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THE EFFECT OF WATER ON THE POSITIVE STREAMER CORONA DISCHARGE IN N_2-NO-CO_2 MIXTURES

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In the last two decades researchers have been trying to remove various types of pollutants using non-thermal plasma. This type of plasma may be generated by electron beam, or electrical discharges (e.g., corona discharge). Electrons in the non-thermal plasma are responsible for the generation of active species – radicals (e.g. N, O, OH, HO_2), which decompose pollutants to harmless compounds. The chemical reactions in a discharge are very complicated and, as well as by-products formation, can be effected by the change of various discharge parameters, e.g. type of HV signal waveform (its amplitude, shape, polarity), input power, initial concentration, residence time, gas flow rate, gas temperature, moisture, chemical additives and impurities [1-6].

The humidity is one of the impurities, which have an important influence of the main corona discharge phases and promotion of the discharge chemistry for gas treatment process. As for the general effect of the water on the discharge physics, it is difficult to derive the effective part belonging to the effect of humidity. The problem is that besides humidity itself, there are also other parameters e.g. the temperature of the mixture, the clustering process, and the gas flow and other parameters, which act simultaneously on the discharge. Numerous techniques have been used in order to single out the role of humidity for the discharge physics. The general assumption is that the onset field decreases and the onset voltage increases with the contents of the water in the system [7,8], while the humidity lead to decrease in the production of initial electrons required for corona discharge onset [9]. According to other sources [10], the effect of water depends on the surface conductivity, where the high field leads to great number of breakdown streamer by cluster disintegration and the pre-onset streamer absent in dry air appeared rapidly after humid air was supplied into a system [11].

For the discharge chemistry in the discharge applications used for gas treatment (e.g. deNO_x), the water vapor in discharge volume is important for promotion of the reactions for NO_x treatment process. The presence of water and also OH and HO_2 radicals, produced by dissociation of H_2O by high-energy electrons or generated by reactions of H_2O with O radicals, is believed to significantly intensify the chemical process. They play important role in the oxidation of NO_2 and formation of acids, thus enhancing the process of deNO_x [8,12,13]. The main products in the humid air are acids HNO_x, which in the presence of NH_3, can easily be converted to NH_4NO_3 [14]. The process of NO_x removal in the humid environment is preferable also because of energy consumption. According to [15], to achieve the same efficiency of the deNOx as in the dry air, much less power is needed and energy necessary for removal of one molecule of NO is smaller. The radicals of water (OH, HO_2) are more effective than e.g. oxygen, as their reactions with NO_x are much faster as those with N or O radicals [16,17]. OH radicals also work as a third body in the process of attachment and play important role in the deSO_2 process [13].

The objective of this paper is to describe the effects of the water on the discharge chemistry in N_2-NO-O_2-CO_2 mixtures, especially with the accent on the by-products formation and analysis. In our previous works [18,19,20] we have described the effect of CO_2 on the discharge character and the chemistry mainly in the dry mixtures, while now we rather give the explanation of the difference between processes in the dry and wet mixtures treated by positive DC streamer corona discharge. The infrared spectrometry is used as the method to analyze the by-products of the process in the gas phase and also for the analysis of solid by-products formed on the electrode surface.

EXPERIMENTAL SETUP

The experimental setup is presented in the Fig.1. A cylindrical type of corona discharge reactor with the total length of 28 cm was employed in the experiment. As the active electrode tungsten wire with the diameter of a 0.1 mm was used, while a brass cylindrical electrode with 21 mm in diameter served as a passive (grounded) electrode. Conventional HV power supply was used together with a rectifying circuit and a RC integrator to produce DC output signal, while streamer mode of corona discharge of positive polarity was used. The discharge voltage was monitored by a high voltage passive probe (Tektronix P6015A) connected to an oscilloscope, while the discharge current (both DC current and pulse waveform) was recorded by an analog microampermeter and oscilloscope (Tektronix TDS380) respectively.

