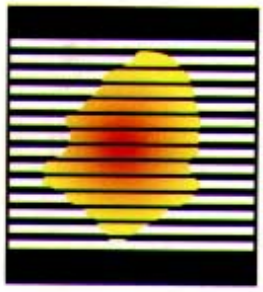

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POSSIBILITIES OF VARIOUS VOC REMOVAL USING CORONA DISCHARGE AND ULTRASONIC AEROSOLATION OF WATER

Zdenko MACHALA[**], Branislav ŠVEHLA[*], Imrich MORVA, Karol HENSEL and Marcela MORVOVÁ

Institute of Physics, Faculty of Mathematics and Physics, Comenius University, Mlynská Dolina, F2, 842 15 Bratislava, Slovak Republic

[*]Departement of Radioelectronics, Faculty of Electrotechnics and Informatics, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovak Republic

[**]Department of Plasma Physics, Faculty of Mathematics and Physics University of Comenius, Mlynská dolina F2, 842 15 Bratislava, Slovak Republic

ABSTRACT:

The effect of „anomal" dc corona discharge on VOC removal was investigated. The experiments were aimed to optimise removal efficiency on following compounds: cyclohexanone, ethyl acetate, toluene, xylene (mixture), ethyl benzene, styrene, monocyclic terpenes (colophony), phenols and their mixtures. The originated products and removal efficiency were estimated by IR absorption spectrometry. The measurements were done both in

- *stable state regime to gain time development of process and products*
- *flowing regime variating flowing velocity, flowing direction and concentrations of VOC in the carrying gas (air)*

The effect of outer electrode material and its diameter on the removal processes was also studied. The influence of ultrasonic aerosolation of water on process efficiency was tested. As in each case the main product was solid polymer mixture in powder form, the new method for electrode cleaning was developed.

Introduction:

Volatile Organic Compounds (VOC) comprise to global ecology by smog production due to specific compound so called peroxyacylnitrate (PAN). The VOC sources are very heterogene and can be found in all sorts of industry, in heavy industry (oil mining and processing, petrochemistry, rubber industry, chemical industry, production and treatment of plastic materials, pulp and paper industry, production and treatment of fat and grease, cosmetic and pharmaceutical industry, energetics) as well in light industry (production, treatment and use of painting, treatment and conservation of wood and others). Not negligible contribution to VOC discharge is brought by communal sources (waste combustion, evaporation and putrefaction of waste) and indoor emissions as gas stoves, smoking and other. The specific place in VOC discharges has traffic. Agriculture contributes to VOC discharges especially due to the animal production.

Experimental:

For measurements we have used the anomal corona discharge stabilised by resistance. The high voltage electrode was in form of internal thread. We suppose, that similarly as glow discharge with hollow cathode, also this discharge probably burns from holes of internal thread. The both electrode surfaces were modified due to action of corona pre-discharge so the convenient areas for the enhanced electron/positive ion emission arise. The transport of metal from HV to LV electrode occurs similar as in arc. From the IR analysis of electrode surface comes out that

surface layer/spots with high dielectric permitivity are probably responsible for this enhanced emission. The discharge travels between these surface spots with high velocity. The anomal corona discharge arises at higher currents after regular dc corona pre-discharge. This process is connected with the fall of voltage from 10 kV (normal corona regime for given electrode configuration) to several hundreds of volts and current rise up to ~ 2 mA. The discharge changes to spontaneously pulsing „brush-like" streamer type of discharge with current pulses frequency about 1 kHz accompanied by an intensive sound. The cathode and anode spots are fully developed in the near electrode region. The current voltage characteristics of anomal corona discharge in the frame of whole characteristics is seen from Fig. 1 (part f and g of the discharge).

