Processes controlling properties of high-voltage nanosecond discharge plasma in combustible mixtures

E M Anokhin¹, M A Popov¹, A Yu Starikovskiy² and N L Aleksandrov¹

¹Moscow Institute of Physics and Technology, Dolgoprudny, 141700, Russia
²Princeton University, Princeton, NJ08544, USA

E-mail: nick_aleksandrov@mail.ru

Abstract. We present the results of the experimental study of high-voltage nanosecond repetitively pulsed discharge and of its afterglow in ethane, dimethyl ether and their mixtures with oxygen. The measurements were made for room temperature and pressures from 2 to 6 Torr. The measured specific deposited energy and mean discharge current varied with the number of voltage pulses monotonously in ethane and dimethyl ether and nonmonotonously in the hydrocarbon:oxygen mixtures. A microwave interferometer was used for time-resolved electron density measurements in the discharge afterglow. The effective recombination coefficients were obtained from the analysis of the measured data. These coefficients varied with the number of voltage pulses monotonously in ethane and peaked in pure dimethyl ether and its mixture with oxygen. Possible mechanisms of the nonmonotonous behavior of the discharge characteristics were discussed.

1. Introduction

Repetitive, nanosecond-pulse discharges are widely used for plasma generation. In such discharges, ionization, dissociation and excitation of molecules efficiently occur because of high reduced electric fields created in the discharge plasmas. Therefore, nanosecond discharges are promising for many applications including aerospace applications. Over the last decades, considerable progress has been made in studies of ignition and combustion by nanosecond discharge plasmas [1-7]. It was shown that, using non-equilibrium nanosecond discharges, it is possible to reduce ignition delay time and ignition temperature, to stabilize flame and to increase flammability limits in various combustible mixtures.

The effect of non-equilibrium discharge plasmas on oxidation and ignition processes are hard to study at temperatures below the self-ignition threshold when fuel is not ignited without plasma. For low temperatures, oxidation processes have been studied in fuel-containing mixtures activated by nanosecond repetitively pulsed discharges [8-14]. Plasma-assisted oxidation was considered for H₂ [8], alkanes [9, 10, 13, 14] and ethylene [11, 12]. In these studies, emission and absorption spectroscopy and gas chromatography were used to measure species density and gas temperature.

Previous studies of fuel oxidation under the action of nanosecond discharge plasmas considered the effect of discharge on oxidation processes. There is also the influence of oxidation on the properties of discharge plasmas. It was shown in [15] that fuel oxidation influences discharge characteristics and the rate of plasma decay in discharge afterglow. The aim of this work was to further study the effect of
oxidation on discharge development and the decay of plasma generated by a nanosecond repetitively
pulsed discharge. Energy deposition, discharge current and electron density history in the discharge
afterglow were measured to obtain information about plasma properties and lifetime for various
numbers of discharge pulses leading to partial or complete fuel oxidation. The study was extended to
oxygenated hydrocarbons (dimethyl ether) to compare the effect of oxidation in these hydrocarbons
with that in saturated hydrocarbons considered in [15]. For the comparison purposes, measurements
were also made in pure hydrocarbons.

2. Experiment
The experimental setup and the methods used to measure the characteristics of a high-voltage
nanosecond repetitively pulsed discharge and electron density in its afterglow are the same as in our
previous work [9, 16]. The discharge developed in a quartz tube with an inner diameter of 47 mm. The
high-voltage electrode and the low-voltage electrode were a cone-shaped one and a grounded ring,
respectively. The distance between the electrodes was 20 cm. The plasmas were generated at gas room
temperature and pressures in the range 2 - 6 Torr. The amplitude of the pulses applied to the high-
voltage electrode was up to 24 kV. The pulse duration was 25 ns and the pulse rise time was 5 ns. The
pulse frequency was 10 or 20 Hz. A back-current shunt was used to measure the voltage amplitude,
the shape of the pulses, the mean discharge current, and the deposited energy.

We also measured the temporal evolution of electron density in the discharge afterglow by a
microwave interferometer with a reference wave frequency of 94 GHz. An incident microwave signal
crossed the plasma volume in the middle of the discharge gap perpendicularly, reflected from the
angle reflector, crossed the plasma volume again and returned to the waveguide. Electron density was
determined using the measured phase shift of the reflected wave. The uncertainty of the electron
density measurements was \( \approx 30\% \).

