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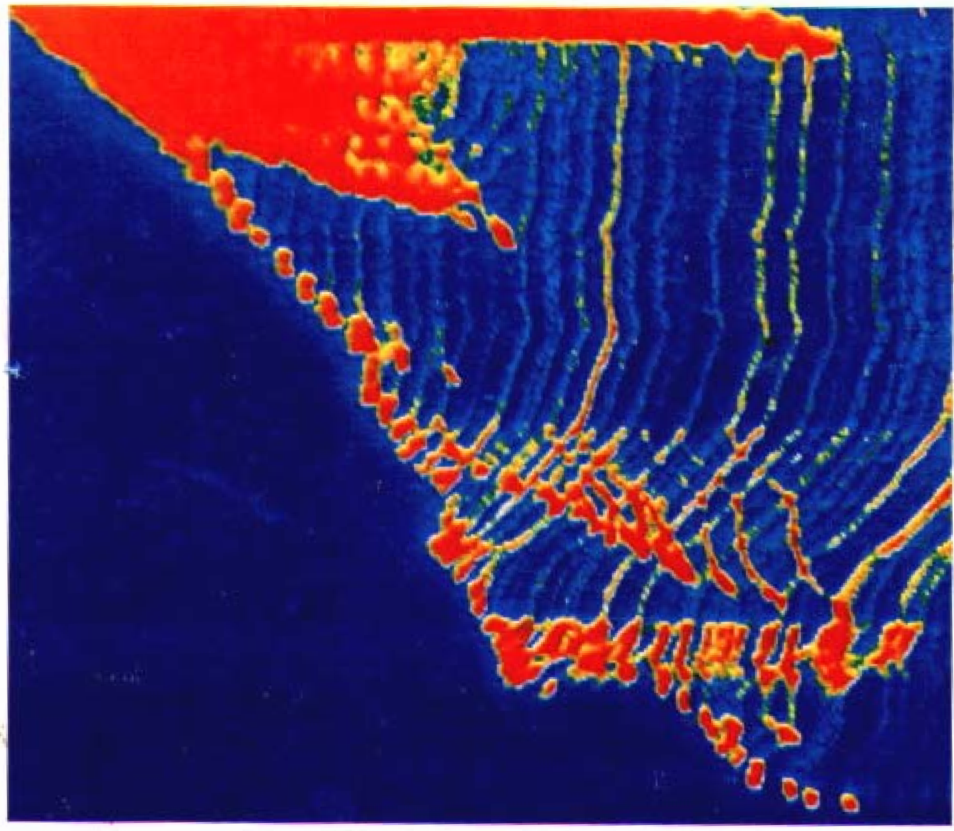

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SPECTROSCOPIC STUDY OF CORONA DISCHARGE IN N_2-NO-CO_2 MIXTURES

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ABSTRACT

The aim of the research was to investigate changes in mixtures containing N_2, NO and CO_2 while using positive DC corona discharge. Hemi cylindrical discharge reactor was employed and infrared spectrometry was used to analyze the products of the process in the discharge chamber. Experimental results describing the influence of CO_2 and other admixtures on discharge, its character and performance are presented.

INTRODUCTION

For several years corona discharge has been used in precipitation and ozonizing techniques and later as a source of charged particles, especially electrons, for the initiation of chemical reactions. Corona discharge is very effective solution to remove compounds such as SO_2, NO_x, CO_x and hydrocarbons (VOC) from exhausts. However it is also important to control not only the emissions of NO_x and SO_2, but, also other compounds, e.g CO_2 and N_2O, two gases which are mainly responsible for greenhouse effect and global warming.

In case of NOx removal, corona discharge has been often used in many laboratory and pilot-scale experiments over last decades. The process of NOx treatment, its chemical reactions, final products, energy consumption and efficiency of the process can be influenced by change of many different parameters and discharge conditions (HV waveform characteristics, discharge polarity, initial gas composition, chemical additives, etc.) [Ami93] [Civ93] [Mas90]

Among different additives with more or less significant effect on deNO$_x$ process (e.g. NH_3, H_2O, hydrocarbons, etc.) influence of CO_2 had been studied only partially. Despite interesting chemical processes and products in NO_x-CO_2 containing mixtures detailed description of CO_2 effect on the process has not been probably published yet.

Individual investigation of CO_2 decomposition process in corona discharge in mixture of CO_2 with air has been widely studied. Especially good results were obtained in a pulsed corona discharge in the presence of granular ferroelectric matter. Many authors are still interested in DC corona discharges in both polarities and conversion of CO_2 to CO [Sig92] [Mor98].

