At low reduced fields, insufficient for the excitation of the mixture components (several hundred volts per centimeter at atmospheric pressure), the so-called “ionic wind” (the electric field-induced redistribution of the charged particles, as well as neutral atoms and molecules, which are set into motion due to the resonance charge-exchange processes, A + A^+ → A^- + A) plays a decisive role. It was shown by Lawton and Weinberg [7] that the electric forces inside a flame can exceed the convective forces by more than two orders of magnitude. This effect is especially pronounced in the case of slow diffusion flames, whose propagation velocities are much lower than those of premixed flames [8].

At higher electric fields, the processes of gas excitation, dissociation, and ionization by electron-impact become important. These processes lead to the appearance of new chemically active species and additional interaction mechanisms that modify and accelerate the kinetics of the entire system. The electron energy should be high enough for electronic and vibrational excitation of the molecules in this case; hence, this range of electric fields, in general, corresponds to the development of a gas discharge.

At present, it is commonly believed that almost all the existing measurements for low-speed diffusion flames can be explained (at least qualitatively) by an ionic wind. Most experiments dealt with dc fields (high-frequency fields do not affect the combustion rate because the ions have no time to move out of their positions during the field period) in the typical “burner-ring” electrode geometry. The ring is placed at a certain distance (from a few millimeters to a few centimeters) above the burner rim, and the potential difference between the electrodes is several kilovolts. It is worth mentioning that it is sensible to talk just about the po-
tential difference (rather than the electric field intensity), because, in such an electrode geometry, the field distribution is highly non-uniform. For example, a significant increase in a flame's blow-off velocity in methane–air mixture (by a factor of 2.0–4.2) was observed when the nozzle was at a negative potential [9]. This was explained by: (i) a change in the temperature distribution within a narrow nozzle region filled with unburned reagents, (ii) the slowing-down and stabilization of the effluent gas near the burner edge due to the ionic wind, and (iii) the intensification of the reaction due to heat transfer and the entry of combustion products into the region where the mixture has not yet burned.

Unfortunately, in spite of the interesting results obtained, such a burner design has some drawbacks. In particular, the thickness of burner wall determines the distance over which the flame is stabilized, and so plays an important role. Hence, it is problematic to use this method to stabilize a flame in an industrial burner. Moreover, because of a highly non-uniform electric field, the main voltage drop occurs at distances of several millimeters from the nozzle. Calculations show that, in this region, the electric field intensity is close to the breakdown field in air, which leads to the formation of a corona at the nozzle’s edge. Therefore, the change in the blow-off velocity is not related to the ionic wind, but is a consequence of the local energy deposition in a few points inside the flow where the ignition of the mixture occurs.

The influence of a corona discharge on the blow-off velocity of a methane–air flame was studied by Bradley and Nasser [10], who applied a voltage between a spiral coil placed above the flame and four tapered points placed inside the nozzle. Three regimes were found for the effect of an electric field: (i) the ionic wind, which slightly increases the blow-off flow rate (by ≈30%); (ii) a corona discharge, in which the flame is stabilized at the burner nozzle; and (iii) an unsteady corona discharge with four inverted-flame cones. As in [9], the mixture was ignited at the cone’s vertexes (at each point); then, the flame propagated due to conventional mechanisms, such as heat transfer and diffusion. In this case, a significant (nearly twofold) increase in the flame propagation velocity was achieved. However, any further increase in the voltage (and, accordingly, the flame velocity) was impossible in this geometry because the corona discharge transformed into a spark mode. Moreover, only a fraction of the flow that was admitted to the cone was burnt. As a result, combustion was incomplete, which led to a decrease in the burner’s power.

Both of the above studies dealt with edge effects, which stemmed from the highly non-uniform electric field; consequently, practical implementation of these studies is rather problematic. It will be shown experimentally below that, in the above geometry, the increase in propagation velocity is not related to the current flowing through the flame, the role of the ionic wind is negligible. Seemingly, the ionic wind is of limited utility as a means of increasing the combustion rate in premixed flames (a possible exception may be specific burners with a thick wall and small inner diameter of the nozzle).