3. Measured results and discussion
The properties of discharge plasmas were studied in pure \( \text{C}_2\text{H}_6 \) (ethane), the stoichiometric \( \text{C}_2\text{H}_6: \text{O}_2 \)
mixture, \( \text{CH}_3\text{OCH}_3 \) (dimethyl ether) and the stoichiometric \( \text{CH}_3\text{OCH}_3: \text{O}_2 \) mixture. Figure 1 shows the
measured average discharge current, \( I \), in pure \( \text{C}_2\text{H}_6 \) and in the \( \text{C}_2\text{H}_6: \text{O}_2 \) mixture versus the number of
voltage pulses. Similar results were obtained in pure \( \text{CH}_3\text{OCH}_3 \) and in the \( \text{CH}_3\text{OCH}_3: \text{O}_2 \) mixture. In pure \( \text{C}_2\text{H}_6 \), the mean current increases monotonously with increasing number of pulses, \( N_p \), and \( I(2 \text{ Torr}) > I(4 \text{ Torr}) \). This behavior changes when \( \text{O}_2 \) is added to \( \text{C}_2\text{H}_6 \). In the \( \text{C}_2\text{H}_6: \text{O}_2 \) mixture, the mean
current varies nonmonotonously with \( N_p \) and shows minimum at \( N_p \approx 1100 \) for 2 Torr and at \( N_p \approx 2000 \)
for 4 Torr. The minimum is pronounced for 2 Torr and less marked for 4 Torr. As a result, we have \( I(2 \text{ Torr}) < I(4 \text{ Torr}) \) at \( N_p < 6000 \) and \( I(2 \text{ Torr}) > I(4 \text{ Torr}) \) for higher values of \( N_p \).

The specific deposited energy, \( W \), in pure \( \text{C}_2\text{H}_6 \) and in the \( \text{C}_2\text{H}_6: \text{O}_2 \) mixture versus the number of
voltage pulses is shown in figure 2. The specific energy input per single voltage pulse is between
0.002 and 0.009 eV per one neutral particle. This quantity, as well as \( I \), depend on gas pressure, gas
composition and the number of voltage pulses. In pure \( \text{C}_2\text{H}_6 \) and \( \text{CH}_3\text{OCH}_3 \), the specific deposited energy is inversely proportional to the gas pressure \( p (W \sim 1/p) \). This energy is independent of \( N_p \) in
pure \( \text{C}_2\text{H}_6 \) and decreases with increasing \( N_p \) in \( \text{CH}_3\text{OCH}_3 \). In the \( \text{O}_2 \)-containing mixtures, the value of \( W \)
varies nonmonotonously when \( N_p \) is increased. This energy shows profound minimum for 2 Torr
and less marked minimum for 4 Torr at the values of \( N_p \) at which the minimum is observed for \( I \) in
these mixtures.

According to our estimates, rapid gas heating during one voltage pulse and discharge afterglow and
gas heating due to energy release in the oxidation processes were less than 15K. Therefore, each new
discharge developed in a room temperature gas. The absence of gas heating was controlled by
measuring gas pressure in the discharge tube.
Using a microwave interferometer we studied how the plasma decay in hydrocarbons and combustible mixtures depends on gas mixture parameters. In our case, recombination with molecular ions is the dominant mechanism of electron loss. From the measurement of electron density history, we obtained the effective recombination coefficient defined as $\alpha_{eff} = (n_e(t_{1/2}))^{-1}$, where $t_{1/2}$ is the time required to halve the electron density, $n_e$. We took $n_{e0} = 2 \times 10^{11}$ cm$^{-3}$; this value is an order of magnitude lower than the value of $n_e$ in the beginning of the afterglow and corresponds to $t \sim 2$ µs.

**Figure 1.** Mean discharge current in C$_2$H$_6$ and stoichiometric C$_2$H$_6$:O$_2$ mixture for various pressures as a function of the number of voltage pulses.

**Figure 2.** Specific deposited energy in the nanosecond discharge in C$_2$H$_6$ and stoichiometric C$_2$H$_6$:O$_2$ mixture for various pressures as a function of the number of voltage pulses.
It is worth noting that the electron temperature $T_e$ in the discharge afterglow in hydrocarbons and hydrocarbon-containing mixtures is close to the gas temperature $T = 300$ K. The calculation showed that the electron temperature is thermalized for 100 ns during plasma decay in ethane and propane at 2 Torr [17]. According to our estimates, the same is also expected in CH$_3$OCH$_3$ and in all mixtures considered in this work.

The effective recombination coefficient in pure CH$_3$OCH$_3$ and in the stoichiometric CH$_3$OCH$_3$:O$_2$ mixture versus $N_p$ is shown in figure 3. In pure CH$_3$OCH$_3$ the recombination coefficient peaks at $N_p \approx 2300$ for 2 Torr and at $N_p \approx 4300$ for 4 Torr. The recombination coefficient in the CH$_3$OCH$_3$:O$_2$ mixture shows much more profound maximum with increasing number of pulses and this peak is observed at much lower number of pulses. Here, this coefficient peaks at $N_p \approx 400$ for 2 Torr and at $N_p \approx 600$ for 4 Torr. The dependence of $\alpha_{\text{eff}}$ on $N_p$ in the CH$_3$OCH$_3$:O$_2$ mixture is similar to that obtained in the mixtures of saturated hydrocarbons with O$_2$ [15]. However, a nonmonotonic dependence of $\alpha_{\text{eff}}$ on $N_p$ was not observed in pure saturated hydrocarbons, whereas this was obtained in pure CH$_3$OCH$_3$.

![Figure 3](image_url)

**Figure 3.** The effective recombination coefficient in CH$_3$OCH$_3$ and stoichiometric CH$_3$OCH$_3$:O$_2$ mixture afterglows as a function of the number of voltage pulses prior to these afterglows.

