NO_x formation in apokamp-type atmospheric pressure plasma jets in air initiated by a pulse-repetitive discharge

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ABSTRACT

The decomposition products of atmospheric pressure plasma of repetitive pulsed discharge in apokamp and corona modes were determined by optical and chemical methods. It is shown, that the decomposition products contain mainly nitrogen oxides NOx. A brief review of the plasma- and thermochemical reactions in the pulsed discharges was made. The review and experimental data allow us to explain the reactive oxygen species formation mechanisms in a potential discharge channel with apokamp. The possible applications of this plasma source for treatment of seeds of agricultural crops are discussed.

Keywords: apokampic discharge, atmospheric pressure, air, nitrogen oxides, ozone, plasma jet

1. INTRODUCTION

Relatively new research areas are pre-sowing seed treatment with the non-equilibrium atmospheric pressure plasma, plasma decomposition products and plasma-activated water[1-4]. Experiments revealed that seed treatment had positive effects on seed germination, seedling growth and productivity. It is shown that fungal and bacterial diseases resistance of agricultural crops is increased[4-8]. Recent research has reported that plasma-activated water (PAW) can also efficiently inactivate a wide variety of microorganisms[9]. This can be used in the food industry, biomedicine, and also for watering plants[10].

For the development of these directions, it is necessary to study the composition of the plasma produced by pulsed and continuous discharges, as well as the decomposition products. At present, it is known that pulsed discharges in atmospheric pressure air are sources of nitrogen oxides[4,11].

The aim of this work is to determine the composition of the decay products of atmospheric pressure plasma of repetitive pulsed discharge in apokamp mode (so-called apokampic discharge), which was described in[12,13]. This is a new plasma source differing from the other pulsed discharges by the formation of one or more plasma jets (apokamps, in Greek: από – from and καμπη – bend, turning) at the bend of the current channel, which propagate normal to the discharge channel without gas flushing and have a length of up to a few centimeters. A photo of this phenomenon is presented in Figure. 1.

2. EXPERIMENTAL EQUIPMENT AND RESEARCH TECHNIQUES

The setup for absorption UV spectroscopy is shown in Figure 2. High-voltage source *1* and step-up transformer *2* produced output voltage pulses of positive polarity with a frequency of f = 53 kHz, duration of τ = 1.5-2.5 μs and amplitude of up to 13 kV. The pulses were applied to a discharge gap of width d = 0.9 cm, formed by two sharp-ended stainless steel electrodes *3* and *4*, with a diameter of 3 mm. Electrode *3* was connected to the high-voltage output of the pulse transformer, and electrode *4* was capacitively decoupled with ground through a capacitor *C* (from 1 to 20 pF). After discharge ignition between electrodes *3* and *4*, the decomposition products of plasma were passed through glass funnel *6* and optical cell *7* (15 cm length and 10 mm diameter). The density of the mixture in the cuvette was regulated by changing the rate of pumping the gas through the pipe *8*, connected to a diaphragm pump, providing a pumping rate of 0.1 to 2 l/min (not shown in the figure). The reference signal from source *10* (SL5 UV-VIS based on deuterium and

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incandescent lamps, the range 200-850 nm) was fed to the input through the light guide 9 with the collimating lens of a cuvette. The absorption spectra were recorded on a StellarNet EPP2000-C25 spectrometer (StellarNet Inc.) based on a Sony ILX511 multichannel CCD-array (operating range 200-850 nm, the spectral half-width of the hardware function does not exceed 1.5 nm).

The Fourier-transform IR spectra of the resulting mixtures were recorded. For this purpose, the gas flow through funnel *6* (Figure 2) was sent to a cuvette with a volume of 125 cm^3 with an optical path length of 10 cm and KBr windows (35 mm in diameter) and further on an interference spectroscope (FT-801, wavelength range 2-18 μm).