For study of CO_2 to CO conversion it is very important to know the amount of positive and negative ions presented. Also concentration of cluster ions is important. For negative corona discharge the dominating ions are O^-, CO_3^- and CO_4^-, while in positive polarity HCO_2^+, CO_2^+, $H^+[H_2O]_n$ [Alg77].

For the process in NO_x and CO_2 containing mixtures, it is believed NCO radical plays an important role. This radical is responsible for removal of NO_x and can also be incorporated in different heterogeneous organo-metal compounds on a surface of electrodes (like copper or brass) having significant catalytic properties. There is also a certain suspicion discharge process in mixtures including CO_2-N_2-H_2O can eventually cause a formation of some essential aminoacids (e.g. glycine) [Mor98]. Based on aforementioned fact a question is raised whether similar process could not also exist in NO_x-CO_2-H_2O mixtures, while NO_x and CO_2 would be simultaneously treated.

The aim of our research project concerning NO_x is to perform measurements in CO_2-N_2 and CO_2-NO_x mixtures (including water) to describe the discharge process, its efficiency and products. The intention was to perform measurements while using different modes of DC corona discharge, however in the first phase we used positive DC streamer corona discharge mainly.

EXPERIMENTAL SETUP

The experimental apparatus and setup is presented (*Fig.1*). Hemi cylindrical type of corona discharge reactor with length 20cm was employed. A copper wire with a diameter of 0.2 mm was used as active electrode, while 35mm in diameter copper hemi cylindrical electrode served as a passive (outer) electrode. To avoid discharge to appear at sharp edges of hemi cylindrical electrode the copper elements with bigger curvature of radius ('Rogowski designed') were mounted at both ends of the cylinder.

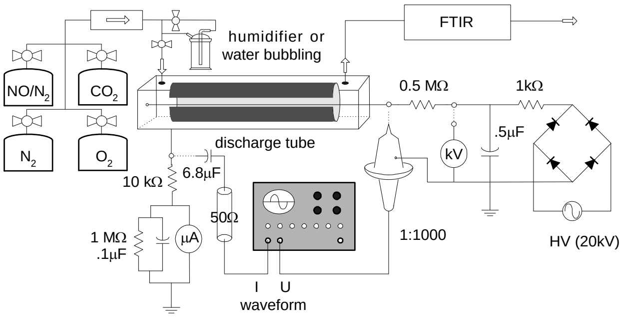

Fig.1.: Hemi cylindrical geometry corona discharge setup

Conventional HV power supply was used together with rectifying circuit and RC circuit integrator to produce DC output signal. DC streamer corona discharge mode of positive polarity was used especially in experiments. The voltage across the discharge chamber and discharge current (both mean current resp. current waveform) were recorded by the analog microampere meter resp. oscilloscope (Tektronix TDS380).

Pressure tanks of N_2, NO in N_2 (500ppm admixture), CO_2 and O_2 were used to prepare various initial mixtures. The measurement were performed in a flow regime where the total gas flow was set to 1 l/min. Gas composition and was continuously monitored by FT-IR spectrometer (using 2.4 m long gas cell) to provide the information about changes in gas mixtures. The use of IR spectrometry is a suitable method how to analyze CO_2 and NO_x gases due to their absorption in IR region.

EXPERIMENTAL RESULTS

In our past experiments [Hen99] with gas mixtures of NO_x and CO_2 we only evaluated deNO and deNO$_x$ treatment efficiency and its change in case of CO_2 addition into the gas mixture by means of NOx chemiluminescence analyzer.

In case gas mixture of N_2 with 500ppm of NO the maximum deNO treatment efficiency more than 80% at energy consumption 256eV/NO was achieved *(Fig.2.)*. At the same time the total deNO$_x$ treatment efficiency was 70% at energy consumption equal 287eV/NO$_x$. Adding CO_2 gas into the gas mixture both deNO and deNO$_x$ treatment effects were diminished, since also oxidative processes took place and also because of a slight change in a discharge character after CO_2 input.

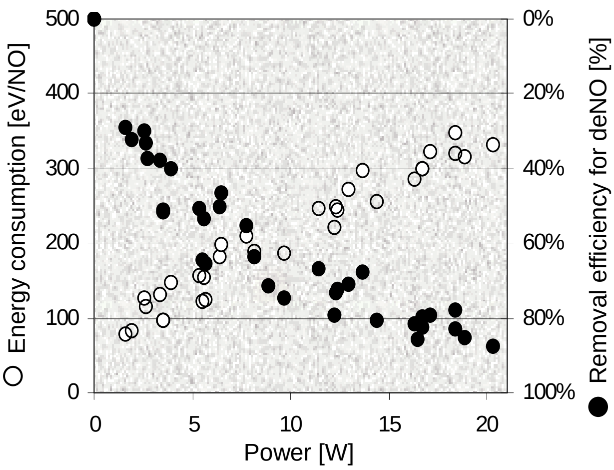

Fig.2.: Efficiency and energy consumption of deNO process in N_2/NO(500pm) mixture

In the present research rather concentrated on overall analyze of all compounds in the mixture as well as the products. The four different groups of measurements were performed where different gas mixtures were treated by positive corona discharge *(Tab.1.)* The admixture of oxygen was used to stabilize discharge, because of some instabilities (see later).

