Fast gas heating in N₂/O₂ mixtures under nanosecond surface dielectric barrier discharge: the effects of gas pressure and composition

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The fractional electron power quickly transferred to heat in non-equilibrium plasmas was studied experimentally and theoretically in N₂/O₂ mixtures subjected to high electric fields. Measurements were performed in and after a nanosecond surface dielectric barrier discharge at various (300–750 Torr) gas pressures and (50–100%) N₂ percentages. Observations showed that the efficiency of fast gas heating is almost independent of pressure and becomes more profound when the fraction of O₂ in N₂/O₂ mixtures increases. The processes that contribute towards the fast transfer of electron energy to thermal energy were numerically simulated under the conditions considered. Calculations were compared with measurements and the main channels of fast gas heating were analysed at the gas pressures, compositions and electric fields under study. It was shown that efficient fast gas heating in the mixtures with high fraction of O₂ is due to a notable contribution of heat release during quenching of electronically excited N₂ states in collisions with O₂ molecules and to ion–ion recombination. The effect of hydrocarbon addition to air on fast gas heating was numerically estimated. It was concluded that the fractional electron power transferred to heat in air, as a first approximation, could be used to estimate this effect in lean and stoichiometric hydrocarbon–air mixtures.
1. Introduction

The mechanisms of gas heating in molecular gas discharges have attracted considerable attention in the last decade due to their importance for different non-equilibrium plasma applications including plasma-assisted combustion, plasma aerodynamics and others. Fast (on a nanosecond scale) gas heating has been well studied in N₂, air and some other N₂/O₂ mixtures when the discharge energy is deposited at moderate (approx. 100 Td) reduced electric fields, \( E/N \) (\( N \) is the gas number density) (see, for instance, [1–4]). Here, the energy is quickly transferred to heat due to electron-impact dissociation of O₂, to quenching of electronically excited triplet N₂ states by O₂ molecules and to quenching of the O(1D) state [5].

The fractional electron power quickly transferred to heat in air plasma increases with the \( E/N \) at which the energy is deposited and can reach up to 40–50% at 10³ Td [6,7]. At such high values of \( E/N \), a high percentage of the discharge energy is spent on ionization and one of the main mechanisms of fast gas heating is associated with electron–ion and ion–ion recombination. These conditions are met in high-voltage nanosecond discharges that are being increasingly used for aerodynamic flow control [8,9], plasma-assisted combustion [10–12], material processing [13] and for some other applications. That is why much attention has been given to experimental [6,14–18] and computational [6,7,19–23] studies of fast gas heating in nanosecond discharges and in their afterglows. Available measurements are usually limited by not-too-high values of \( E/N \). Experimental studies of fast gas heating in the discharges developed at \( E/N \sim 10³ \) Td are difficult to perform and have been made only in air at 20 Torr (a pulse high-voltage nanosecond discharge) and 1 atm (a surface dielectric barrier discharge) [6]. Available kinetic models for fast energy transfer from electrons to gas translational degrees of freedom can lead to different conclusions. For instance, from [6], the effect of gas pressure on the fractional electron power rapidly transferred to heat in air plasma is notable when the discharge energy is deposited at high (approx. 10³ Td) reduced electric fields, whereas, according to Popov [7], this effect is expected to be small in this case. Additional studies are required to clarify the mechanisms and efficiency of fast energy release in nanosecond discharges developed in ultra-high electric fields under practically important cases.

The purpose of this work was to extend the measurements made in a nanosecond surface dielectric barrier discharge in atmospheric pressure air [6] to lower pressures and to other N₂/O₂ mixtures. At lower pressures, the plasma in a surface dielectric barrier discharge becomes more uniform and this could favour the analysis of observations and validation of available kinetic schemes for fast gas heating. We also carry out the simulation of fast energy release at high reduced electric fields in different gas mixtures to show how this phenomenon depends on the O₂ percentage and hydrocarbon addition.