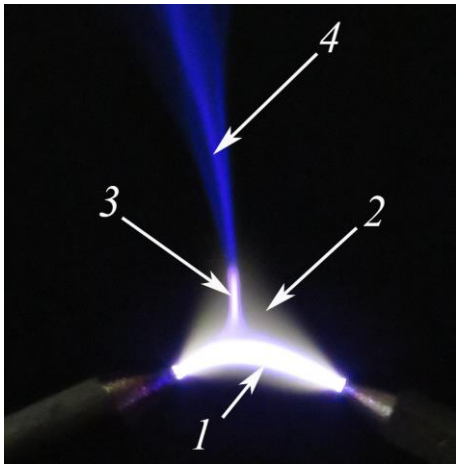

Figure 1. Image of apokampic discharge: 1 – current channel; 2 - halo; 3 - bright shoot; 4 – plasma jet

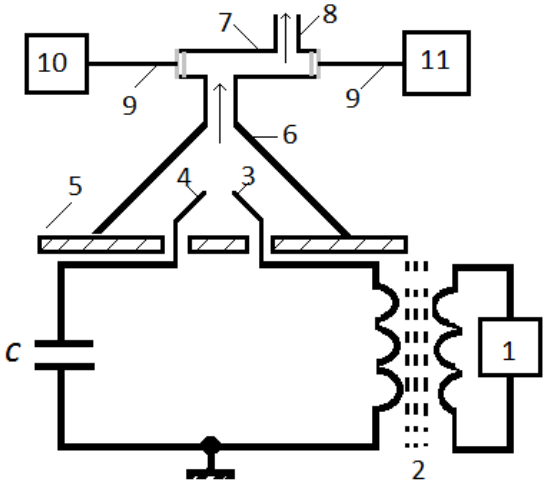

Figure 2. Experimental setup for absorption spectroscopy of the plasma decay products: 1 – high-voltage source; 2 – step-up transformer; 3 – high-voltage electrode: 4 – electrode with capacitively decoupled with ground: 5 – dielectric plate; 6 – funnel; 7 – optical cell; 8 – pipe for pumping out the gas mixture; 9 – optical fibers; 10 – reference light source; 11 – spectrophotometer. Arrows indicate the motion of air through the setup. Arrows show the direction of air movement through the installation

3. RESULTS AND DISCUSSION

The absorption spectra are shown in Figure 3. They correspond to the absorption spectra of gases NO_2 and N_2O_4 [15]. The intensity of formation of plasma products in the case of C = 20 pF (Figure 3 (2)) was several times higher than at C = 1.65 pF (Fig. 3 (1)). Accordingly, in the first case, the power dissipated about 7 W, and in the second case ~ 2.5 W. The output of nitrogen oxides in the plant can be regulated.

The spectrum in Fig. 3 (3) corresponds to the corona discharge mode, when high voltage pulses are applied to electrode 3 (Fig. 2), but the discharge gap is increased to d = 14 mm. As a result, a discharge channel not forms and electrode 3 produce a crown. This absorption spectrum corresponds to intensive generation of ozone under normal conditions in air (for example, [16]).

When in the apokampic discharge mode the forming gas collects in a 5 l glass flask, brown gas was accumulated in it within one minute of operation. According to [17], it is known, that NO_2 is a brown, poisonous and corrosive gas. At 100 °C and 760 Torr the NO_2 decomposes to NO_2 (90%) and N_2O_4 (10%) [17].

Further we performed a few experiments in which the plasma decay products from the apokampic and corona discharges were captured by distilled water poured into Petri dishes (5 ml per dish), which were placed under a 5-liter glass cap

covering the discharge gap, which was tightly pressed to the dielectric plate 5 (Figure 2). Water captured the decomposition products of plasma. As a result, water was subjected to the following changes:

- Water solution acidity had changed. A five-minute treatment of water resulted to decrease of pH from 6.8 to 2.1 (C = 1.65 pF) in apokamp mode and from 6 to 4.6 (C = 10 pF) in corona mode.

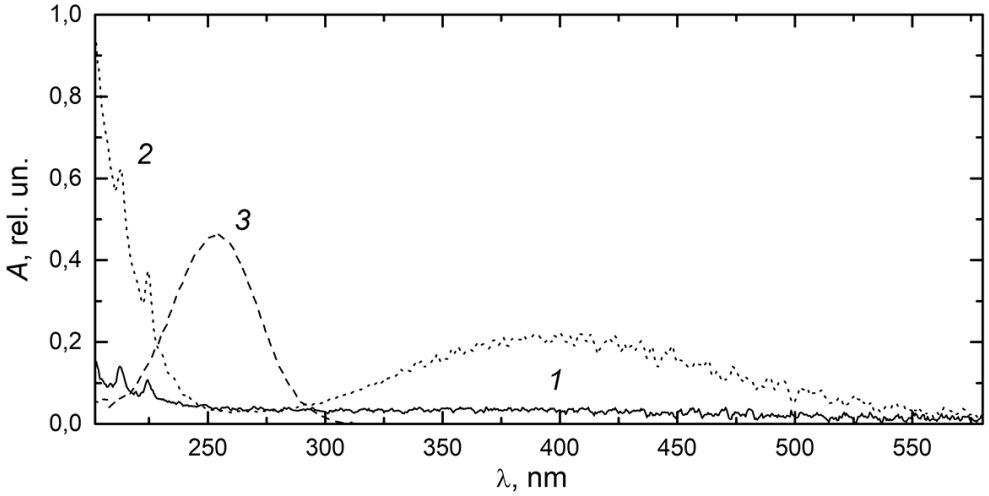

Figure 3. Absorption spectra of plasma products in the apokampic mode (1, 2) and in corona discharge mode (3)