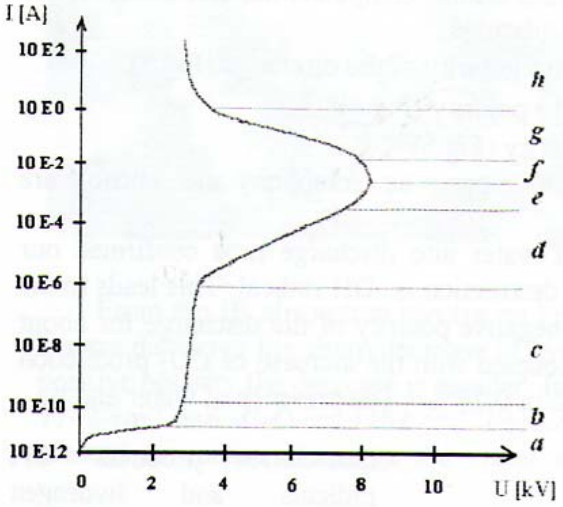


Fig. 1 The current-voltage characteriscs of the anomal corona discharge - part f and g

The investigated form of the discharge is important for good parameters concerning chemical reactions especially in VOC removal. The energy accumulated in the discharge is lower comparing to glidarc so only particular destruction of organic compound occurs. After destruction process polymerisation in outer corona region take place. This type of VOC removal is important concerning the CO_2 minimisation in atmosphere.

Measurements were made in static regime in gas cell discharge tube described on Fig.2 (to gain time development of process and products) or in flowing regime in coaxial corona discharge system both in positive and negative polarities of dc corona discharge. Flowing mixture of air with VOC up to saturated vapour pressure was realised by bubbling of air from pressure tank through flowmeter with needle valve and temperable bubbler with studied solution. For tests were used following solvents: cyclohexanone, toluene, xylene (mixture), ethyl acetate, ethyl benzene, styrene, monocyclic terpenes (colophony), phenols and their mixtures. The necessary water for process was introduced via ultrasonic aerosolator. For each mixture gas before/after the discharge and the surface of used plane LV electrode was analysed using IR absorption spectrometry of gas and reflection IR spectrometry. The water from process was accumulated and liquid or solid products soluted or suspended in water were analysed by ATR reflection spectrometry on KRS5 crystals with 45° reflecting angle. The solid product (if was originated) was separated from water, dried and treated by the KBr pellet making technology for scanning of IR absorption spectra.

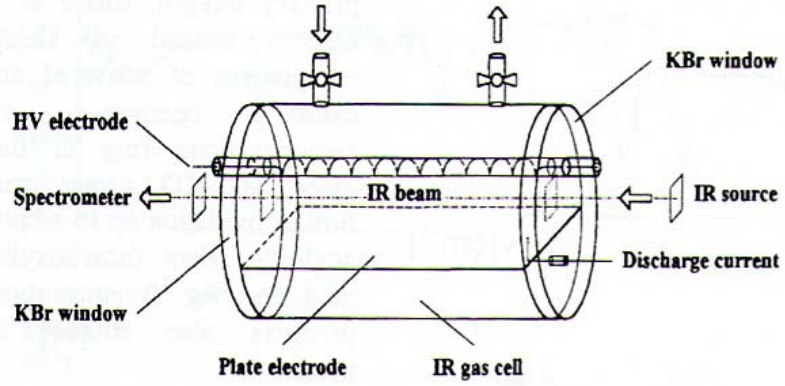


Fig. 2 Gas cell discharge tube

Results and discussion:

We present spectra, where the efficiency of liquidation process is greater, the product on the low voltage electrode is significant or the changes of the studied compound are characteristic for this group of compounds. From this point of view the mixtures

- air plus cyclohexanone and applied negative polarity of the discharge (Fig.3),
- air plus ethyl acetate and negative discharge polarity (Fig.4),
- air plus toluene and positive discharge polarity (Fig.5)

are important and presented here. Styrene, monocyclic terpenes as colophony and phenols are more in details described in [1].

Measurements with ultrasonic aerosolidation of water into discharge tube confirmed our hypothesis that main initiation factor of hydrocarbon destruction is -OH radical. This leads to the increase of removal efficiency for both positive and negative polarity of the discharge for about 25-30% comparing to dry process. The process is coupled with the increase of CO_2 production of about 3% and decrease of CO production to less than 0,25%. The presence of water and its dissociation products -OH radicals and hydrogen influenced the type of reaction products. Nitrogen as the air component is dissociated to nitrogen atoms, which can bc activated. In spite of this functional groups -NH and -NH_2 are produced. Their presence leads to the creation of oxime of cyclohexanone. Air oxygen is activated to primary oxygen, ozone or -OH radical. These components of activated air cause opening of cyclohexanone ring in the place of -CO group and further oxidation up to adipic acid or other dicarboxylic acid. Among fragmentation products also ethanol is present.