2. Experiment

The installation used in this work is shown in figure 1 and is similar to that used in [6,8,9]. The main difference is that, in this work, the experiments were conducted in a vacuum cubic chamber of 220 mm side, whereas in [6,8,9] the experiments were performed in open air. The system was evacuated by a 2NVR-5DM for vacuum pump down to \( 10^{-1} \) Torr. The gas supply system allowed the chamber to be filled with different working mixtures up to a maximum pressure of 2 atm. We studied N₂/O₂ mixtures of spectral purity.

A surface dielectric barrier discharge was initiated using a magnetic compression generator with a pulse amplitude of 50 kV, a rise time of 7 ns and a pulse duration of 25 ns. A scheme of the discharge gap and dimensions of the high- and low-voltage electrodes are shown in figure 2. The discharge was ignited in a typical asymmetric plasma actuator geometry. The electrodes were separated by a 0.3 mm thick fluorocarbon film.

To determine the reduced electric field, \( E/N \), in the discharge gap, we measured the emission profiles of the first negative system (391.7 nm) of N₂⁺ ions and the second positive system (337.1 nm) of N₂ molecules. Typical oscillograms of the first negative and second positive systems...
Figure 1. Scheme of experimental set-up: (1) actuator in a chamber, (2) focus system, (3) monochromator (4) high-speed ICCD camera PicoStar HR12, (5) back-current shunt, (6) coaxial cable from the high-voltage generator, (7) back-current shunt, (8) coaxial cable and (9) oscilloscope Tektronix TDS 3054.

Figure 2. Scheme of the discharge gap: (1) low-voltage electrode, (2) dielectric layer, (3) high-voltage electrode, (4) zone of discharge propagation, and (5) insulating layer. (Online version in colour.)

are shown in figure 3 for the discharge in an N$_2$/O$_2$ = 1:1 mixture at 0.4 atm. The emission spectral range was selected using a monochromator (grating 3000 lines mm$^{-1}$, $f = 300$ mm and dispersion 0.95 nm mm$^{-1}$) that was placed in front of the plasma actuator. The widths of the front and back slits of the monochromator were 0.2 and 0.35 mm, respectively. The measurements were made with a nanosecond temporal resolution and with and without the aperture in order to remove the emission from some discharge regions. Observations showed that the peak value of $E/N$ is approximately uniform and is around $10^3$ Td over the streamer zone and is somewhat higher in the vicinity of the high-voltage electrode edge, in qualitative agreement with previous electric field measurements in surface dielectric barrier discharge plasmas [8,9,24,25].

The discharge development had been studied in detail with an intensified charge-coupled device (ICCD) camera [8,9]. According to the ICCD images presented in [8,9], the discharge developed in the following manner. Firstly, ‘streamers’ progressed along the dielectric surface from the upper high-voltage electrode with a velocity of approximately $10^8$ cm s$^{-1}$. In this phase, the streamer channels radiated emission and a charge was accumulated on the dielectric surface. The discharge progression slowed down when the streamer channels reached the opposite edge of the covered electrode. In this phase, no emission was observed in the discharge gap. Then, during the trailing edge of the high-voltage pulse, a second flash was initiated and the surface charge was removed from the dielectric surface. Typical integral images of the discharge are shown in figure 4 for gas pressures from 0.4 to 1 atm.

The plasma volume was determined using discharge images taken with nanosecond resolution by a PicoStar HR-12 ICCD camera from the side and top views. Discharge emission was non-uniform and decreased with distance from the dielectric surface and from the edge of the high-voltage electrode. From the images, we calculated the effective area of the surface covered with the plasma and the effective thickness of the plasma layer and estimated the volume
occupied by the plasma. The density of deposited energy was determined under the assumption that the energy input in a given point is proportional to the emission of the second positive system of N$_2$ molecules, the dominant radiation system in our case. It was assumed that 50% of the discharge energy was deposited in the part of the plasma volume that emitted 50% of the radiation. This assumption means that the discharge develops at sufficiently high $E/N$ when most of the deposited discharge energy is spent on the electron-impact excitation of electronic N$_2$ and O$_2$ levels and on ionization. Under the conditions studied, electron-impact excitation of the rotational and vibrational states of molecules was negligible and it was reasonable to assume that the discharge energy is distributed proportionally to the radiating electronic states of molecules and ions. The assumption used was validated by high (around 10$^3$ Td) measured reduced electric fields in the discharge plasma. The effective plasma volume was estimated as a product of the area of the effective surface covered with plasma and the effective thickness of the plasma layer (for more details, see [6]).

