

DC GLOW DISCHARGE IN ATMOSPHERIC AIR AS A SOURCE FOR VOC ABATEMENT

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ABSTRACT. We present experimental investigations of a direct-current (DC) discharge in atmospheric pressure air with the aim of producing nonequilibrium plasma applicable for air pollution control. This pulseless continuous discharge occurs between two metal electrodes. Spectroscopic and electrical measurements confirm that the discharge is of the glow type. It operates with currents from 2 mA, voltages of some kV, current densities of 1-10 A/cm², and gap lengths from a few mm to a few cm. Its voltage–current characteristics is descending. The gas temperature in the discharge is controlled by the current and by the gas flow velocity. The discharge generates highly ionized nonequilibrium air plasma with electron number densities of 10^{12} - 10^{13} cm⁻³ and gas temperatures of 1500-2500 K. We have successfully tested single and multiple discharges of this type in glass and copper tube reactors for the abatement of selected VOCs (cyclohexanone and toluene). Depending on the reactor type, discharge parameters and the injected energy density we obtained removal efficiencies of 30-95 %, with energy costs of 50-800 eV/molecule. In the VOC decomposition process, thermal discharge effects couple with volume reactions induced by radicals and other active species formed in the plasma, and with reactions occurring on electrode surfaces.

INTRODUCTION

Atmospheric pressure nonequilibrium air plasmas present considerable interest for a wide range of applications such as air pollution control, bio-decontamination, plasma-assisted combustion, material processing, surface treatment, and electromagnetic wave shielding. Desirable conditions are high electron densities (above 10^{12} cm⁻³) and relatively low gas temperatures (below 2000 K).

Various types of atmospheric DC or AC glow discharges as sources of nonequilibrium plasmas have received renewed attention during the past few years. The subject of our research is a direct current (DC) glow discharge in atmospheric pressure air as a source for VOC abatement. This type of atmospheric air DC glow discharges was studied previously in [1-4]. This discharge, also called high pressure glow discharge (HPGD), does not use dielectric barrier layers, and as such should not be identified with the recently widely investigated atmospheric pressure glow discharges (APGD). Our DC glow discharge has the advantage of producing relatively large volumes of fairly homogeneous plasma. In addition, DC operation enables an easy control of the current and plasma properties, making it attractive for various applications. Similar atmospheric air DC discharges were applied for the VOC abatement in [5-6].

In this paper, we provide general characteristics of a DC glow discharge in ambient atmospheric pressure air obtained by electrical and spectroscopic measurements. We then present this discharge type at low currents as a source for the abatement of volatile organic compounds (VOCs), following our previous studies [3,4]. Results from the original study performed at the LPGP, University Paris XI, France are combined with results obtained at Comenius University, Slovakia.

EXPERIMENTAL

We used two DC power supplies, placed in series with ballast resistors, to sustain the discharge: a Del High Voltage RHVS (60 kV, 5 mA) and Universal Voltronics Mintrol (30 kV, 150 mA). The ballast resistor was used to stabilize the discharge. Its value was chosen experimentally, typically about $500\text{ k}\Omega$, depending on the operating current. The discharge voltage was measured with a high voltage probe Tektronix T6015A (1000 x, 3 pF, 100 M Ω). The discharge current recorded across a $50\text{ }\Omega$ resistor and the discharge voltage measured by the probe were processed by digitizing oscilloscopes (400 MHz Tektronix DSA 602 and 500 MHz Tektronix TDS 544 A). The discharge was typically applied in point-to-plane geometry; we used rhodium points opposite to copper planes as electrodes.

Spatially resolved optical emission spectroscopy and electrical diagnostics were employed to characterize the discharge properties. An optical set-up shown in Figure 1 consists of a Jobin Yvon monochromator HR 640 (200-700 nm, resolution 0.1 nm) combined with a photomultiplier tube Hamamatsu C659S. The PMT signal is processed by a 400 MHz digitizing oscilloscope Tektronix DSA 602 linked with a PC. A digital camera Nikon Coolpix 990 was used for photo-documentation of discharges.

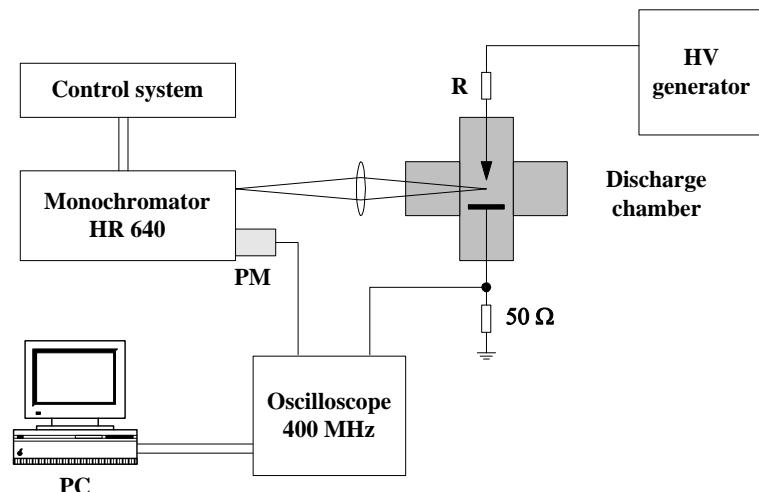


Figure 1 Schematic of the experimental set-up used for the emission spectroscopy of the DC discharge