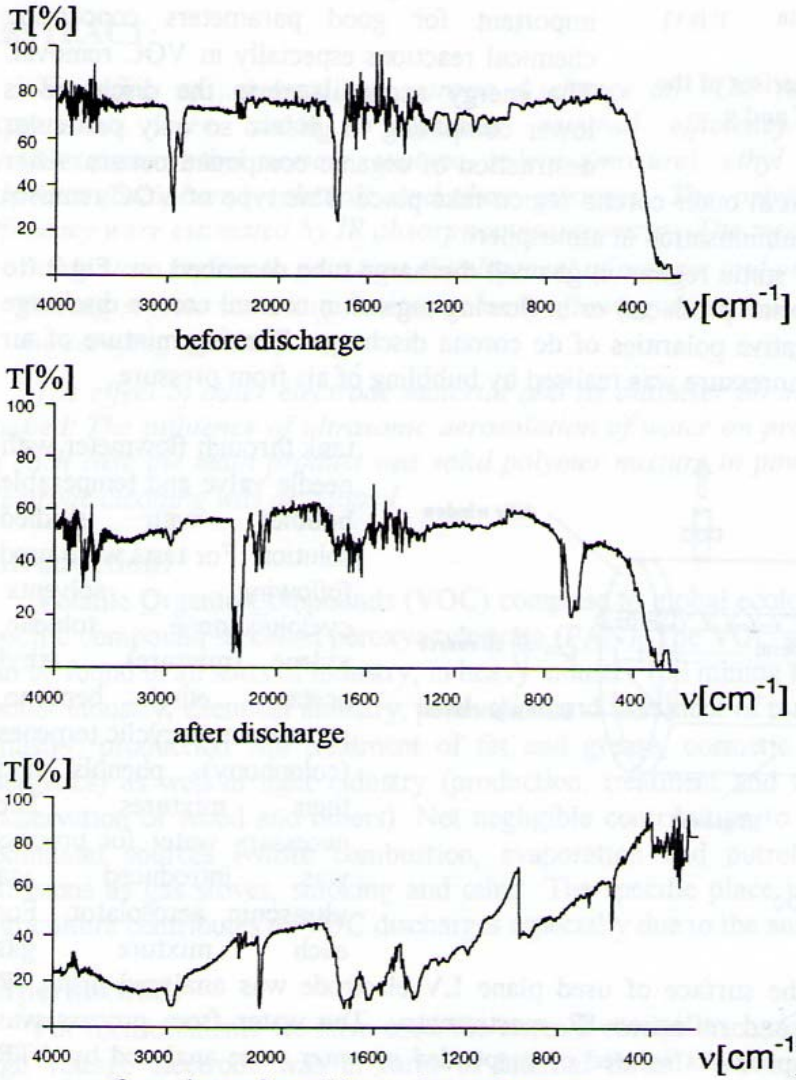


Fig.3 IR absorption spectra of gas before and after negative corona discharge in the mixture of air plus cyclohexanone and reflection IR absorption spectrum of the surface of low voltage electrode

The microscopic photography of the solid dark white product created in negative corona discharge in the mixture of air with cyclohexanone is in the figure. The powder was a mixed copolymer with following structural components: polyamide, polyimidoester, polyimide, aminoacid and oxamidato complexes and malone acid anhydrid.