Figure 5 shows the measured volume occupied by the plasma in air at various applied voltages as a function of the gas pressure. This volume decreases with increasing gas pressure because, at high pressures, to maintain high values of $E/N$, the characteristic dimensions of the plasma layer should be decreased. The plasma is less uniform and the filamentary structure is more pronounced for higher gas pressures and fractions of O$_2$ in N$_2$/$O_2$ mixtures (see figure 4 and ICCD images of the discharge in air and pure N$_2$ [26]). An increase in the applied voltage leads to some increase of the plasma volume. This relation is explained in the following way. An increase
Figure 5. The effective plasma volume in air at various applied voltages as a function of the gas pressure.

Figure 6. The measured energy input in the discharge in air as a function of the gas pressure.

The energy deposited in the discharge was determined when subtracting the energy in the pulse after the actuator from the energy stored in the incident pulse. The pulse energy after the actuator and the energy in the incident pulse were measured by back-current shunts ((7) and (5) in figure 1, respectively). The accuracy of these measurements depends on the ratio of the discharge energy to the incident pulse energy. Under typical conditions of our experiments, this ratio was about 50% and the discharge energy was measured with an accuracy of about 20%. Figure 6 shows the energy input in the discharge in air as a function of the gas pressure. The deposited energy increases with the applied voltage and depends on the pressure only slightly. The typical specific energy input in the discharge is around $Q = 0.5 \text{ mJ mm}^{-3}$. 

in the pulse voltage results in an increase in the longitudinal and transverse components of the local electric fields in the gas. The increase of the transverse electric field causes an increase in the thickness of the plasma layer, whereas the increase of the longitudinal field leads to an increase in the ionization wave speed and hence to an increase in the plasma layer length. As a result, the plasma volume increases with the applied voltage.
Figure 7. Gas temperature in the air plasma layer as a function of the gas pressure. The measurements were made immediately after the discharge and 1 μs later.

Figure 8. Fractional electron power transferred to heat during the discharge phase and 1 μs after the discharge as a function of the gas pressure. The discharge is initiated in atmospheric pressure air by voltage pulses of 17.5 and 20.5 kV.

The evolution in time of the gas temperature was studied using emission spectra of the 0–0 transition of the second positive system of N₂ molecules. For this purpose, the emission of the discharge was focused onto the slit of the input monochromator. The optical plane of the output monochromator was adjusted to the photocathode of the high-speed camera, which was synchronized with the high-voltage pulses. The time gate was 100 ns. The full spectrum of the 0–0 transition of the second positive system of N₂ was obtained in each experiment. To increase the signal-to-noise ratio, 1000 spectra were collected in one regime. To study the temporal evolution of the gas temperature, a weak ‘diagnostic’ discharge was ignited with some delay after the main discharge. A delay line was developed using an additional long coaxial cable ((8) in figure 1). The length of this cable was varied from 0 to 100 m; this corresponded to a delay time between the main and secondary pulses of 0–1 μs. Propagation of the high-voltage pulse travelling through
the additional coaxial line led to ignition of an additional weak discharge. The deposited energy of this discharge was only about 10% of the main discharge.

Direct temperature measurements with nanosecond resolution were made to estimate the fraction of the discharge energy that is quickly transferred to heat (figure 7). According to our measurements, the gas temperature increase is small in the discharge phase. However, in the afterglow, the temperature increases for 1 μs up to 50–70 K at 300 Torr and up to 140–180 K at 1 atm.

For a short relaxation time, the gas was assumed to be motionless; that is, the gas was heated at constant volume. Under this assumption, we compared the specific discharge energy and the energy spent on the gas heating in the plasma layer for various delay times. Our observations showed that more than 50% of the discharge energy was transferred to heat for 1 μs (figure 8). The fraction of energy conversion during the discharge phase was several times lower.