Some authors [11] suppose that the kinetics of combustion can be affected by a relatively weak (1–2 kV/cm) alternating electric field and explain the change in the normal flame velocity by an acceleration of the reaction:

\[
H + O_2 \rightarrow OH + O \quad (1)
\]

This reaction is one of the most important in a flame [21], and its rate substantially determines the oxidation of CO and the production of OH radicals, which play a major role in branching combustion of a hydrocarbon. Measurements [22] show that the effect of an increase in the flame’s propagation velocity takes place at reduced electric fields \(E/N\) (where \(E\) is the electric field intensity and \(N\) is the density of molecules in a mixture) as low as 10 Td (1 Td = \(10^{-17}\) V cm\(^2\)).

\[
N_2(v = 0) + e \rightarrow N_2(v > 0) + e \quad (2)
\]

The process is likely to be the main way a field can influence a flame. Subsequently, a vibrationally excited nitrogen molecule can transfer vibrational quanta to other molecules (in particular, \(O_2\) in:

\[
N_2(v = 0) + O_2(v' = 0) \rightarrow N_2(v - 1) + O_2(v' = 1) \quad (3)
\]

Such vibrational excitation of oxygen molecules can accelerate chemical reactions, in particular, reaction (1), and, accordingly, the combustion process as a whole. An indirect confirmation of this mechanism is the fact that an increase in the combustion rate was observed in mixtures of \(CH_4, O_2 + N_2\), whereas in flames of \(CH_4, O_2 + Ar\) this effect was much less pronounced, although the electron density was the same. Unfortunately, it is not yet quite clear to what extent this mechanism can accelerate reaction (1), because, in a typical flame, the relaxation and deactivation processes competing with the vibrational excitation of \(N_2\) and \(O_2\) are fairly fast. Hence, further experimental study of such mechanisms is required to verify the above statements. Nevertheless, one can assert that a reduced electric field of 10 Td is insufficient to enable the electron-impact excitation of higher \((v > 3)\) vibrational levels (to saying nothing of electronic ones) of both nitrogen and oxygen. In addition, the discharges at such a low reduced electric field are not self-sustained. This reduces the efficiency of this type of discharge.

The problem of the uniform and fast ignition of combustible mixtures is of crucial importance...
mixed with air ignited by transient plasma discharge were investigated and compared with spark discharge ignition in [13]. Multi-ignition site effect and high-electron energy are suggested to contribute to shortening of rise and delay times.

The paper [14] presents the results of non-equilibrium RF plasma-assisted ignition and combustion experiments in premixed methane–air, ethylene–air, and CO–air flows. The results show that large volume ignition of these mixtures by the uniform and diffuse RF plasma can be achieved at significantly higher flow velocities (up to \( u = 25 \, \text{m/s} \)) and lower pressures (\( P = 60–130 \, \text{torr} \)) compared to both a spark discharge and a DC arc discharge. The experiments also demonstrated flame stabilization by the RF plasma, without the use of any physical obstacle flameholders. Temperature measurements in the stable diffuse RF discharge using Fourier transform infrared spectroscopy show that the flow temperature in the plasma prior to ignition (\( T = 250–550 \, \text{°C} \) at \( P = 60–120 \, \text{torr} \)) is considerably lower than the autoignition temperatures for both ethylene–air and CO–air mixtures at these pressures (\( T = 600–700 \, \text{°C} \)). Spatially resolved temperature measurements show the transverse temperature non-uniformity in the RF discharge to be insignificant. Visible emission spectroscopy measurements in \( \text{C}_2\text{H}_4 \)-air flows in the RF discharge detected the presence of radical species such as CN, CH, \( \text{C}_2 \), and OH, as well as O atoms. In CO–air flows, O and H atoms have been detected in the RF plasma region and \( \text{CO}_2 \) emission (carbon monoxide flame bands) in the flame downstream of the RF plasma [14].

Recent progress in developing a detailed kinetic mechanism for \( \text{C}_8\text{H}_{18} \) hydrocarbons and practical plasma igniters for plasma-assisted combustion is discussed in [15]. Shock tube validation experiments made in argon using a fixed stoichiometry (\( \phi = 1.0 \)), pressures of approximately 0.95 and 1.05 atm, and temperatures ranging from 850 to 1200 K (post-reflected shock) are presented. The mechanism is being expanded to include electron kinetics and to allow for a degree of non-equilibrium modelled with separate electron and gas temperatures. Quantum calculations used to derive needed electron-impact ionization/dissociation cross-sections for hydrocarbons are discussed. In addition, ignition of ethylene fuel in a Mach 2 supersonic flow with a total temperature of 590 K and pressure of 5.4 atm is demonstrated using a low frequency discharge with peak and average powers reaching 8 and 2.8 kW, respectively [15].