The composition of simulated gas was controlled by flow regulators on each of the high-pressure cylinders containing N_2, NO (1000 ppm admixture in N_2 gas), CO_2 and O_2. The mixtures under investigation were N_2-NO(500ppm)-O_2(0,10,20%)-CO_2(0,3,10,30%) with and without the presence of the water. For the

measurements with H_2O, a simple water bubbling system at the room temperature was used, so the maximum concentration of the water vapor in the mixture was limited to about 3%. All measurements were performed in a flow regime with the total gas flow set to 1 l/min respectively. The concentrations of the gas components and the overall analysis of the products with regards to discharge power were performed using a FT/IR spectrometer (Herschel/Jasco FT/IR-430) and the 2.4 m long gas cell (Gemini Mercury Cell #0.1L/2.4M). Besides the analysis of the gas mixture changes also analysis of the solid products formed on the surface of the passive electrode was performed using KBr tabletting technique.

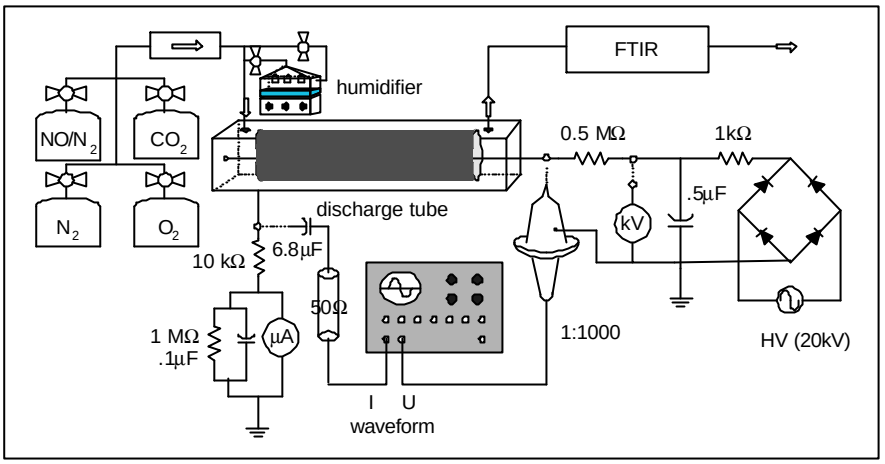

Fig.1: Experimental setup

EXPERIMENTAL RESULTS

The presence of the water in the system caused small decrease of the onset voltage as well as the operation voltage (Fig.2). Also breakdown voltage slightly decreased in the presence of water (caused by its condensation on the surface of electrodes and its high ε_r). As for the discharge character, the discharge became more homogenized (distribution of discharge in the gap) in the presence of water, although the probability of discharge instability (spark breakdown) increased at the same time. The water influenced the discharge current waveform. The amplitude of the pulses increased in the presence of water, as well as the rise time of the pulse, while the duration of a single pulse decreases (Fig.3, Fig.4).

The addition of other components into the gas mixture also led to certain changes in the character of the discharge, which influenced the discharge chemistry and by-products formation. The oxygen stabilized the discharge, transferring it from a streamer mode to a glow mode and delaying the breakdown. On the other hand carbon dioxide caused the streamer and the pulse behavior of the discharge was recovered, while emission spots and discharge channels in the discharge gap, their number, amplitude and repetition rate progressively grew and discharge spatial distribution improved filling up the whole discharge gap. The increase of CO_2 concentration, the amplitude of the streamer pulse characteristic increase further also the pulse duration decreases. Very large amount of CO_2, however, the onset voltage could be significantly increased and streamer corona may terminate.