Similar measurements were made in an N₂/O₂ = 1 : 1 mixture and in pure N₂. It may be concluded that the fractional electron power transferred to heat in N₂/O₂ mixtures increases with increasing O₂ fraction (figure 9). This conclusion agrees qualitatively with previous observations at lower (approx. 10² Td) electric fields [1,3,4].

3. Computational model

To show the mechanisms of fast gas heating under the conditions studied, we made a numerical simulation of heat release on nanosecond and microsecond scales. Fractional electron power transferred to heat in N₂/O₂ mixtures was calculated using the computational model developed in [6]. The kinetics of charged and excited particles in the discharge and in its afterglow was studied under the assumption that the value of E/N is constant during the discharge phase. In reality, the electric field varied with time in the discharge plasma. However, most of the discharge energy was deposited for the time interval when the electric field was close to its peak value because at lower E/N the discharge current decreased drastically due to a decrease in the electron density and electron drift velocity. Therefore, the assumption of constant electric field in the discharge phase is reasonable to estimate the deposited energy and fractional electron power transferred to heat in the surface dielectric barrier discharge developing in high reduced electric fields.
The initial electron density was assumed to be \( n_{e0} = 10^5 \text{ cm}^{-3} \). The time of the discharge, \( \tau_d \), was selected such that the electron density \( n_e \) at \( t = \tau_d \), \( n_{ef} \), was \( 10^{14} - 10^{15} \text{ cm}^{-3} \), values that are close to the typical values of \( n_e \) in a surface dielectric barrier discharge [27]. We calculated the temporal evolution of the densities of active species from a numerical simulation of the corresponding balance equations. In addition, we simultaneously solved the gas energy conservation equation to determine the evolution of gas temperature under the assumption of constant volume. To simulate plasma decay in the discharge afterglow, the evolution of the effective electron temperature, \( T_e \), was simulated based on a numerical solution of the electron energy conservation equation. All balance equations were solved on the zero-dimensional approximation. Active species considered in this work were N, O, H, OH, O(1D), O(1S), N(2D), N(2Σ+), N2(2B', 2B), N2(4σ+), N2(3Π), N2(ΔE = 13 eV) (singlet N2 states with a threshold of around 13 eV), electrons, O2+, O4+, N2+, N4+ and O22+.

The reactions considered in our kinetic model and their rate constants have been given elsewhere [6]. The only difference was that, in this work, we took into account the energy release in the reaction [1,3,28]

\[
N_2(A) + N_2(A) \rightarrow N_2 + N_2(B) + 4eV.
\]  

This effect is negligible in air plasma considered in [6] and can make a notable contribution to the fast gas heating in pure N2.

We considered electron-impact dissociation, excitation and ionization of neutral particles, quenching of electronically excited particles, charge exchange in collisions between ions and neutral particles, dissociative and three-body electron–ion recombination, and electron attachment and detachment from negative ions. The rate coefficients for electron processes were calculated from a numerical solution of the electron Boltzmann equation in the classical two-term approximation with the BOLSIG+ code [29]. This approximation is acceptable when plasma modelling requires a not-too-high accuracy for electron transport and rate coefficients [30,31]. For instance, calculations on the basis of a more accurate approach showed that the error introduced by the two-term theory into the rates of electron-impact excitation of the N2(A) state and electron-impact ionization in pure nitrogen does not exceed 15% at \( E/N < 1.5 \times 10^3 \text{ Td} \) [32]. A similar error is expected for other electron-impact processes in nitrogen, air and other N2/O2 mixtures. This accuracy was sufficient in our simulation. To calculate the rate coefficients for electron processes, we used self-consistent sets of electron collision cross-sections for O2 and N2 that allowed good agreement between measurements and calculations for electron transport and rate coefficients in pure gases.