Experimental researches on the internal plasma-assisted combustion are carried out in the hot wind tunnel in [16]. Supersonic airflow (\( M < 2, \, P < 1 \, \text{bar}, \, \text{and} \, T < 1000 \, \text{K} \)) is created in the test section of this experimental setup. Powerful streamer HF discharge (mean power up to
10 kW) is used for airflow preheating and fuel-airflow radial generation. Modulated HF streamer discharge is used to accelerate fuel-airflow mixing and plasma-assisted combustion in some experiments. Optical and IR spectroscopy analyses are used to study plasma and radical generation in airflow. Gas flow parameters are measured in the combustion region and after it by pressure and temperature sensors. Experimental results on power balance (calorimetric measurements) and fuel combustion completeness are considered. It was revealed that combustion completeness is increased by a factor of 2–3 at plasma the in comparison with one at plasma off [16]. External plasma-assisted combustion is studied in the wind tunnel experiment. Airflow parameters are as follows: Mach number $M < 2$, stagnation temperature $T = 300$ K, and static pressure $P < 1$ bar. Surface pressure distribution on the model surface is measured in the plasma-aerodynamic experiment. Model drag is also measured in this experiment. Supersonic flow around the model is studied by the shadow optical method. Considerable drag decrease up to 30–40% and surface pressure decrease up to 50% were measured at local external plasma-assisted combustion generation [16].

Effects of the number of ignition site on burning times and comparison between pulsed corona and spark discharges with single ignition site and the same energy show that there are two possible mechanisms—chemical and geometric effects, which contribute to shortening delay and rise times of pulsed corona ignitions, respectively [17]. Burning time shortening has also been demonstrated in a geometrically IC engine like combustion chamber at elevated pressure. Discharge efficiency of pulsed corona discharge is observed to be much higher than spark discharge [17].

In [18], the ignition of supersonic propane–butane–air mixture with the help of transversal surface discharge and stabilizing action of a stagnant zone in the aerodynamic channel of rectangular section on the process of propane–butane–air mixture combustion were investigated. Under the experimental conditions of [18], the stable burning of supersonic (flow Mach number $M = 2$) mixtures of propane–butane with air has been received at use of a stagnant zone.

Experiments with deeply undercritical microwave discharges in high-speed airflow and the effects of the discharge on propane–air ignition are described in [19]. The discharge was excited in the quasi-optical beam of a linearly polarized microwave radiation with power 1 kW at a wavelength of 12.5 cm, which was generated using a magnetron-type generator of continuous radiation. The discharge was initiated by an electric vibrator located within a submerged airstream at velocities varying from zero to supersonic speeds. The propane jet was injected into the discharge region through a hole in the base of the vibrator. The experiments [19] demonstrate the possibility of propane ignition and combustion at supersonic speeds following propane injection into a discharge region.

The interaction between a nanosecond pulsed plasma discharge and a hydrocarbon diffusion flame is investigated in [20]. An atmospheric-pressure coaxial burner made of electrically non-conductive material, allowing the use of high-voltage discharges in its vicinity, was designed and built. A triggered pulse generator with a 10 ns jitter was built with a hydrogen thyratron as the main switch. The generator can reach a pulse amplitude of 45 kV at 100 Hz or more, with a pulse width of about 40 ns and a rise time of 15–20 ns. The pulsed discharge plasma was able to attach a lifted turbulent methane diffusion flame. OH-PLIF was performed in the afterglow of a pulsed discharge in a methane diffusion flame, and the images obtained show that the discharge creates OH radicals. Emission spectra of a pulsed discharge operated at room temperature in propane and methane showed that carbonaceous species ($C_2$, CH, and $C_3$) are created in the plasma. The “rotational” temperature of CH excited states was measured. It was shown that the rotational distribution corresponds to temperature higher than translational one. It was pointed out that the recombination of C and H into CH through inverse predissociation pathways may explain the apparent rotational non-equilibrium of CH A and B electronic states [20].

Nowadays, it seems that the most challenging method for accelerating combustion is the non-equilibrium excitation of the gas-mixture components, which allows one to affect the chemical reaction kinetics. To enable more efficient excitation of the electronic and vibrational degrees of freedom, one should use short-duration”) pulses with a highly reduced electric field [23,24]. In pulsed discharges, the reduced electric field at the front of an ionization wave (e.g., in the streamer head) attains hundreds of Td, whereas the electric field in the streamer channel is significantly lower and certainly insufficient for the production of active particles. The experiments of [25] demonstrated that it is the region with a strong field in the streamer head in which the active particles are mainly produced.