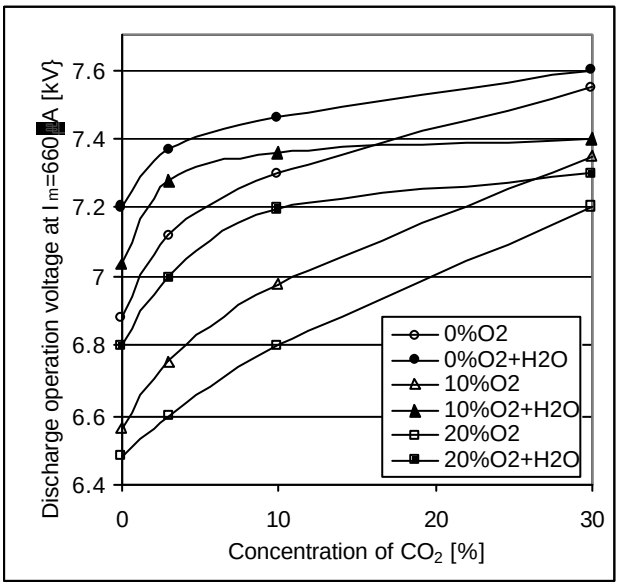

Fig.2: Effect of H_2O and other gas components of the N_2-NO-O_2-CO_2-H_2O mixtures on the operating voltage of the discharge at I_m=660μA

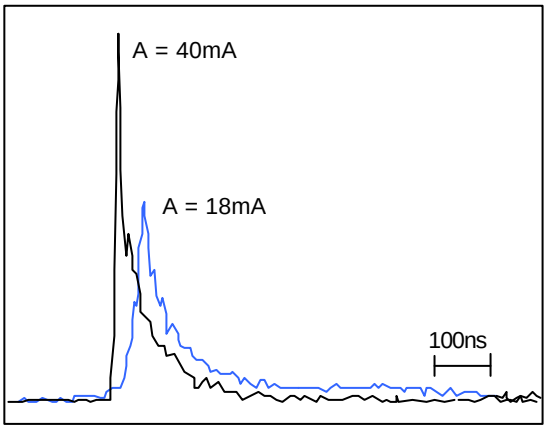

Fig.3: Effect of H_2O on the discharge current waveform characteristic in the mixture of N_2-NO-20%O_2-10%CO_2 at I_m=660μA

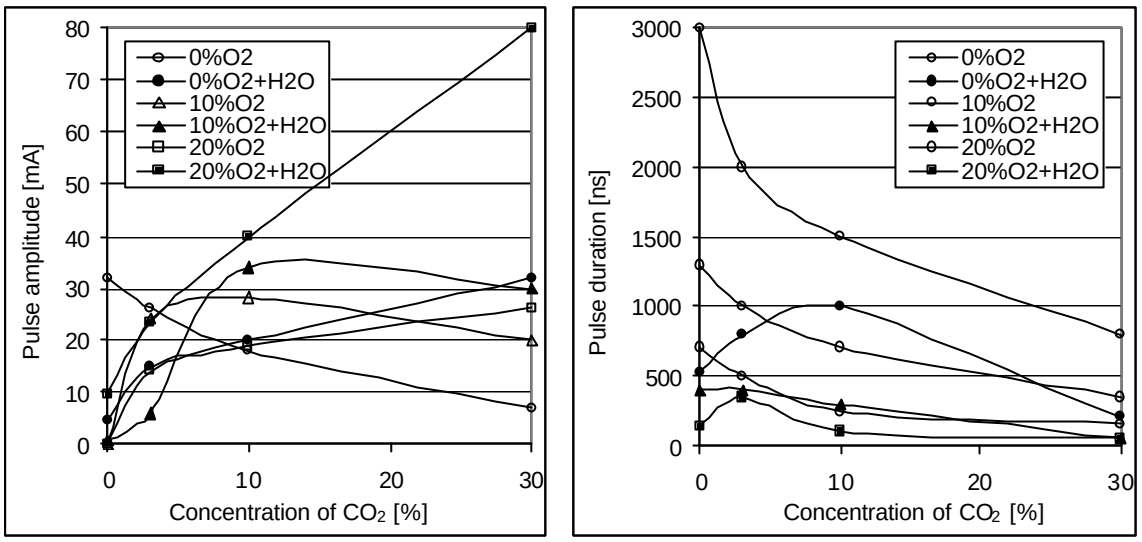

Fig.4: Effect of H_2O and other gas components on the discharge current pulse waveform characteristic, its amplitude (left) and duration (right) at I_m=660μA

The analysis of the gas mixture was done by means of infrared spectrometry, which is very effective method for monitoring the changes of the gas mixture composition caused by electric discharge and by-products identification. The spectra of different kinds of initial gas mixtures treated by corona discharge were recorded continuously with an increasing discharge power. Although the molecules of O_2 and N_2 are infrared inactive, the absorption bands of NO, NO_2, CO, CO_2 and other chemical compounds and functional groups were detectable and relatively well visible in the spectra (Fig.5).