From the IR absorption spectra on Fig. 4 for mixture of air with ethyl acetate after negative corona discharge the sharp decrease of hydrocarbon groups $-CH_3$ and CH_2 is seen. In the case of positive polarity the decrease is smaller. In the same time the decrease of carbonyl group-C=O at 1742 cm^{-1} and -C-O- at 1182 cm^{-1} occured. All these changes were initiated by the -OH radical created in corona discharge via water activation. Similar as by cyclohexanone also in ethyl acetate ethanol was produced in fragmentation process. In IR absorption spectrum of gas products rise the band group at 1300-1450 cm^{-1}. Activated nitrogen created in the discharge broke the hydrocarbone string and past into carbonyl group to produce -C=N=O, or oxim group -C=N-O-. Due to dimerization bright group of compounds with IR bands in the described region of IR spectrum are produced. These group of gas and liquid compound are responsible for origin of copolymers on the surface of LV electrode containing polyimid, polyaminoacid, polyurethan and polyamid groups.

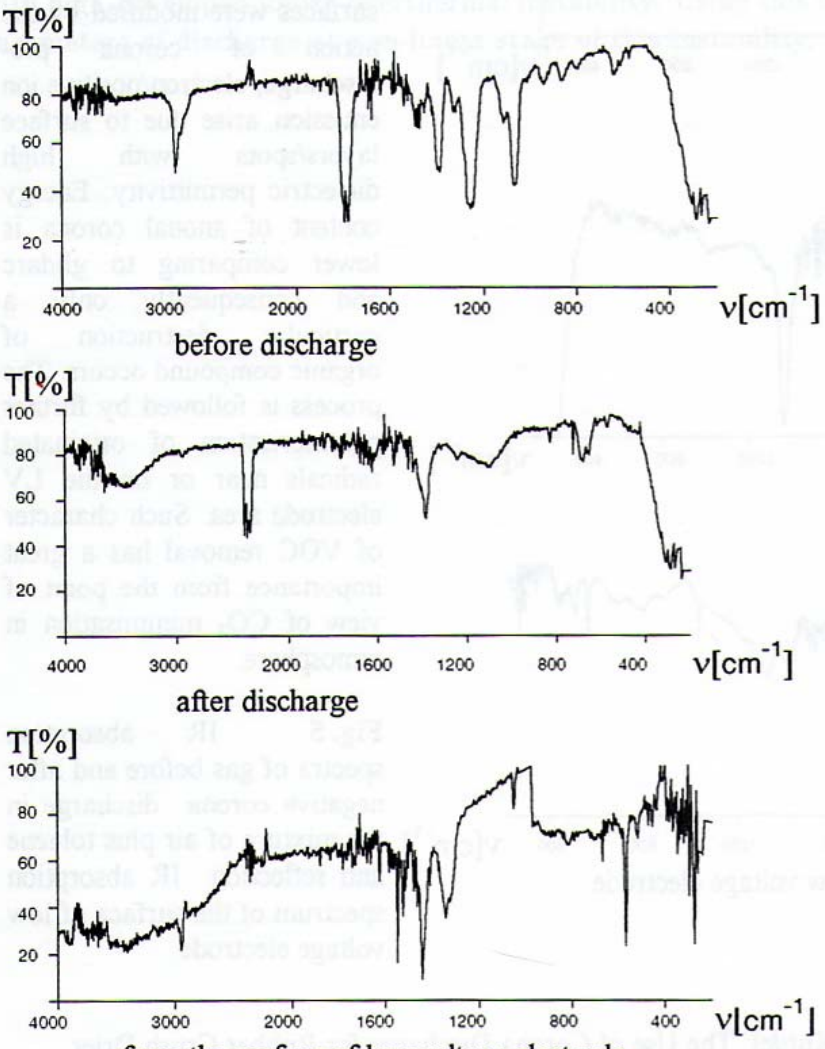
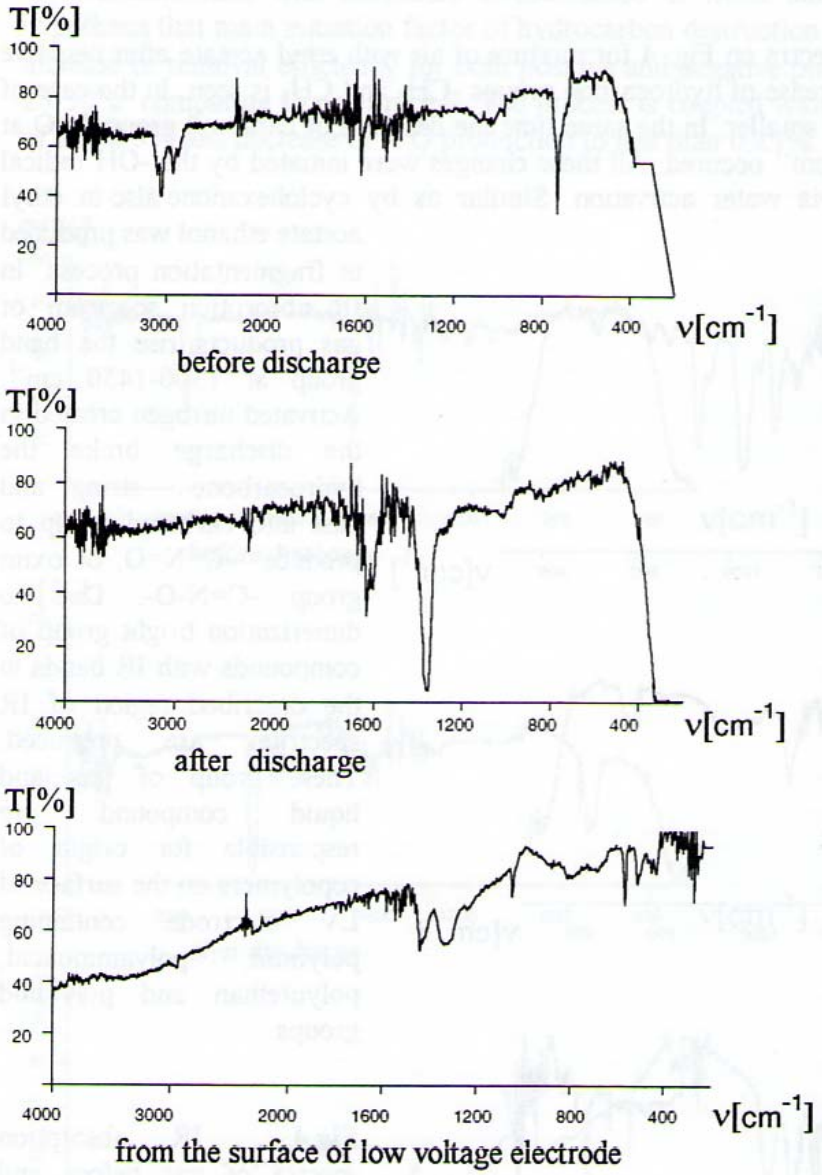