Employing a pulsed barrier discharge allows one to avoid the transition of a streamer discharge to a spark form because the dielectric barrier limits the maximum charge transmitted through a channel. This type of discharge is non-equilibrium: the electron temperature is rather high (4–5 eV), whereas the translational temperature of the neutral gas is close to the temperature of the electrodes [26]. Thus, the gas is heated only slightly, and the energy is mainly deposited in
the vibrational and electronic (rather than translational) degrees of freedom of the gas molecules.

A comprehensive study of the discharge parameters [27] allows one to analyze the efficiency of the produced plasma as a generator of active particles. Present-day methods of recording high-voltage nanosecond pulses enable measurements of the current and voltage waveforms with a sub-nanosecond time resolution. The aim of this study was a detailed analysis of the electric parameters of the discharge and their influence on the efficiency of mixture ignition, as well as the possibility of optimizing discharges used to ignite combustible mixtures.

2. Plasmachemical processes in low-temperature non-equilibrium plasma of fuel–air mixtures

The question “How to describe role of the discharge in a case of using of low-temperature non-equilibrium plasma for the ignition” still remains without clear unambiguous answer. The importance and role of atoms, excited species, and ions are under discussion. There is the only way to clarify this: direct measurements of fuel destruction under the discharge to understand kinetic peculiarities of the system. In this section, we briefly represent our investigation of the decomposition of different hydrocarbons by the nanosecond discharge. In Table 1, percentage of hydrocarbon in investigated mixtures is represented for hydrocarbon–oxygen and hydrocarbon–air mixtures.

The plasmachemical reactor described in [28] was used in these experiments. Uniform discharge was initiated in discharge cell 500 cm³ in volume at a pressure of mixture of 1–12 torr. The electric pulse was 25 ns in a half-width, 11 kV in amplitude, at a repetition rate of 40 Hz. Time-resolved (in nanosecond and second ranges) profiles of emission produced by different excited species and electrical parameters, such as dynamics of electric field, energy consumption per pulse, and current, were measured. The absorption of methane was controlled on the wavelength of 3.3922 μm. As a result, we obtain kinetic curves of active species and a full set of electrical parameters of discharge. After uniform electric field establishing in the discharge tube, the discharge current increases during several nanoseconds up to maximal value (about of 200 A). At the same time, the electric field decreases. This time interval corresponds to the maximum of dissipated power, which was measured by the back-current shunt technique. Total energy of high-voltage pulse was about 60 mJ. We measured and analyzed energy input into the gas in the beginning and in the end of the oxidation process.

Emission spectra of mixtures represented in Table 1 were controlled during the oxidation in the wavelength range of 200–800 nm. As an example, we represent in Fig. 1 the emission spectra of the methane and of the products in methane–oxygen mixture. In methane, we observe strong molecular hydrogen continuum emission. Lines of OH, CO⁺, and CH are clearly seen in the mixture.

On the basis of the experiments, we concluded that all investigated mixtures excluding mixtures with methane give approximately the same oxidation time. For methane–air and for methane–oxygen mixture, typical oxidation time is two times higher than for the other mixtures (Fig. 2).

3. High-temperature ignition by nanosecond pulsed discharges

Accounting for the fact that experiments should be induced at high temperatures, in the problem under consideration the shock wave serves to prepare the gas mixture (Table 2) at the specified temperature and pressure. Because the gas dynamic times (1–100 ms) are significantly more than the characteristic time of gas excitation by the pulsed breakdown (1–100 ns), the gas in the shock wave may be regarded as motionless from the viewpoint of discharge development. A great difference of the characteristic gas dynamic times and the time of discharge development makes it also possible to

Table 1
Mixtures used for low-temperature oxidation experiments by pulsed nanosecond discharge

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>CH₄ (%)</th>
<th>C₂H₆ (%)</th>
<th>C₃H₈ (%)</th>
<th>C₄H₁₀ (%)</th>
<th>C₅H₁₂ (%)</th>
<th>C₆H₁₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With O₂</td>
<td>33.3</td>
<td>22.2</td>
<td>16.6</td>
<td>13.3</td>
<td>11.1</td>
<td>9.5</td>
</tr>
<tr>
<td>With air</td>
<td>11.11</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.03</td>
<td>2.56</td>
</tr>
</tbody>
</table>
consider that FIW propagates in gas with the parameter distribution \((P, T, \rho)\) corresponding to their instantaneous values behind the shock wave.

