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Spectroscopic Study of Positive Corona Discharge in Mixtures Containing N_2, NO, CO_2, O_2 and H_2O

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Abstract

The positive DC corona discharge in the hemi cylindrical discharge reactor was applied to mixtures containing N_2, NO, O_2 CO_2 and H_2O, while infrared spectrometry was used to analyze the products of the process in the discharge chamber. The attention was paid to the influence of CO_2 on discharge, its character, performance and products of the process. Besides the main components of the mixtures (NO, NO_2, CO_2 etc.) also other compounds and functional groups (e.g. amides I-III, amines, imides, NCO) had been identified in the spectra.

Introduction

The corona discharge is one of solutions how to remove nitrogen oxides and other toxic compounds from flue gases. This technique has been widely used in many laboratory and pilot-scale experiments over last decades [1-3]. The process of NO_x treatment, chemical reactions, final products, energy consumption and process efficiency can be influenced by change of many different parameters and discharge conditions (shape of HV waveform, discharge polarity, initial gas composition, chemical additives, etc.). Among different chemical additives used in deNO_x process (e.g. NH_3 or hydrocarbons) influence of CO_2 had been studied only partially, detailed description of CO_2 effect on the process has not been probably published yet as well as the chemical reactions and products of the process.

The aim of the research was to perform measurements in the mixtures containing N_2, NO, CO_2, O_2 and water and describe the discharge process, its efficiency and products. Our intention was to provide measurements using positive DC corona discharge in different modes, while positive DC streamer corona discharge was used mainly. Although the elementary process and chemical reactions are very complicated, several ideas about the discharge process and the analysis of the products are presented at least.

Experimental Setup

The experimental setup is presented in the **Fig.1**. Hemi cylindrical type of corona discharge reactor with length 20 cm was employed in the experiment and DC corona discharge of positive polarity was used in all experiments. The gases mixtures of N_2, NO (250 ppm), CO_2 (0-50%), O_2 (20%) and water were used. All measurements were performed in a flow regime with the total gas flow set to 2 l/min. The overall analysis of the gas products was done by FT-IR spectrometer using 2.4 m long gas cell.

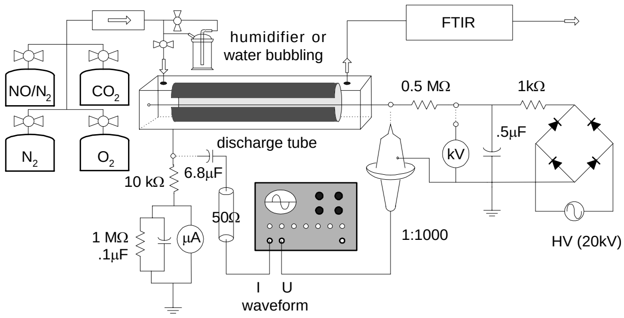

Fig.1 Experimental apparatus

Experimental Results

The effect of individual components of the mixture on the *discharge character* was very significant. Compared with pure N_2, an admixture of NO caused a decrease of the corona onset voltage V_o and hindered breakdown. Increasing discharge current, streamers gradually appeared with fast growing amplitude and frequency. An increase of CO_2 concentration in the mixture (3-5% of CO_2) caused the discharge volume utilization by streamers and their distribution in discharge gap became more homogenous. In the mixtures with initial NO, streamers appeared from early stages of the discharge and an admixture of CO only enhanced the streamers improving their space distribution in the discharge gap, while in the mixtures without initial NO steamers appeared only after CO_2 was introduced. Too much of CO_2 however, caused the streamers gradually died out in the gap and also led to discharge instabilities. With very large amount of CO_2, corona discharge onset voltage could be significantly increased and streamer corona may terminate.

The *analysis of the gas mixture* by means of IR spectrometry is very effective method for monitoring the changes of the gas mixture composition caused by electric discharge and products identification. The absorption bands of the main components of the initial gas mixtures are presented in the **Tab. I**.

Tab. I Characteristic absorption bands [cm^{-1}]	
NO	**1920-1900** monomer, 1840 dimer
NO_2	1750, **1630**, 2930-2900 overtone
N_2O	**2240** (between CO_2 and CO bands)
CO_2	3800-3700, **2400-2300**, 677
CO	**2220-2020**

Except the absorption bands of the main components of the gas mixture, there were also other bands, which appeared in the spectra. Analyzing spectra complexly, considering all possibilities, discharge conditions, initial gas composition and intensity of absorption bands also other interesting compounds and functional group were identified (**Fig.2**).