As shown in Fig. 4 water solution absorption spectra changed. According to the reference data [18], the absorption spectrum of water exposed to the plasma decay products in the apokampic discharge (Fig. 4, curve 1), corresponds to a water solution of nitrous acid HONO. Under the action of the plasma decay products in the corona discharge, a water solution of hydrogen peroxide is formed H_2O_2 (Fig. 4, curve 2).

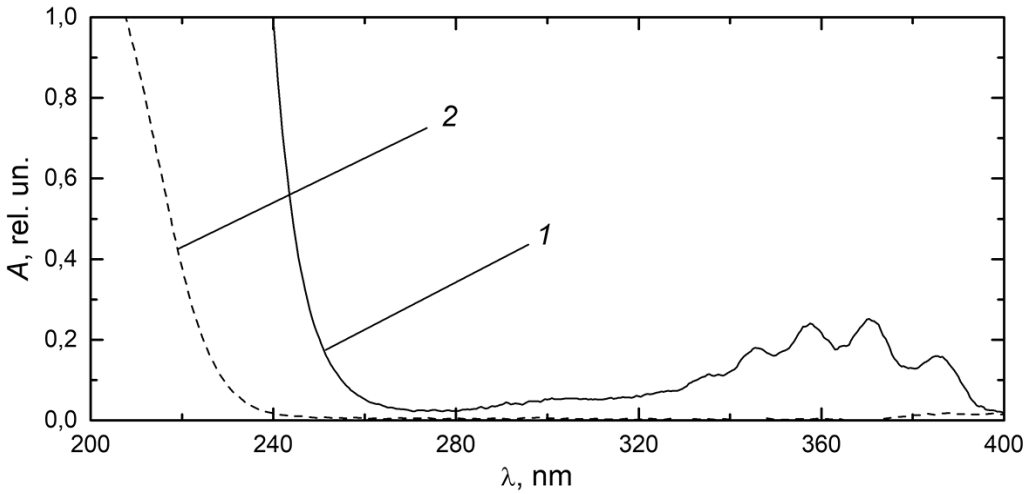

Figure 4. Absorption spectra of water solution absorbing the decay products in apokamp (1) and corona (2) modes

It is known that the bactericidal activity of plasma-activated water is due to the combined action of a high oxidation-reduction potential and a low level of pH acidity[10,19].

Moreover, we obtain Fourier spectra from apokamp and apokampless modes. They were recorded after 10 minutes of pumping gases through a cuvette with a gas flow rate of 0.15 l/min. As it can be seen from Figure 5 and Figure 6 the spectra differ in intensity in both cases. The peaks obtained correspond (as their concentration decreases) to the following oxides: NO_2, N_2O_4 and NO.

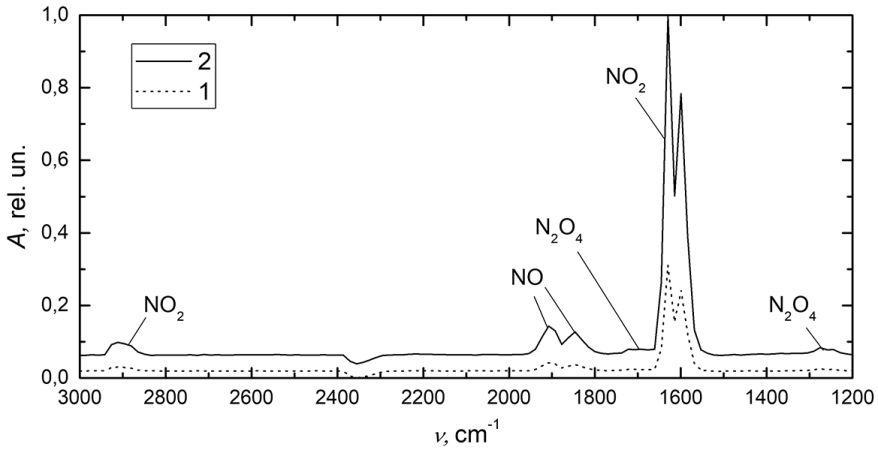

Figure 5. Fourier-transform IR spectra of discharge plasma products *(C* = 5 pF): 1) without apokamp (*U* = 8 kV); 2) with apokamp (*U* = 9.7 kV)