In all experiments, nanosecond discharge was initiated behind the front of a reflected shock wave. The experimental setup (Fig. 3) consisted of a shock tube (ST) with a discharge cell (DC), a gas evacuation and supply system, a system for discharge ignition, and a diagnostic system.

The shock tube with a \(25 \times 25\) mm\(^2\) cross-section had a 1.6-m-long working channel. The length of the high-pressure cell (HPC) was 60 cm. There were two pairs of windows for optical diagnostics along the stainless-steel working channel. The last 20-cm-long section of the shock tube with a \(25 \times 25\) mm\(^2\) cross-section was made from 20-mm-thick organic glass and had eight optical windows (five of which were made of quartz and three were made of MgF\(_2\)). The metal end plate (EP) of the tube served as a high-voltage electrode. Another electrode was the grounded steel section of the shock tube.

The nanosecond discharge was initiated at the instant at which the reflected shock wave arrived at the observation point (point \(A\) in Fig. 3). High-voltage pulses were produced with a ten-stage GIN-9 Marks generator. To enable the operation of the spark gap, the generator was filled with nitrogen at a pressure of 3 atm, which provided a starting voltage in the range 100–160 kV. To sharpen the high-voltage pulse applied to the discharge gap, a forming ferrite line with a wave impedance of \(Z = 40 \Omega\) was used. At the output of the forming line, the voltage growth rate was 8 kV/ns, which enabled the operation of the gas discharge in the form of a fast ionization wave in the dielectric section of the shock tube. The propagation velocity of the ionization wave front was \(10^9–10^{10}\) cm/s, depending on the experimental parameters.

The diagnostic system consisted of four components: a system for monitoring the shock wave parameters, a system for detecting ignition, a system for studying the spatial structure of the discharge and combustion, and a system for monitoring the electric parameters of the nanosecond discharge.

To study the spatial structure of the discharge and the uniformity of combustion, we carried out an additional series of experiments in which the emission intensity (integrated over the wavelength range 300–800 nm) was measured with a PicoStar HR12 (La Vision) ICCD camera.

Figure 4 schematically shows two different regimes of camera operation. After the initiation of the discharge (a rectangular pulse in the upper left of the figure), which was synchronized with the instant at which the reflected shock wave arrived at the measurement cross section, we observed an intense short-duration emission pulse from the discharge with a characteristic decay time of a few tens of nanoseconds and a relatively long-duration emission pulse related to combustion with a characteristic duration of about 10–100 \(\mu\)s. When obtaining images of a nanosecond discharge, the gate time of the ICCD camera was set to 1 ns. The triggering of the CCD camera
was synchronized with the instant of discharge ignition. The intensifier was triggered by the signal from a coaxial photoelectric cell (PEC) through a delay line with an adjustable delay time $D_t$. When obtaining images of gas combustion, the CCD gate time was 30–50 ms, and the intensifier was triggered by a microsecond pulse generator with an adjustable delay time.

Simultaneous with the measurements of current and voltage, the emission from the second positive system of molecular nitrogen ($\lambda = 337.1$ nm, $C^3\Pi_u(v' = 0)\rightarrow B^3\Pi_g(v'' = 0)$ transition) was monitored with a nanosecond time resolution. Such measurements in the nanosecond range allowed us to trace the discharge development and to determine the energy deposited in the gas under different experimental conditions. Since the main purpose of our study was to find the most favorable conditions for igniting a combustible mixture by a nanosecond discharge, we chose as a basic regime one of the experimental regimes of [23]. All the experiments were carried out with the CH$_4$:O$_2$:N$_2$:Ar = 1:4:15:80 mixture. The temperature behind the reflected shock wave ($T_5$) varied from 1000 to 2250 K, and the pressure ($P_5$) varied from 0.4 to 2.3 atm.

The time delay of ignition versus temperature is shown in Fig. 5. In addition to the experimental data, the dependences of the self-ignition time by the GRIMech 3.0 mechanism are also shown. The computations were performed at a constant pressure. It can be seen that the simulation and experimental results are in good agreement for pressures of about 2 atm behind the reflected shock wave. With a discharge, both the ignition time and the minimum temperature needed for ignition decrease. At a pressure of 2 atm, the decrease in the ignition temperature is 100 K, whereas at a pressure of 0.5 atm, the ignition temperature decreases by 600 K. One of the aims of our experiments with a detailed monitoring of the electric parameters of the discharge was to reveal a reason for such a discrepancy.

