

# APPLIED ELECTROSTATICS

PROCEEDINGS OF THE FOURTH INTERNATIONAL  
CONFERENCE ON APPLIED ELECTROSTATICS

2001 DALIAN, CHINA

WU YAN, LI JIE

DALIAN UNIVERSITY OF TECHNOLOGY PRESS

# The Analysis of Dry and Wet Gas Mixtures Containing NO<sub>x</sub>-CO<sub>2</sub> Treated by Positive DC Streamer Corona Discharge

Hensel K, Yamabe C, Morvová M

Faculty of Electrical Engineering, Saga University, Saga, 840 Japan

\* Faculty of Mathematics, Physics & Informatics, Comenius University, Bratislava, 84215 Slovakia

**Abstract:** The corona discharge is widely used to promote chemical reactions leading to reduction of NO<sub>x</sub> and production of different products depending on various parameters of the discharge and composition of the initial gas mixture. Among various chemical additives the influence of CO<sub>2</sub> has been studied only partially. Therefore, laboratory experiments were carried out to investigate and describe the changes in mixtures containing NO<sub>x</sub>, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> in the presence of H<sub>2</sub>O (ultrasonic humidifier was used for this purpose) or without while using positive DC corona discharge. The products of the process were analyzed by infrared spectrometry. Besides the concentration changes of the main gas components of the gas mixture, the products as ozone, amides, amines, imides and other compounds or functional group were detected in the spectra.

**Key words:** corona discharge, nitrogen oxides, carbon dioxide, water, IR spectrometry

## 0. Introduction

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<sub>2</sub>), which decompose pollutants to harmless compounds. The chemical reactions in the 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 influence the corona discharge mode 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 source [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<sub>x</sub>), the water vapor in discharge volume is important for promotion of the reactions for NO<sub>x</sub> treatment process. The presence of water and also OH and HO<sub>2</sub> radicals, produced by dissociation of H<sub>2</sub>O by high-energy electrons or generated by reactions of H<sub>2</sub>O with O radicals, is believed to significantly intensify the chemical process. They play important role in the oxidation of NO<sub>2</sub> and formation of acids, thus enhancing the process of deNO<sub>x</sub> [8,12]. The main products in the humid air are acids HNO<sub>x</sub> which in the presence of NH<sub>3</sub>, can easily be converted to NH<sub>4</sub>NO<sub>3</sub> [14]. The process of NO<sub>x</sub> removal in the humid

environment is preferable also because of energy consumption. According to [15], to achieve the same efficiency of the deNO<sub>x</sub> 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<sub>2</sub>) are more effective than e.g. oxygen, as their reactions with NO<sub>x</sub> 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<sub>2</sub> process [13].

The objective of this paper is to describe the effects of the water on the discharge chemistry in N<sub>2</sub>-NO-O<sub>2</sub>-CO<sub>2</sub> 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<sub>2</sub> 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.

## 1. Experimental setup

The experimental setup is presented in the Fig.1. A cylindrical respectively hemi-cylindrical type of corona discharge reactor were 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 (21 mm in diameter) respectively copper hemi-cylindrical electrode (36 mm) served as a passive (grounded) electrode. Conventional HV power supply was used for the positive streamer mode of corona discharge of positive generation. 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 microammeter and oscilloscope (Tektronix TDS380) respectively.

The composition of simulated gas was controlled by flow regulators on each of the high-pressure cylinders containing N<sub>2</sub>, NO (500/1000 ppm

admixture in N<sub>2</sub> gas), CO<sub>2</sub> and O<sub>2</sub>. The mixtures under investigation were N<sub>2</sub>-NO(250/500ppm)-O<sub>2</sub>(0,10,20%)-CO<sub>2</sub>(0,1,3,5,10,20,30,50%) with and without the presence of the water. For the measurements with H<sub>2</sub>O, either a simple water bubbling system or ultrasonic humidifier were used at the room temperature, 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. 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 tableting technique.