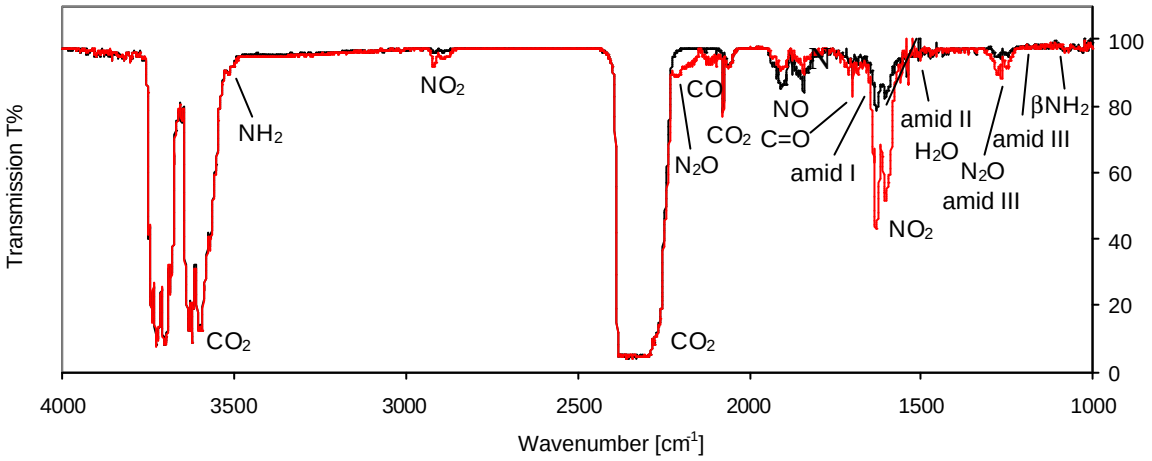

Fig. 5: Typical IR absorption spectra of gas mixture treated by positive corona discharge at I_m=1000μA (N_2 + 500 ppm NO + 10% O_2 + 10% CO_2)

As for the discharge chemistry in the N_2-NO-O_2-CO_2 mixtures and the character of the chemical process, the presence of water vapor in the mixture, as well as OH and HO_2 radicals, is believed to significantly intensify the chemical process and lead to the improved decomposition of NO_x. In the process without initial CO_2 presence (mixture of N_2-NO-O_2), when the process in the mixture has an oxidative character and lead to formation of acids at last, the water is important for the step of N_2O_5 (NO_2•NO_3) oxidation and formation of $2HNO_3$. The OH radicals can also play important role in the oxidation process if they supplement the role of $O(^1D)$ radicals. In such case HNO_3 is formed directly from NO_2 without NO_3 formation step. Generally, the more HNO_3 is formed in the liquid phase, the more NO_2 and NO_3 can be formed in the gas phase and so the efficiency growths. The energy consumption of such process increases more or less linearly with the number of oxidized molecules. In the mixtures with CO_2, the discharge chemistry is the gas phase is a little different and in the presence of the water lead to the formation of H_2CO_3 [21]. If the water and the oxygen are present in the mixture, H_2O_2 is produced and its reaction with CO_2 leads to formation of $(HCO)_4$ acid. This process also lead to decrease of the ozone production, as oxygen in $O(^3P)$ state is necessary for H_2O_2 formation. As for the OH radicals, although for their production only one oxygen atom is needed, the oxygen must be in the $O(^1D)$ state, which unfortunately requires more energy.