Tab.1. : Groups of measurements	
1	**N_2 + x% CO_2** (x = 0,1,3,5,10,20,30,50%)
2	N_2 + 20% O_2 + x%CO_2 (x =0,1,3,5,10,20,30,50%)
3	**N_2 + 250ppm NO + x% CO_2** (x = 0,1,3,5,10,20,30%)
4	N_2 + 250ppm NO + 20% O_2 + x% CO_2 (x = 0,1,3,5,10,20,30%)

Discharge Character

[N_2+CO_2] Discharge in pure N_2 gas had a pulse character until the breakdown V_b (at 400μA). An admixture of CO_2 to N_2 however caused strong vibrations of the wire (already at current of 50μA) what avoid to go further then 150μA and so to investigate mixtures. Anyhow generally speaking the addition of CO_2 caused an increase of onset voltage V_o. Increasing the power of the discharge the amplitude of current pulses increased (up to 20mA) as well as the frequency.

[N_2+O_2+CO_2] Addition of O_2 into the gas mixture helped to stabilize the discharge, transferring discharge from streamer mode to glow mode (*Fig.4a*), decreasing V_o and hindering breakdown (until 1.2mA). Increasing concentration of CO_2, however, V_o increases and the pulse behavior is gradually recovered. Bright homogenous light of corona glow discharge along the wire step-by-step changes, while emission spots on the wire and channels in the gap grows. Going further and increasing the concentration of CO_2 (up to 20-30%) causes still bigger number of streamer channels to appear filling up whole discharge volume between electrodes (alike *Fig.4c*).

Streamer pulse duration decreases with increasing concentration of CO_2. Amplitude of the pulse (although bigger than in pure N_2), decreases too.

[N_2+NO+CO_2] NO in the mixtures with N_2 caused, alike O_2, decrease of V_o and hindered breakdown. Increasing discharge current streamers appeared with fast growing amplitude and frequency. The channels in the discharge volume are visually more intensive then those in N_2+O_2+CO_2 mixtures, though concentrated at several places along the wire (*Fig.4b*). By adding CO_2 into a mixture the discharge volume utilization by streamer 'showers' gets even better (3-5% of CO_2), however further increase of CO_2 causes an decrease in discharge light intensity and also leads to vibrations of the wire.

[N_2+NO+O_2+CO_2] Character of discharge in these mixtures is jointly influenced by each of its component. While O_2 and NO cause decrease of V_o, CO_2 does opposite. While NO and CO_2 support streamer mode, O_2 leads discharge to a glow mode. In general the character of the discharge - VA characteristics (*Fig.3*)), pulse waveforms and light emission (*Fig.4c*) are about the same as in N_2+O_2+CO_2 group of measurements.

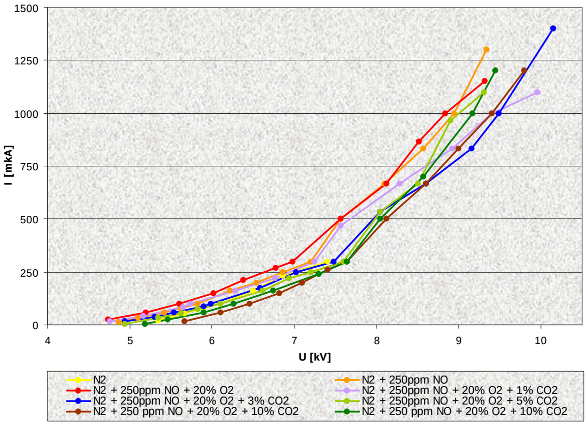

Fig.3.: Current - Voltage characteristics of N_2+NO+O_2+CO_2 gas mixtures

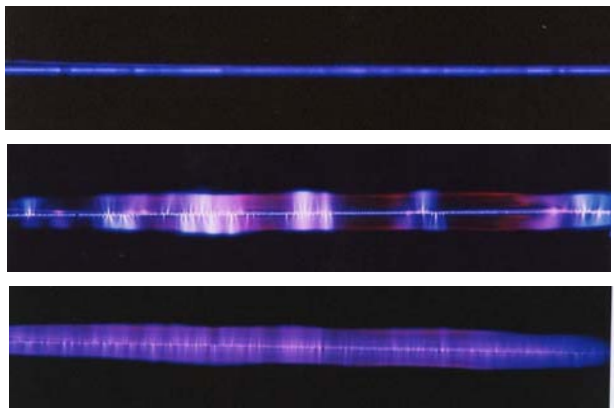

Fig.4.: Photographs of typical light conditions of discharge in different gas mixtures (I_m =1.5 mA) :