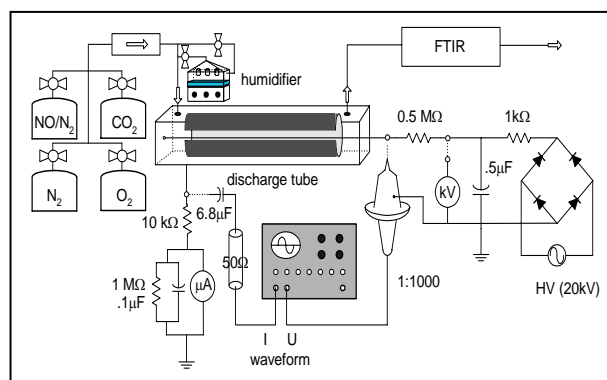


Fig.1: Experimental setup

## 2. Experimental results

The presence of the water in the system caused small decrease of the onset voltage as well as the operation voltage. Also breakdown voltage slightly decreased in the presence of water (caused by its condensation on the surface of electrodes and its high  $\epsilon_r$ ). 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

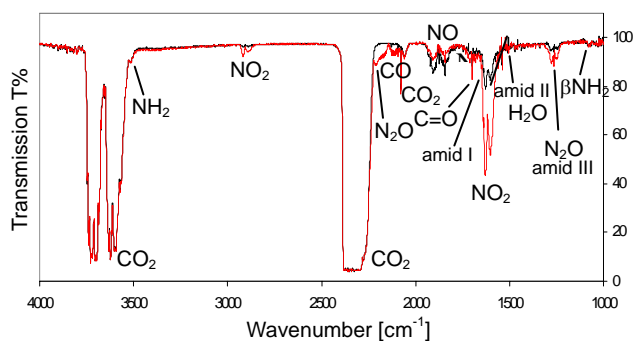
pulse decreases.

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 significantly intensified the chemical process and lead to the improved decomposition of  $NO_x$ . In the process without initial  $CO_2$  presence, 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. 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 grows. 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 in 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.

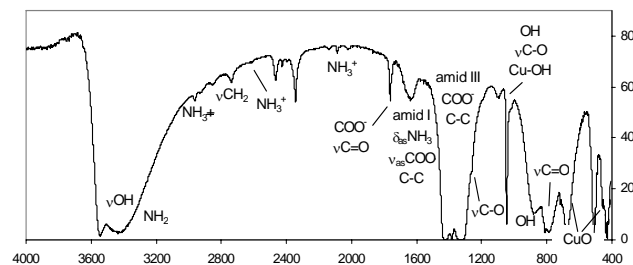
However generally to compare the two processes with and without water and evaluate the influence of the water on the removal process of  $NO_x$  in the mixtures  $N_2$ -NO- $O_2$ - $CO_2$ , is far more complicated than that. The reasons are different mechanisms, time developments and by-products of the 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 [22,20].

The process of amino acid formation in the

mixtures containing  $N_2$ , NO,  $CO_2$ ,  $O_2$  and  $H_2O$  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. 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 accumulated in by metastable states is released and can be used again, if the residence time of the gas mixture in the discharge system is long enough. In the longer discharge reactors, the energy is recuperated [22]. Because of relatively short residence time, as it is unfortunately also in the presented system, some reactions may remain unaccomplished. Therefore to evaluate the energy consumptions and 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, the process consists of many chain reactions in the non-equilibrium conditions.



**Fig. 3:** IR absorption spectra of gas mixture at  $I_m=1000\mu A$  ( $N_2 + 500 \text{ ppm NO} + 10\% O_2 + 10\% CO_2$ )



**Fig. 4:** IR absorption spectra of solid product formed on the electrode in  $N_2$ -NO- $O_2$ - $CO_2$ - $H_2O$  system