However generally to compare the two processes with and without water and evaluate the influence of the water on the removal process of NO_x in the mixtures N_2-NO-O_2-CO_2, is far more complicated than that. The reasons are different mechanisms, time developments and by-products of the processes in different gas mixtures, where besides processes in the gas phase, also surface and heterogeneous reactions take a place and where addition of a single component into a gas mixture may change the whole discharge chemistry. For example, while in the case without CO_2, the process goes through the production of N_2O_5 to formation of acids in the reaction with water, on the contrary the presence of initial CO_2 and water, lead to the NCO radical, respectively ON-NCO intermediate followed by the formation of amino acids and later the formation of polymers. In the discharge system of mixtures containing N_2, NO, CO_2, O_2 and H_2O, the reactions responsible for the removal of NO can also lead to formation of amino acids [22,20].

This process starts with the formation of electronically excited metastable state of molecular nitrogen $A^3\Sigma_u^?$ with energy 6.85 eV and a relatively long lifetime between 1.3-1.9 s [22,23,24]. Likely NO can also form metastable with the energy of 5.1 eV, simply by energy transfer with the metastable N_2 ($A^3\Sigma_u^?$). In the discharge with the high frequency of pulses, these metastable states are accumulated and serve as an energy reservoir for the subsequent chemical process. The activated N_2* and NO* are in the next step incorporated into the CO_2. For this process the accumulated energy is necessary, however it is released after the stable molecule is formed (the process of recuperation of the energy). The reaction of N_2* respectively NO* with CO_2 leads to formation of long-living NCO, ON-NCO or similar intermediates. If the water is present in the system, the NCO reacts with it and trivial amino acids may be formed. In the case the amino acid is formed the energy is released and can be used again, however only if the residence time of the gas mixture in the discharge system is long enough. In the longer discharge reactors, the energy is recuperated and the total energy consumption does not increase anymore, yet it may decrease [22]. Because of relatively short residence time, as it is unfortunately also in the presented system, some reactions remain unaccomplished. Therefore to evaluate the energy consumptions and to describe the influence of the water in such complex process and compare it with the simple one, as the formation of acid in the system without CO_2, is not appropriate. Moreover, as the process consists of many chain reactions in the non-equilibrium conditions (as plasmochemical reactions are usually non-equilibrium reactions) to determine the reaction rate coefficient is principally impossible and also for such process rate coefficients cannot be used.

For the possible formation of trivial amino acids in the discharge the presence of water is necessary, as the reaction of NCO radical with the water leads to the formation of an amide group, the essential part of amino acids. The identification of amino acids or their traces in the discharge volume is complicated due to their possible polarization and formation of zwitter ions in the presence of the electric field. This phenomenon results in the shifts of bands in the infrared spectra making possible analysis more difficult. Furthermore amino acids can be neutral, acidic or basic, depending on the number of NH_2^+ respectively COO^- groups in the structure of the molecule, which can also cause different effects in the infrared spectra. Although the presence of amino acids may be expected especially in the liquid phase, the analysis of the gas mixtures (Fig.5) and solid products formed on the passive electrode during the discharge measurements in the mixtures N_2-NO-O_2-CO_2 with water (Fig.6) gave some interesting results and findings as many of identified functional groups were evidently connected with the process and so confirmed the assumption of the possible formation of the amino acids or their fractions in the discharge process.

In the spectra of the gas product, except the absorption band of the main gas components, also the following bands were detected - amine NH_2 (3490, 3467 cm^{-1}), NH_3^+ (2580, 2550 cm^{-1}), C=O of carboxylic acid (1720 cm^{-1}), C=O of imide (1700 cm^{-1}), C=O of non-specified neutral amino acids (1680 cm^{-1}), C=C, C=N and