4. Calculated results

The evolution in time of active species densities was numerically calculated during the discharge and its afterglow and the power transferred to heat via different collisional channels was determined. Figure 10 shows the temporal evolution of the total fractional electron power transferred to heat in air at \( E/N = 10^3 \text{ Td} \) and different pressures. The calculated results turned out to be almost independent of \( n_{ef} \) in the range \( 10^{14} - 10^{15} \text{ cm}^{-3} \), whereas the curves in figure 10 are similar for various pressures. The characteristic time of gas heating is in the nanosecond range and is approximately inversely proportional to pressure. The total fractional electron power transferred to heat by 1 μs increases only slightly when the gas pressure rises from 300 to 760 Torr, in agreement with our observations (figure 8).

An important channel of fast heating in air at \( E/N \sim 10^3 \text{ Td} \) is energy release in electron–ion recombination [6] with the rate that depends on the electron temperature \( T_e \) and ion composition. Under the conditions studied, the characteristic time of electron thermalization and plasma lifetime are of the same order of magnitude. Therefore, it is required to simulate simultaneously plasma decay and electron energy relaxation in the discharge afterglow. According to our calculations, the loss of electrons in the afterglow of the discharge initiated at \( E/N \sim 10^3 \text{ Td} \) is dominated by recombination with O2+ and O4+ ions and by three-body attachment to O2.
Figure 10. The evolution in time of the total fractional electron power transferred to heat in air at $E/N = 10^3$ Td and different pressures. The calculations were made for $n_e = 10^{14} \text{ cm}^{-3}$. Time is reckoned from the end of the discharge.

Figure 11. The calculated fractional electron power transferred to heat in $N_2/O_2$ mixtures at 300 Torr and 1 atm as a function of the $O_2$ mole fraction. The calculations were carried out for $n_e = 10^{14}$ and $10^{15} \text{ cm}^{-3}$ at $E/N = 10^3$ Td.

molecules to form $O_2^-$ ions. In nitrogen with a small (approx. 1%) addition of $O_2$, the electron recombination with $N_2^+$ ions is also important, whereas the role of negative ions is much smaller. This affected the dependence of the fractional electron power transferred to heat on the gas composition.

Figure 11 shows the calculated fractional electron power transferred to heat at various gas pressures as a function of the mole fraction of $O_2$ in $N_2/O_2$ mixtures. The effect of fast gas heating becomes somewhat smaller at lower pressures due to the lower contribution of three-body processes [6]. A notable decrease of the fractional electron power transferred to heat with a decreasing mole fraction of $O_2$ is associated with a decrease in gas heating via quenching of electronically excited $N_2$ states in collisions with $O_2$ molecules [7] and via ion–ion recombination. The rates of these processes increase with increasing fraction of $O_2$ in the mixtures. The calculated
effect of gas composition on the fractional electron power transferred to heat agrees qualitatively with our observations (figure 9).

Figure 12 shows the calculated fractional electron power transferred to heat for various \( \text{N}_2/\text{O}_2 \) mixtures and gas pressures as a function of the reduced electric field at which the energy was deposited in a high-voltage nanosecond discharge. The relative effects of gas pressure and composition depend on the values of \( E/N \) only slightly.

5. Fast gas heating in hydrocarbon–air mixtures

To numerically simulate plasma-assisted ignition and combustion, information about fast gas heating in combustible mixtures is required [11,12]. In particular, this effect can be important for ignition by high-voltage nanosecond discharges [19,31,33–35]. The efficiency of fast gas heating can increase with addition of hydrocarbons due to a high rate of vibrational–translational relaxation of hydrocarbon molecules [33]. In this work, to estimate the effect of hydrocarbon addition on fast gas heating in gas mixtures under the action of high-voltage nanosecond discharges, we calculated the fractional electron power spent on gas heating in a stoichiometric \( \text{C}_2\text{H}_2/\text{air} \) mixture at sufficiently high \( E/N \) when electron-impact vibrational excitation of molecules is small. For this purpose, the mechanism used in this work for heating in air was generalized to take into account reactions with \( \text{C}_2\text{H}_2 \) molecules. These reactions and their rates were taken from the kinetic scheme used to study fast gas heating in \( \text{C}_2\text{H}_2/\text{O}_2/\text{Ar} \) mixtures under shock-tube conditions [31]. In addition, we took into account the quenching collisions between excited \( \text{N}_2 \) molecules and \( \text{C}_2\text{H}_2 \),

\[
\text{N}_2(A) + \text{C}_2\text{H}_2 \rightarrow \text{N}_2 + \text{C}_2\text{H} + \text{H}
\]

and

\[
\text{N}_2(a') + \text{C}_2\text{H}_2 \rightarrow \text{N}_2 + \text{C}_2\text{H} + \text{H}.
\]

The rates for these reactions were taken from [36].