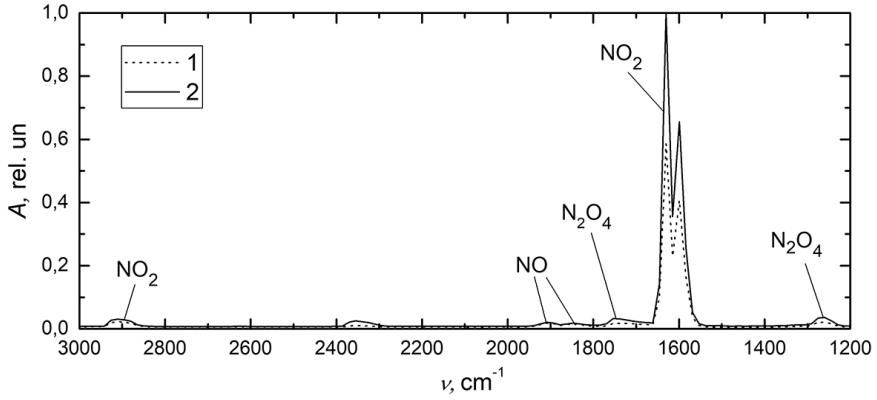

Figure 6. Fourier-transform IR spectra of discharge plasma products (*C* = 10 pF): 1) mode without apokamp (*U* = 8 kV); 2) the mode with apokamp (*U* = 9.7 kV)

What mechanisms lead to the formation of identified decay products of plasma? To understand the formation of reactive particles (ROS) in the plasma of atmospheric pressure discharges, it is necessary to take into account three factors: discharge channel temperature, processes initiated by electrons and photoprocesses. Each of them contributes to the kinetics of the formation of decomposition products of plasma.

To describe the kinetics of chemical reactions at temperatures of 2000 K and higher, the Zeldovich model and its modifications[21,22] are most often applied for description of thermal formation of NOx particles, in the reactions:

$$N_2 + O \rightarrow NO + N, \quad (1)$$

$$N + O_2 \rightarrow NO + O, \quad (2)$$

$$N_2 + OH \rightarrow NO + H. \quad (3)$$

In [23], the apokampic discharge parts temperatures were carrying out. It is shown that the gas temperature in current channel exceeds 1340±170 ºC) and 110±14 ºC at the end of plasma jet. According to the calculated data given in [22] for normal conditions in this temperature range, the volume content of NO obtained in the course of thermochemical conversions varies from ~ 10^{-5} to 10^{-3}.

The other way for the formation of nitrogen oxides is electrochemical processes. The type of discharge, or more precisely, the average energy values that electrons take in an accelerating field, critically affect to kinetics of air plasma products at atmospheric pressure. It is known that in a barrier discharge at an electron energy of 1 to 10 eV ozone O_3 is

mainly formed (which is used in industrial production of ozone[23,24]). At the same time, the concentrations of oxides N_2O and N_2O_5 are two orders of magnitude smaller than for ozone. On the other hand, as the electron energy increases, the production of ozone can completely stop and change to the predominant formation of nitrogen oxides (NO, NO_2 and N_2O), which is figuratively called «discharge poisoning». Numerical simulation has shown that the formation of ozone ceases at a critical concentration of NO_x oxides, in which oxygen atoms react with nitrogen oxides more rapidly than in reactions with O_2 and O_3. As a result, a «catalytic» recombination of oxygen atoms into nitrogen oxides occurs[24]:

$$O + NO + M \rightarrow NO_2 + M, \quad (4)$$

$$O + NO_2 \rightarrow NO + O_2, \quad (5)$$

$$NO + O_3 \rightarrow NO2 + O_2. \quad (6)$$

Also, we list the key reactions of the formation of nitrogen oxides, with the participation of electrons and excited particles, known from[26]:

$$O_2 + e \rightarrow O + O + e, \quad (7)$$

$$O_2 + e \rightarrow O + O^* + e, \quad (8)$$

$$N_2 + e \rightarrow N_2^* + e, \quad (9)$$

$$N_2^* + O_2 \rightarrow N_2 + O + O, \quad (10)$$

$$O_2 + O + M \rightarrow O_3 + M, \quad (11)$$

$$N_2^* + O \rightarrow NO + N^*, \quad (12)$$

$$N^* + O_2 \rightarrow NO + O, \quad (13)$$

$$N_2^* + NO \rightarrow N_2 + N + O, \quad (14)$$

$$N + NO \rightarrow N_2 + O, \quad (15)$$

$$O^* + NO \rightarrow N + O_2, \quad (16)$$

$$NO_2 + M \rightarrow N_2O_4 + M. \quad (17)$$

Due to electron impact, O_2 dissociates into atoms (reactions 7, 8) and, at the same time, excitation and ionization take place with the formation of excited N_2^* molecules (reaction 9) and N_2^+ ions, namely $N_2(A)$, $N_2(B)$, $N_2(C)$, $N_2(a)$, $N_2^+(B)$ [27]. The population of the $N_2(A)$ states is due to the relatively low excitation energy (6.17 eV) for the reaction $e + N_2(X^1\Sigma^+_g) \rightarrow N2(A^3\Sigma^+_u) + e'$ and due to collisions of vibrationally excited nitrogen molecules $N_2(v_1) + N_2(v_2) \rightarrow N_2(A^3\Sigma^+_u) + N_2(X^1\Sigma^+_g)$). In addition, a partial population of the metastable state $N_2(B)$ occurs. The spectra of plasma jet in apokampic discharge and the initiating discharge were obtained in[14]. The fact that the emission of the second positive nitrogen system $N_2(C^3\Pi_u - B^3\Pi_g)$ show that the most intense in the spectrum means that the electron temperature under these conditions is close to the optimum for the population of the $N_2(C)$ state. The emission of this band (giving a characteristic bluish glow in the visible part of the spectrum) and quenching (reaction 10) ensure the formation of atomic oxygen.

As a rule, the formation of ozone requires a three-particle reaction (11). NO are formed mainly during the reactions (12) and (13) and then enter the reactions (4)-(6), (14)-(17).

On the basis of the facts obtained in this paper, in[23], and in the above review of reaction kinetics, the following hypothesis for the formation of reactive active species (ROS) in apokampic discharge can be proposed:

Under our experimental conditions at $E/p < 2.6$ V/cm·Torr the average electron energy in the high-voltage discharge channel should not be large. Otherwise, there would be a predominant generation of ozone (which we observe when going to the corona or barrier discharge under normal conditions). In this case the formation of atomic oxygen (7, 8) and its association in O_3 (11) should trigger under the action of an electron impact. Emission spectra also confirm the intense formation of N_2^* molecules, which also contribute to atomic oxygen formation (reaction 10). However, in experiments, ozone is almost not formed. What is the reason for this? We believe that the thermochemical formation of NO (reactions 1, 2, 3) has a significant effect on this. And further, the NO produced becomes a source of « discharge poisoning» (reactions 4, 5, 6). Apparently, the nitrogen oxides formed in this way start the process of discharge poisoning in both in

shoot and in plasma jet. If it were not so, then plasma jet and shoot might be the ozone sources, supplying the atomic oxygen for reaction 11.

The proposed hypothesis agrees with the FT-IR spectra of plasma decay products in apokampic mode, although it does not take into account the contribution to the kinetics of their formation the reactions of dissociative attachment of electrons to oxygen, as well as photochemical reactions in which visible and ultraviolet radiation of discharge.

4. CONCLUSION

Thus, the experiments carried out in this work revealed the predominant decay products of plasma in two discharge regimes. These are nitrogen dioxide NO_2 in the apokampic mode and ozone O_3 under conditions of the corona discharge. Both gases keep well in glass flasks. In the water medium, they form dilute solutions of nitrous acid and hydrogen peroxide, respectively. All these reagents exhibit the etching property, which allows us to conclude that the plasma processing facility proposed in this study is useful for conducting experiments on antibacterial and fungicidal treatment of seeds and for increasing their germinating power. Plasma-activated water can be used to treat any surface on which bacteria, viruses or other microorganisms can be found, and it can be watered and processed with fresh products[20]. It is important that our plasma setup produce active chemicals directly from the air.

In treating the seeds, one has to take into account the fact that in addition to the plasma decay products, the source exerts its influence due to the UV and visible radiation at the nitrogen transitions and might be a source of mild X-rays, which has to be verified in the future studies.

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