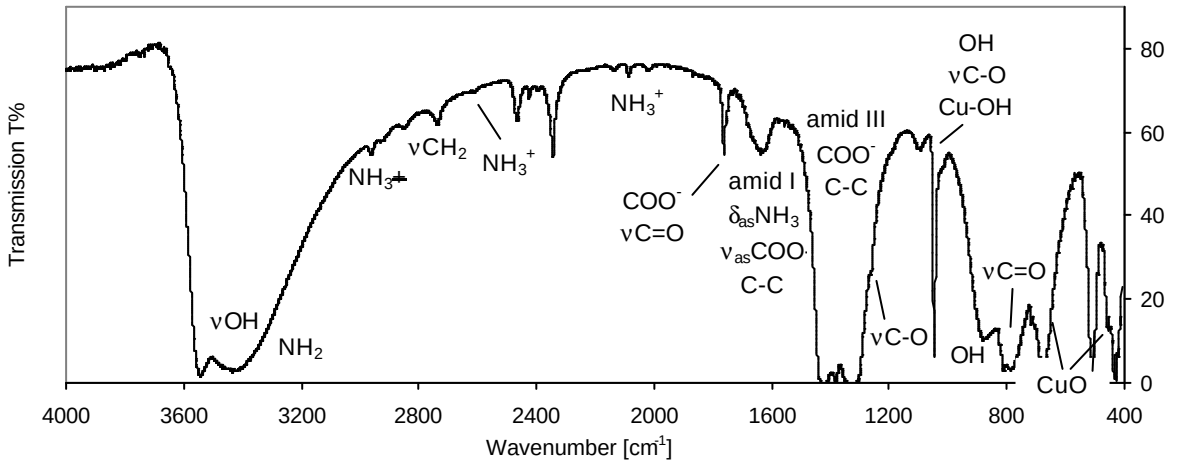

Fig. 6 IR absorption spectra of solid product formed on the electrode during the measurements in N_2-NO-O_2-CO_2 system treated by positive corona discharge

carboxylate ion COO^- (ν_{as}) along with the NO_2 (1630-1620 cm^{-1}), amide I (1640 cm^{-1}), amide II (1600-1500 cm^{-1}), amide III and NCO (1460 cm^{-1}), imide (1490 cm^{-1}) carboxylate ion COO^- (ν_s) (1465 cm^{-1}), amide III with C-N and C-O (1300-1250 cm^{-1}). Unfortunately, it is not possible to describe the relationship between the gas composition and products like amides (monomers), imides (dimmers), NCO, amino acids appearance directly. As already mentioned, the problem is very complicated for several reasons. The analysis would be possible for the chemical reactions of the first order (i.e. those dependent on the initial concentrations) in the equilibrium conditions, however the plasmochemistry in the discharge is much more complicated. The conditions of equilibrium in the discharge are barely fulfilled, many chain reactions take place and many of reactions sequences remain unfinished for limited residence time of the mixture in the discharge reactor. The oxidation reactions in the initial phase of the process have a low activation energy and in such case the impact of a single electron is usually enough for the reaction to proceed. For such processes it is easy to evaluate the energy consumption and dependence on the initial concentration. However, the process in the N_2-NO-CO_2-O_2-(H_2O) system consists mainly of chain reactions. The activation energy for molecular nitrogen is relatively high and several electrons are needed for its formation. The metastables are accumulating in the discharge (energy reservoir). It causes the time shift of the chemistry concerning electric parameters, what makes the evaluation based on the electrical parameters impracticable. The realization of chemical process is postponed and causes the deformation of dependence on energy delivery. As for the reaction kinetics, we suppose that for the formation of amino acids about 10-15 reaction steps are needed, depending on the type of the amino acid. For the formation of the solid products even more reactions. This is also very strong argument against any possible determination of the reaction constant.

CONCLUSIONS

The positive DC corona discharge in the cylindrical type reactor geometry was used. The experimental results and performed analysis demonstrated the influence of the water on the discharge character and the chemical processes inside the reactor and so the final products. Among the products of the process the amides I-III, amines, imide, NCO and were found, which confirmed the assumption of the possible formation of the amino acids or their fractions in the discharge process.

The paper has explained that the measurements in the simple N_2-NO system are not relevant enough to evaluate deNO_x process for the practical use as the addition of a particular component into the gas mixture can change the mechanism of the discharge and its influence on the gas mixture completely. This fact is very important, as in the combustion process, along with the forming nitrogen oxides, the water and CO_2 are present too. The water stabilizes the formation of the amino acids and it also supports the formation of the solid product insoluble in the water.

The process described in the paper and leading to formation of amino acids is possible and is closely connected with the process in the primary atmosphere, very similar to flue gases, which lead to the origin of life on the Earth [25].

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