The analysis of other compounds of the mixture also took into account the fact of possible formation of aminoacids or at least some traces or functional groups. The formation of aminoacids was confirmed earlier [4]. The formation is launched with excitation of N_2 molecules (metastable state $A^3\Sigma^+_u$) later incorporated into CO_2 while forming important radicals NCO respectively ON-NCO. For possible formation of trivial aminoacids in the discharge the process of water dissociation on electrode surface is necessary to form an amide group. The identification of aminoacids or their traces in the discharge is complicated by their polarization in the volume and formation of zwitter ions, i.e. $NH_2^+COO^-$ or NH_3COO^- in the presence of the electric field. It results in the band shifts in the infrared spectra (e.g. protonated amino cation NH_3^+ is shifted down to 2500cm^{-1} and NH_2^+ 2700cm^{-1}) making possible analysis more difficult. Furthermore aminoacids can be neutral, acidic or basic, depending on the number of NH_2^+ respectively COO^- groups in the structure of the molecule, which might also lead to different effects in the infrared spectra.

In the upper region, there are visible bands of amine NH_2 resp. zwitter ion NH_3^+ in the spectra in the range of 3490, 3467 resp. 2580, 2550 cm^{-1}, while the region around 1900 cm^{-1} belongs to NO, namely NO monomer band at 1920-1900 cm^{-1} and NO dimmer at 1840 cm^{-1}.

The region from 2000 cm^{-1} down to 1600 cm^{-1} is the region of carbonyls (ketones, esters, carboxyl acids, etc.), i.e. the compounds including C=O group. Especially the range of 1850-1600 cm^{-1} is very important as this is the range of carbonyls with the double bond, which are very strongly dependent on their surrounding and associations resulting in the shift and position of the absorption bands in the spectra. In our case the following bands are visible in the spectra: carbonyl of carboxyl acid at 1720 cm^{-1}, carbonyl of imide at 1700 cm^{-1} (which is stronger as it is twice in one compound), then carbonyl of non-specified neutral aminoacids at 1680 cm^{-1}.

At the bottom side of this region a strong band of NO_2 is present at 1630-1620 cm^{-1}, along with C=C conjugated resp. C=C, C=N conjugated and carboxylate ion COO^- (ν_{as}). At the right side of the NO_2 absorption band a small band representing amide I (1640 cm^{-1}) is well visible especially in the spectra of N_2-NO-CO_2 mixture. In the mixtures with initial concentration of O_2

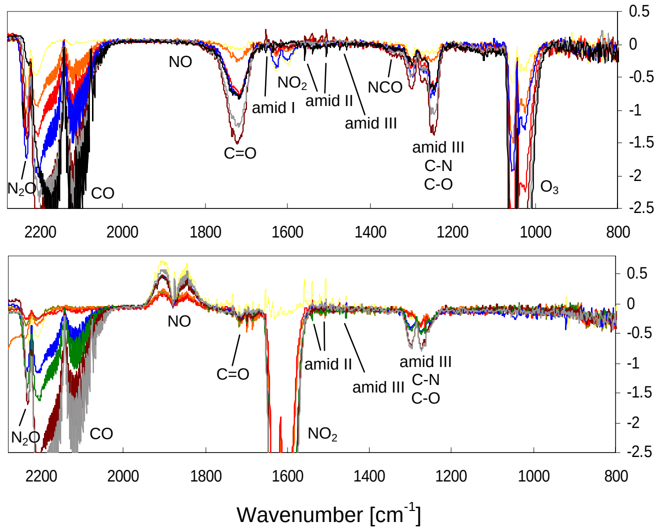

Fig.2 Part of differential spectra of mixtures N_2-O_2-CO_2 and N_2-NO-O_2-CO_2, where each curve represents the same discharge power while concentration of CO_2 varies from 0 to 30%

and comparably bigger production of NO_2 caused the band interfered with band of NO_2 and so the band is invisible.

Then in the range of 1600-1500 cm^{-1} absorption band of amide II (β, δ NH_x) can be seen. Especially the region of 1560-1510cm^{-1} is full of sometimes small but sharp bands, which corresponded to amide II.

Further in all three types of mixtures a small band at 1460 cm^{-1} appeared, which represented the combination of bands of standard amide III band in his neutral state. This band is associated with the band of NCO radical, imide group 1490 cm^{-1} and carboxylate ion COO^- (ν_s) at 1465 cm^{-1}. In the polarized state of zwitter ion aminoacid the band is shifted down to region 1300-1250 cm^{-1}, where it interferes with C-N and C-O bands.

Finally a small and sometimes hardly visible absorption in the range 1140-1130 cm^{-1} represented βNH_2 amine and amide III, which usually appears in the range of 1190-1038cm^{-1}.

Conclusions

The positive DC corona discharge in the hemi cylindrical discharge was applied to mixtures containing N_2, NO, O_2 CO_2 and H_2O. Except the main gas components also other bands were identified in the spectra including amides I, II and III, βNH_2 amines, NCO radical and imide.

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