In experiments on discharge-induced ignition behind the reflected shock wave, the problem of the spatial uniformity of the discharge and subsequent combustion is of crucial importance.

In fact, these intensities differ by a factor of only 1.3. Hence, we conclude that the discharge is nearly uniform. Similar measurements were performed at the parameters corresponding to curve 2 (a pressure of $\approx$2 atm) and curves 3–5 (a pressure of $\approx$0.5 atm) in Fig. 5. Figure 6 presents two photographs taken at different temperatures and pressures. It can be seen that, at $T_5 = 1337$ K and $P_5 = 0.6$ atm, the discharge emission intensity is almost uniform. As the temperature increases to $T_5 = 1598$ K and the pressure increases to $P_5 = 1.9$ atm, a stratified structure resembling a horizontal flow appears. Most likely, this structure is related to gas density variations behind the shock wave.

The spatial uniformity of discharge-induced combustion was studied for the parameters corresponding to the above curves in Fig. 5. Two photographs of the combustion process for different $T_5$ are shown in Fig. 7. At $T_5 = 1290$ K (which corresponds to a uniform discharge), one can see a uniformly glowing domain and, at $T_5 = 1707$ K, a characteristic spotted structure is seen.

Thus, employing a high-voltage nanosecond volume discharge at pressures of about 0.5 atm significantly reduces the ignition temperature.
and results in spatially uniform combustion. At pressures of 1.5–2 atm, the ignition temperature decreases only slightly; however, the number of combustion sites and their spatial uniformity increase greatly as compared to the case of self-ignition at the same pressure.

4. Effect of the pulsed electric discharge plasma on a flame

We examined different electric field configurations to choose such that it is optimum for determining the most efficient mechanisms for flame control and, at the same time, allows us to avoid excess electric energy losses and gas heating. The key requirements to the discharge section geometry are as follows: (1) accounting for the fact that the energy deposition in the discharge is much lower than the burner power, it is necessary that the discharge affects the preflame zone rather than the ignited mixture. (2) The discharge should occupy the entire cross-section of the nozzle. This enables a nearly uniform gas excitation and significantly facilitates the interpretation of the results obtained.

In the burner, we used a rectangular glass nozzle (30 × 2 mm), inside which a high-voltage electrode was placed (Fig. 8). The low-voltage electrodes were positioned near the nozzle edge; to prevent a transition of the discharge into a spark form, they were set tightly into quartz tubes. On applying a voltage to the gap, a barrier discharge occurred, whose current was limited by the dielectric layers.

The amplitude of the incident voltage pulse was $U_{\text{max}} = 12$ kV, the pulse duration at a half-height was $\tau_{1/2} = 77$ ns, the rise time was $\tau_{\text{inc}} = 10$ ns, and the pulse repetition rate was $f = 1.2$ kHz. The pulsed voltage polarity could be varied. The design of the voltage supply also allowed us to apply a dc voltage of either polarity to the discharge gap. In the experiments, the waveforms of both the discharge current and voltage were recorded, which allowed us to determine the energy input in the discharge.

We have found that the action of a barrier discharge on a flame leads to an increase in the flame propagation velocity. The higher the discharge power, the higher the increase. (It should be noted, however, that, in all the regimes, the discharge power did not exceed 1% of the burner chemical power.)

A comparative analysis of these discharges and their effect on the blow-off velocity is presented in Fig. 9. From the standpoint of increasing the flame propagation velocity, a positive-polarity pulsed barrier discharge is the most efficient. The higher efficiency of this discharge as compared to a negative-polarity barrier discharge stems from the fact that, at the same pulse voltages, a cathode-directed streamer develops faster and produces a larger number of active particles than an anode-directed one because of the different mechanisms for their propagation [25]. In the case of a dc discharge, the situation is opposite. At a negative-polarity, the tapered electrode in a hot gas efficiently emits electrons, which leads to the formation of a dc corona with a high current density near the points. In the given geometry, a positive dc voltage only slightly affects the flame propagation velocity.

In the case of a positive-polarity pulsed discharge, which is the most efficient from the stand-
point of increasing the flame propagation velocity, the change in the flame blow-off velocity is shown in Fig. 9 for a wider range of the equivalence ratios $\phi$ (the ratio of the fuel percentage in the mixture under study to the fuel percentage in a stoichiometric mixture). It can be seen that the effect of the discharge is strongest at $\phi = 0.65–0.75$. In a system with a barrier discharge, the increase in the flame propagation velocity is higher than 100%.