It was suggested in [15] that the nonmonotonic behaviors of discharge characteristics and $\alpha_{\text{eff}}$ with increasing $N_p$ in hydrocarbon:oxygen mixtures can be associated with the production of some neutral intermediates that favor plasma decay. A number of neutral hydrocarbon intermediate species have been detected during oxidation of C$_1$ – C$_5$ alkanes after a high-voltage nanosecond discharge. These intermediates include CH$_2$O, CH$_3$OH, CH$_3$CHO, and CH$_3$CH$_2$CHO (see, for instance [13, 14]). Some hydrocarbon intermediate species have high dipole moments. The production of such intermediates is followed by the formation of cluster ions for which the recombination coefficients with electrons are anomalously high [19]. The observed increase of the effective recombination coefficient with increasing gas pressure (see figure 3) can be associated with the production of more complicated cluster ions in three-body reactions and with the increased contribution of three-body electron-ion recombination to the total rate of plasma decay.

In [15], it was suggested that the intermediates favoring plasma decay are formed in saturated hydrocarbon:oxygen mixtures and are absent in pure saturated hydrocarbons. It was shown in this work that the nonmonotonic behavior of the effective recombination coefficient with increasing $N_p$ also can be observed in pure oxygenated hydrocarbons. We suggest that the intermediates leading to
the increase in the recombination rate can be also produced in these hydrocarbons without the presence of oxygen in the initial gases.

4. Conclusions
The discharge characteristics of a high-voltage nanosecond repetitively pulsed discharge in ethane, dimethyl ether and their mixtures with oxygen were measured at room gas temperature and at pressures from 2 to 6 Torr. In addition, time-resolved electron density was measured in the afterglow of this discharge. Observations were made after various number of voltage pulses when the neutral composition of the gaseous mixtures was changed due to partial fuel oxidation. Observations showed that the mean discharge current and specific deposited energy varied with the number of voltage pulses monotonously in pure hydrocarbons and nonmonotonously in the hydrocarbon:oxygen mixtures.

The effective recombination coefficients were obtained from the analysis of the measured electron density histories. These coefficients peaked with the number of voltage pulses in the ethane:oxygen mixtures, in pure dimethyl ether and in its mixture with oxygen. In pure ethane, the recombination coefficient varied monotonously with the number of voltage pulses. We suggest that the nonmonotonous behaviors of the discharge characteristics and of the recombination coefficients are associated with the formation of dipole intermediate species in hydrocarbon:oxygen mixtures and in pure oxygenated hydrocarbons. As a result, electron-ion recombination is more efficient due to the formation of cluster ions and due to three-body electron-ion collisions.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research under the project No. 17-02-00481.

References
[1] Starikovskaia S M 2006 J. Phys.D: Appl. Phys. 39 R265
[2] Popov N A 2007 High Temp. 45 261
[3] Adamovich I V, Choi I, Jiang N, Kim J-H, Keshav S, Lempert W R, Mintusov E, Nishihara M, Samimy M and Uddi M 2009 Plasma Sources Sci. Technol. 18 034018
[4] Starikovskiy A and Aleksandrov N 2013 Progr. Energy Combust. Sci. 39 61
[5] Starikovskaia S M 2014 J. Phys. D: Appl. Phys. 47 353001
[6] Ju Y and Sun W 2015 Progr. Energy Combust. Sci. 48 21
[7] Adamovich I V and Lempert W R 2015 Plasma Phys. Control. Fusion 57 014001
[8] Zatsepin D V, Starikovskaia S M and Starikovskii A Yu 2001 Combust. Theory Modelling 5 97
[9] Anikin N B, Starikovskaia S M and Starikovskii A Yu 2004 Plasma Phys. Rep. 30 1028
[10] Anikin N B, Starikovskaia S M and Starikovskii A Yu 2006 J. Phys. D: Appl. Phys. 39 3244
[11] Mintusov E, Serdyuchenko A, Choi I, Lempert W R and Adamovich I V 2009 Proc. Combust. Inst. 32 3181
[12] Lefkowitz J K, Uddi M, Windom B C, Lou C and Ju Y 2015 Proc. Combust. Inst. 35 3505
[13] Lefkowitz J K, Guo P, Rousso A and Ju Y 2015 Phys. Trans. R. Soc. A 373 20140333
[14] Tsolas N, Lee J G and Yetter R A 2015 Phys. Trans. R. Soc. A 373 20140344
[15] Anokhin E M, Popov M A, Starikovskiy A Yu and Aleksandrov N L 2017 Combust. Flame 185 301
[16] Aleksandrov N L, Kindysheva S V, Kirpichnikov A A, Kosarev I N, Starikovskaia S M and Starikovskii A Yu 2007 J. Phys. D: Appl. Phys. 40 4493
[17] Anokhin E M, Popov M A, Kochetov I V, Starikovskiy A Yu and Aleksandrov N L 2016 Plasma Sources Sci. Technol. 25 044006
[18] Anokhin E M, Popov M A, Kochetov I V, Aleksandrov N L and Starikovskii A Yu 2016 Plasma Phys. Rep. 42 59
[19] Florescu-Mitchell A I and Mitchell J B A 2008 Phys. Rep. 430 277