a) N_2 + O_2
b) N_2 + 250 ppm NO
c) N_2 + 250 ppm NO + 20%O_2 + 20% CO_2

IR Spectra Analyze

Analyze of mixtures containing compounds N_2, NO, CO_2, O_2, with the help of IR absorption spectrometry turned out to be very effective method. The changes in gas mixtures were recorded in-situ for different types of mixtures and discharge power. Molecules O_2 and N_2 are however symmetric and so no absorption bands in spectra might be visible. On the other hand, NO and CO_2 (resp. NO_2, CO and other compounds) have several absorption bands. Main absorption bands that appeared in spectra are presented in *Fig.5.* and *Tab.2*

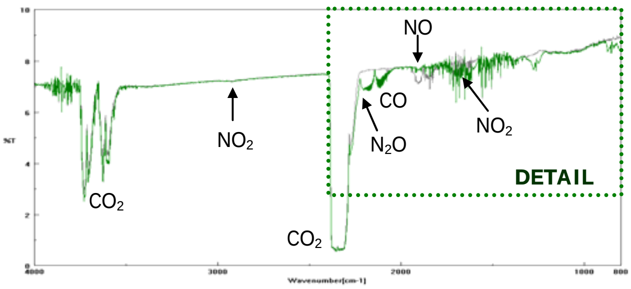

Fig.5.: Typical spectra of mixture containing CO_2 and NO treated by corona discharge

Tab.2.: IR absorption bands [cm^{-1}]	
NO	1920-1900 monomer, 1840 dimer
NO_2	1750,1620, 2990-2900 overtone
N_2O	2240 in-between CO2 and CO bands
CO_2	3800-3700, 2400-2300, 670
CO	2220-2020

Figures (*Fig.6a,b*) show changes in contents of initial mixtures of $N_2+O_2+CO_2$,N_2+NO+O_2+ $+CO_2$. Each curve in a figure represents change in mixtures caused by discharge action at current equal to 1000μA compared with the situation without discharge action. Comparing all three groups of measurements following conclusions might be made:

- Production of N_2O seen in N_2+NO mixtures (probable production way here is the reaction $N+NO_2 \rightarrow N_2O+O$) was intensified by adding either CO_2 or O_2 into mixture ($N_2(A)+O_2 \rightarrow N_2O+O$).
- Increase of CO_2 concentration in initial mixture caused increase of CO produced by discharge action.
- Production of NO_2 is the biggest in case of $N_2+NO+O_2+CO_2$ mixtures as here the source of also reactions between O_2 and N_2 lead to formation of NO and further to NO_2

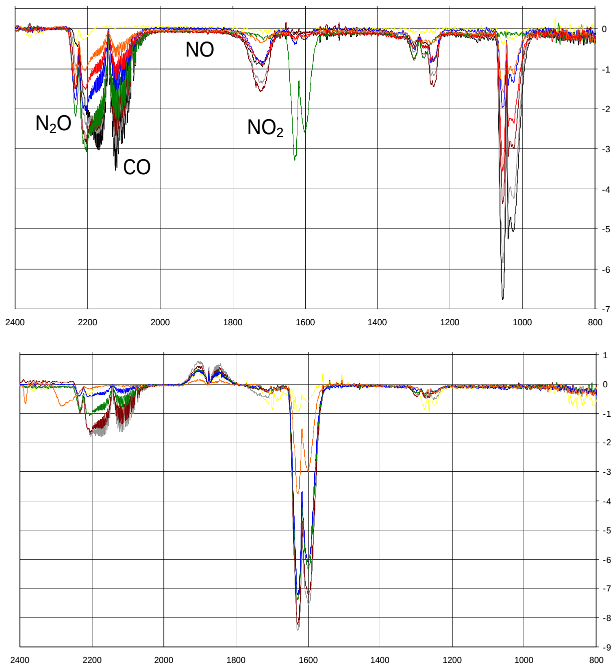

Fig.6.: Gas composition changes in $N_2+O_2+CO_2$, $N_2+NO+O_2+CO_2$ mixtures caused by discharge

- Change of NO concentration was not significant in $N_2+O_2+CO_2$ mixtures, while in mixtures containing NO relatively strong effect of deNOx removal occured.

Objective of the presented paper was to show a possible influence of CO_2 on the deNO$_x$ process. The experimental results confirmed its effect however in future further experiments are required to find out more about the problem. CO_2 addition affected discharge behavior and had influence on final energy consumption and treatment efficiency.

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