Figure 13 compares the fractional electron power transferred to heat by 1 μs in a stoichiometric \( \text{C}_2\text{H}_2/\text{air} \) mixture and in air at 300 K and 1 atm versus the reduced electric field, \( E/N \), at which the energy was deposited. Calculations were carried out by analogy with those described in §§3 and 4. The curves in figure 13 are very close to each other. The difference between the curves increases with \( E/N \) and reaches only 9% for \( E/N = 10^3 \) Td. This difference is due to a change in positive-ion composition that can affect the rates and products of electron–ion and ion–ion recombination. It is worth noting that the calculated results for high \( E/N \) are not reliable because little is known about ion–molecule reactions and their products in hydrocarbon-containing mixtures.

It may be concluded that the results obtained for the fractional electron power transferred to heat in air could be applied to estimate the same effect in lean and stoichiometric hydrocarbon/air mixtures. We have considered only the \( \text{C}_2\text{H}_2 \)-containing mixture. In stoichiometric and lean mixtures of air with heavy hydrocarbons, the hydrocarbon fraction is lower and in this case the efficiency of fast gas heating is expected to be close to that in air.

6. Conclusion

We measured the fractional electron power quickly transferred to heat in a nanosecond surface dielectric barrier discharge initiated in air and other \( \text{N}_2/\text{O}_2 \) mixtures at various gas pressures. It was experimentally shown that fast gas heating is almost independent of pressure in the range 450–760 Torr and becomes more efficient with increasing fraction of \( \text{O}_2 \) in the mixtures.

The fast heating of non-equilibrium plasma was numerically simulated under the conditions studied. The calculated fractional electron power transferred to heat agrees qualitatively with the observations. The analysis of the calculated results showed that, at high (approx. \( 10^3 \) Td) reduced electric fields, the main contributions to fast gas heating are associated with (i) electron-impact excitation of molecules followed by dissociation and quenching of the excited states and
(ii) electron-impact ionization followed by the recombination of charged particles and other ion–molecule reactions. The observed increase in the efficiency of fast gas heating with increasing O\textsubscript{2} percentage in N\textsubscript{2}/O\textsubscript{2} mixtures is associated with the mechanisms of gas heating via quenching of electronically excited N\textsubscript{2} states in collisions with O\textsubscript{2} molecules and via ion–ion recombination. The rates of these processes increase with the O\textsubscript{2} percentage in the mixtures. Calculations showed that the fractional electron power quickly transferred to heat in air is close to the same quantity in the stoichiometric C\textsubscript{2}H\textsubscript{2}/air mixture. This means that the results obtained for the fractional electron power transferred to heat in air, as a first approximation, could be applied to estimate this effect in lean and stoichiometric hydrocarbon–air mixtures.

Figure 12. The calculated fractional electron power transferred to heat for various N\textsubscript{2}/O\textsubscript{2} mixtures and gas pressures as a function of the reduced electric field at which the energy was deposited in a high-voltage nanosecond discharge. The calculations were carried out for \( n_{ef} = 10^{14} \text{ cm}^{-3} \).

Figure 13. The calculated fractional electron power transferred to heat in a C\textsubscript{2}H\textsubscript{2}/air mixture and in air at 300 K and 1 atm as a function of \( E/N \). The calculations were carried out for \( n_{ef} = 10^{14} \text{ cm}^{-3} \).
**Authors’ contributions.** M.M.N. carried out measurements and analysis of the obtained data; S.V.K. carried out numerical calculations and analysis of the calculated data; N.L.A. designed the numerical study, coordinated the study and drafted the manuscript; A.Yu.S. conceived of the study, designed the experimental part of the study and helped draft the manuscript. All authors gave final approval for publication.

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