To estimate the energy deposited in the fuel mixture, the waveforms of the discharge voltage and current were monitored with the help of a back-current shunt and a digital Tektronix TDS-3054 oscilloscope. The energy deposited in one pulse is approximately 8 mJ, which corresponds to an average power of 9 W at a pulse repetition rate of 1200 Hz. This is less than 1% of the chemical energy released in the combustion of a propane–air mixture.

The emission intensity profiles from C$_2$ ($\lambda = 517.8$ nm), CH ($\lambda = 431.5$ nm), and OH ($\lambda = 306.4$ nm) without a discharge and with a barrier discharge at $U = 20$ kW were measured. It can be seen that, in the presence of a barrier discharge, the peaks of the emission intensity from C$_2$ and CH increase, shift toward the nozzle, and become narrower. This indicates the intensification of the combustion process and the acceleration of the chemical reactions occurring in the flame. For the OH radical, besides the above change in the emission profile, applying a barrier discharge results in the appearance of the second emission maximum located in the discharge region, which reflects the production of this radical under the action of the discharge.

Figure 10 shows the OH emission intensity versus the height above the burner edge in the presence of a discharge at $\phi = 0.6$ and different flow rates of the combustible mixture. It can be seen from this figure that the profile of the OH radical emission changes as the flow rate increases. For the sake of comparison, the dashed curve shows a similar dependence for the same value of the parameter $\phi$ but without a discharge.

To find mechanisms responsible for the influence of a non-equilibrium discharge on the flame velocity, it is necessary to determine the role of plasmachemical processes in the discharge and the preflame zone. As was mentioned above, the flame propagation velocity depends on the rates of chemical reactions in the gas and, especially, in the preflame zone. Hence, the excitation of reactants can significantly affect the flame propagation velocity. In this study, we first calculate the production of active particles in the barrier discharge gap; then, the densities obtained are used as initial conditions for the one-dimensional task of flame propagation. After applying periodical high-voltage pulses, plasmachemical reactions in the flame can be divided into three spatially separated stages: (1) electron-impact excitation of molecules in a barrier discharge, (2) kinetics of the excited states in the preflame zone, and (3) flame propagation through the pre-excited mixture.

One-dimensional simulations of the combustion and propagation of a premixed propane–air flame were performed. Atomic oxygen produced in the discharge zone near the nozzle edge participates in chain branching reactions. At low temperatures, the rate at which chain reactions are broken exceeds the formation rate of new chains, and the initial O concentration is insufficient to ignite the mixture and, sustain combustion. Hence, the efficiency of the discharge energy utilization is primarily determined by the temperature growth related to the heat flux from the region where the chemical energy is released. The radicals created in the preheated flow give rise to significantly longer chains, which leads to an increase in the energy released in a single act of oxygen dissociation in the discharge. Thus, applying a discharge to the adjacent to the flame front region significantly increases the efficiency with which the flame can be controlled. The concentration profiles of other active particles (O, CH, and others) behave similarly to the OH concentration profile. The increase in the flame propagation velocity depends on the discharge power (the concentration of atomic oxygen); for a relatively small concentration of atomic oxygen ($0.1\%$), it is about 20%.

5. Conclusions

Slow oxidation of hydrocarbons under the action of repetitive nanosecond discharge has been investigated for mixtures of methane, propane, butane, pentane, and hexane mixtures with air and oxygen. Parameters, which are suitable for the control of oxidation process, are analyzed.
The most important processes have been determined, and the principal role of processes with the formation of excited molecules that support the development of the chain oxidation mechanism has been shown.

The results of experiments on the ignition of a methane–air–argon mixture with the help of a nanosecond volume discharge behind the reflected shock wave at temperatures of 1000–2250 K and pressures of 0.3–2.4 atm allow us to draw the following conclusions:

A spatially uniform single-pulse nanosecond discharge can be achieved at high (1000–2000 K) translational gas temperatures.

The simultaneous monitoring of the time evolution of the discharge voltage and current allows one to determine the total energy deposited in the gas during the discharge.

A detailed analysis of the time evolution of the discharge voltage, current, and emission intensity allows one to determine the characteristic features of the discharge development and to optimize the discharge as a plasmochemical source by varying its parameters.

It is shown that, under the given experimental conditions, a spatially uniform high-current nanosecond discharge initiates uniform combustion. In this case, the ignition temperature turns out to be significantly reduced (by hundreds of Kelvin). A corona discharge initiated on the high-voltage electrode only slightly affects the ignition temperature and the delay time of ignition at the same deposited energy. Thus, the system can be significantly optimized by properly choosing the parameters of a non-equilibrium low-temperature discharge plasma initiating combustion.