Although the presence of amino acids may be expected especially in the liquid phase, the analysis of

the gas mixtures (Fig.3) and solid products formed on the passive electrode during the discharge measurements in the wet mixtures  $N_2$ -NO- $O_2$ - $CO_2$  (Fig.4) had interesting results 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  $NH_2$  ( $3490, 3467\text{ cm}^{-1}$ ),  $NH_3^+$  ( $2580, 2550\text{ cm}^{-1}$ ), C=O of carboxylic acid ( $1720\text{ cm}^{-1}$ ), C=O of imide ( $1700\text{ cm}^{-1}$ ), C=O of non-specified neutral amino acids ( $1680\text{ cm}^{-1}$ ), C=C, C=N and carboxylate ion  $COO^-$  ( $\nu_{as}$ ) along with the  $NO_2$  ( $1630\text{-}1620\text{ cm}^{-1}$ ), amide I ( $1640\text{ cm}^{-1}$ ), amide II ( $1600\text{-}1500\text{ cm}^{-1}$ ), amide III and NCO ( $1460\text{ cm}^{-1}$ ), imide ( $1490\text{ cm}^{-1}$ ) carboxylate ion  $COO^-$  ( $\nu_s$ ) ( $1465\text{ cm}^{-1}$ ), amide III with C-N and C-O ( $1300\text{-}1250\text{ cm}^{-1}$ ).

### 3. 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 deNOx 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 <sup>[25]</sup>.

### References

- [1] J.S. Chang: IEEE Trans. Plasma Sci. 19 (1991) p.1152
- [2] S. Masuda, H. Nakao: IEEE Trans. Indust. Appl. 26 (1990) 2, p.374
- [3] R.H. Amirov : Proc. 21st ICPIG vol.2 (Bochum, 1993), pp.114
- [4] B.M. Penetrante, M.C. Hsiao, B.T. Merritt: IEEE Trans. Plasma Sc. 23 (1995), p.679
- [5] M. Rea, K. Yan (1993) Non-Thermal Plasma Techniques for Pollution Control, eds. B.Penetrante and S.E. Schultheis vol. 1 (NATO Series, New York, 1993) p.191
- [6] E.M. Veldhuizen, W.R. Rutgers, V.A. Bityurin : Plasma Chem. & Plasma Proc. 16 (1996) p.227
- [7] G. Hartman: IEEE Trans. Indust. Appl. IA-20 (1984) 6, p.1647
- [8] J.J. Lowke, R. Morrow: IEEE Trans. On Plasma Sci. 23 (1995) 4
- [9] Y. Goshō, M. Saeki: Proc. 9th Gas Discharges & Their Applications (Venezia, 1988) p.171
- [10] R. Messaoudi, F. Massines, A. Younsi, B. Despax: Proc. 10th Gas Discharges & Their Applications (Swansea, 1992) p.318
- [11] L.B. Loeb: Electrical Coronas, Their Basic Physical Mechanism (Berkley Press, Univ. of California, 1965)
- [12] S. Masuda, H. Nakao: IEEE Trans. On Indust. Appl. 26(1990) 2, p.374
- [13] Dahyia, Mishra, Veetkind: IEEE Transactions on Plasma Science, 21 (1993) p.346
- [14] L. Civitano: Proc. Hakone IV vol.1 (Bratislava, 1993) p.vii
- [15] M. Dors, J. Mizeraczyk, M. Rea: Proc. 18th Symp. on Plasma Phys. and Tech (Prague, 1997) p.169
- [16] M. Dors, G.V. Nichipor, J. Mizeraczyk: Proc. 23rd ICPIG (Toulouse, 1997), p.250
- [17] J.S. Chang IEEE Trans. on Plasma Sci. 19 (1991) p.1152
- [18] K. Hensel, C. Yamabe, M. Morvová : Proc. 1999 Japan-Korea Joint Symposium on Electrical Discharge (Kitakyushu, 1999) p.141
- [19] K. Hensel, N. Hayashi, C. Yamabe: Proc. ACED-2000 (Kyoto, 2000) p.103
- [20] K. Hensel, N. Hayashi, C. Yamabe, M. Morvová: Proc. ISNPT-3 (Seogwipo, 2001), p.219
- [21] M. Morvová: J. Phys. D: Appl. Phys. 31 (1998), p.1865
- [22] F. Hanic, M. Morvová, M. Morva: J. Therm. Analys. Calor. 60 (2000) p.1111
- [23] A. Lofthus, P.H. Krupenie: J. Phys. Chem. Ref. Data 6 (1977) p.113
- [24] W.F. Cooper and J.F. Hershberger: J. Phys. Chem 96 (1992) p.771
- [25] S.L. Miller: J. Am. Chem. Soc. 77 (1955) p.2351