Fig.4 IR absorption spectra of gas before and after negative corona discharge in the mixture of air plus ethyl acetate and reflection IR absorption spectrum of the surface of low voltage electrode

In the case of positive corona discharge in both ethyl benzene and toluene (Fig.5) is seen different character of changes as in the case of ethyl acetate and negative polarity of the discharge. Similar as in ethyl acetate the decrease of hydrocarbon groups is voluminous concerning to band at 3000 cm^{-1}. The CO and CO_2 are not present between the products. The character of products is dependent on the destruction degree of benzene ring. The destruction products concerning the degree of destruction are benzoic acid, adipic acid, malone acid anhydrid. Also disubstiuated aromatic izocyanates are present. In negative polarity the removal efficiency is lower. The destruction products have other composition. Between the products dominate CO_2, CO, water and alcoholes.



Conclusions:

The investigated form of discharge is important from the point of view of suitable parameters concerning a chemical reactions especially for VOC removal. In anomal corona discharge electrode surfaces were modified by the action of corona pre-discharge, electron/positive ion emission arise due to surface layers/spots with high dielectric permittivity. Energy content of anonal corona is lower comparing to glidarc and consequently only a particular destruction of organic compound occurs. The process is followed by further polymerisation of originated radicals near or on the LV electrode area. Such character of VOC removal has a great importance from the point of view of CO_2 minimisation in atmosphere.

Fig. 5 IR absorption spectra of gas before and after negative corona discharge in the mixture of air plus toluene and reflection IR absorption spectrum of the surface of low voltage electrode

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