The effect of different types of discharge on the combustion rate of a premixed gas mixture has been studied. A comparative analysis of the influence of the polarity and type of the discharge on the flame propagation velocity has been performed. Using a pulsed nanosecond barrier discharge, stable flame propagation through a lean propane–air mixture (φ = 0.55) is achieved with the same velocity as in the case of a mixture with φ = 1.1 but without discharge excitation. More than twofold increase in the flame propagation velocity is achieved at the same fuel content in the mixtures. At a pulse voltage amplitude of $U_{\text{max}} = 20–25$ kV, pulse duration of $\tau_{1/2} = 77$ ns, rise time of $\tau_{\text{rise}} = 10$ ns, and repetition rate of $f = 1.2$ kHz, the energy input in the mixture from the discharge is less than 1% of the burner chemical power. The parameters of the system can be improved further by optimizing the parameters of the pulsed voltage generator.

It is shown that the main mechanism through which the discharge plasma affects the flame parameters is the change in the initial mixture composition, which results in the onset of additional chain reactions in the pre-flame zone.

Applying a non-equilibrium discharge leads to the electronic excitation of the gas components, the production of active particles (in particular, atomic oxygen), and the acceleration of the processes governing the combustion rate and the flame propagation velocity. An advantage of employing a strongly non-equilibrium plasma of a nanosecond discharge is the efficiency of energy deposition as compared to other methods for flame control.

One-dimensional numerical simulations of the propagation of a premixed flame with additional gas excitation in a discharge have been performed. The simulation results (the density profiles of atoms and radicals, as well as the profiles of the flame temperature and velocity) are in qualitative agreement with the experimental data. This confirms the proposed mechanism for combustion control.

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**References**

The efficiency of plasma production depends on two factors: generator efficiency and efficiency of energy deposition into the plasma. Modern solid-state nanosecond pulse generators have the overall efficiency up to 90% (with resonant charging). More difficult to answer is the question about the efficiency of energy transfer from generator to plasma. This requires very accurate resistance matching. For short nanosecond pulses this condition is of crucial importance. We can adjust the discharge gap parameters for a wide range of discharge frequencies and pulse voltage amplitude to reach the efficiency of energy transfer up to 80–90%. Thus, the overall efficiency of plasma production system may be as high as 70–80%.
tenth of thousand of reactions. The attempt of such mechanism construction for \( \text{H}_2 \)-air mixture was made, for example, in [1]. For hydrocarbon-air flames ion chemistry kinetics was constructed in part, for example, in work of Williams [2]. Unfortunately, up to now there are no full kinetic data for ion chemistry and chemistry of excited states for hydrocarbons.

**References**


**Reply.** Electronically excited states play a very important role in the process of ignition under plasma-supported conditions. Because of large amount of molecular nitrogen in fuel–air mixtures, a significant amount of the discharge energy goes to the excited states of \( \text{N}_2 \). Among them there are triplet states \( \text{C}_3^\pi, \text{B}_3^\pi, \text{A}_3^\pi \), singlet states, etc. In the presence of molecular oxygen the main channel of triplet states depopulation is collisional quenching by \( \text{O}_2 \). This process leads to atomic oxygen production.

Direct excitation of molecular oxygen by electron impact in the discharge leads to \( \text{O}_2(\text{A}_1\text{D}) \) and \( \text{O}(\text{4D}) \) formation. Electronic excitation of molecular and atomic oxygen leads to a decrease of the activation energy of reactions with these components and increase the oxidation rate at low temperatures. Thus, both short-lived and metastable states play important role in the ignition development under the discharge conditions.

**Reply.** The ionic wind could produce additional force on the gas and may change the velocity of the flow. If we reduce the gas velocity we force the flame closer to the burner rim and reduce the dead space. In our experiments we control the flow velocity separately and ionic wind cannot change this value. Moreover, in our experiments the electric field was directed almost perpendicular to the gas flow velocity and the ionic wind can only stretch the flame in this direction. In the case of nanosecond pulsed periodic discharge the efficiency of momentum transfer from electric field to the gas is very low and almost does not change the flow velocity.

On the other hand the efficiency of gas ionization and excitation by pulsed nanosecond discharge is very high. Numerical analysis proves that this mechanism controls the flame propagation under strong electric field conditions.