Several types of discharge reactors were used for the VOC abatement. The principal reactor is a glass tube with 5 parallel rhodium points and one plane copper electrode, as shown in Figure 2. It allows operating from 1 to 5 parallel discharges. Each point is equipped with its own series resistor (usually $500\text{ k}\Omega$). All points are supplied from one high voltage generator. The interelectrode distance can be varied at each point independently.

The second discharge reactor is a glass tube with 5 point-to-plane gaps placed in series. It was developed in order to decrease the energy losses in the series resistors of each discharge. Another type of discharge reactor is a 50 cm long copper tube with a copper threaded rod central electrode. In this reactor, a long contact of the treated gas with the catalytic copper surfaces is allowed.

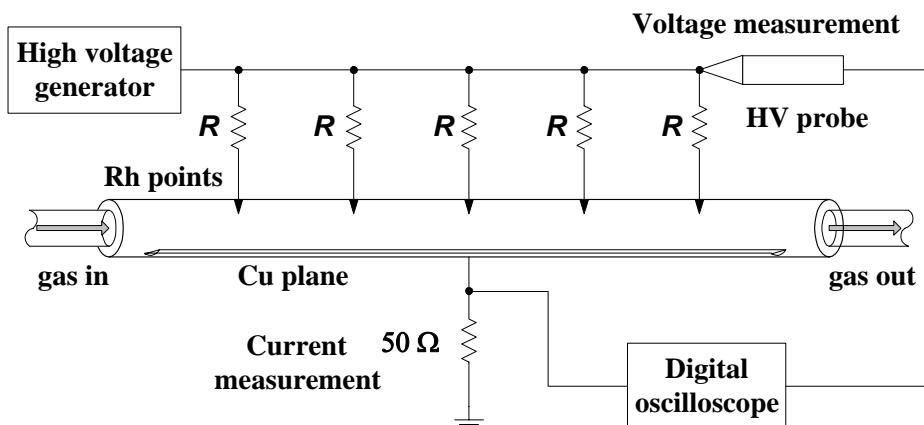


Figure 2 Glass tube reactor with 5 parallel points and its electric circuit

Cyclohexanone and toluene were chosen as VOC representatives due to their wide industry use and different properties. Their chemical structures are shown in Figure 3. Cyclohexanone is a non-aromatic cyclic compound that has been studied for the plasma abatement only in our previous work [3,4]. Toluene is an aromatic hydrocarbon that is the most typically studied VOC in plasma abatement processes.



Figure 3 Structural formulae of cyclohexanone and toluene

Experiments aimed at VOC destruction were carried out in the flowing dry or humid air. The gas flow system is shown in Figure 4. The air flux was divided into two or three branches controlled by the flowmeters Sho RATE Brooks with different ranges. One branch passes through a bubbler with a liquid VOC, thus enriching the air with the VOC vapours at their saturated vapour pressure. Another branch can optionally pass through the bubbler with water, thus providing water vapours at their saturated pressure. The adjustment of the flowmeters allows setting the VOC and H₂O concentrations in the gas. Usually, the relative humidity of the humid air was close to 100 % at a given temperature. The three branches rejoin in the mixing chamber. The air containing VOC vapours is then lead into the discharge reactor. The total gas flow rate can be varied; we typically operated within 1-10 slpm (standard litres per minute).

The infrared absorption spectroscopy was used as a main diagnostic method. We employed a Fourier transform infrared spectrometer (FTIR) Bruker IFS 45 working in the middle infrared region (4000-600 cm⁻¹) with best resolution of 0.5 cm⁻¹ and controlled with a PC, and a 10-cm long brass gas cell with KBr or CaF₂ windows. We alternatively used a long-path gas cell with adjustable optical length between 0.8 and 8 m, with gold mirrors and ZnSe windows. The long path cell allows detecting very low concentrations of the gaseous by-products. The spectrometer was equipped with the infrared microscope able to work in transmission or reflection regime. It allows analyzing liquid and solid samples and surfaces, especially deposits formed in the process and surfaces of the treated electrodes.

The concentration of VOCs was calculated from the absorbance of their calibrated characteristic bands in the infrared spectra. The calibration was based on their saturated vapour pressure. We used VOC concentrations from 500 to 6000 ppm, typically 2000 ppm. The temperature and the relative humidity were measured in the mixing chamber by a capacitive hygroscopic and thermometric probe Hanna HI 8564.

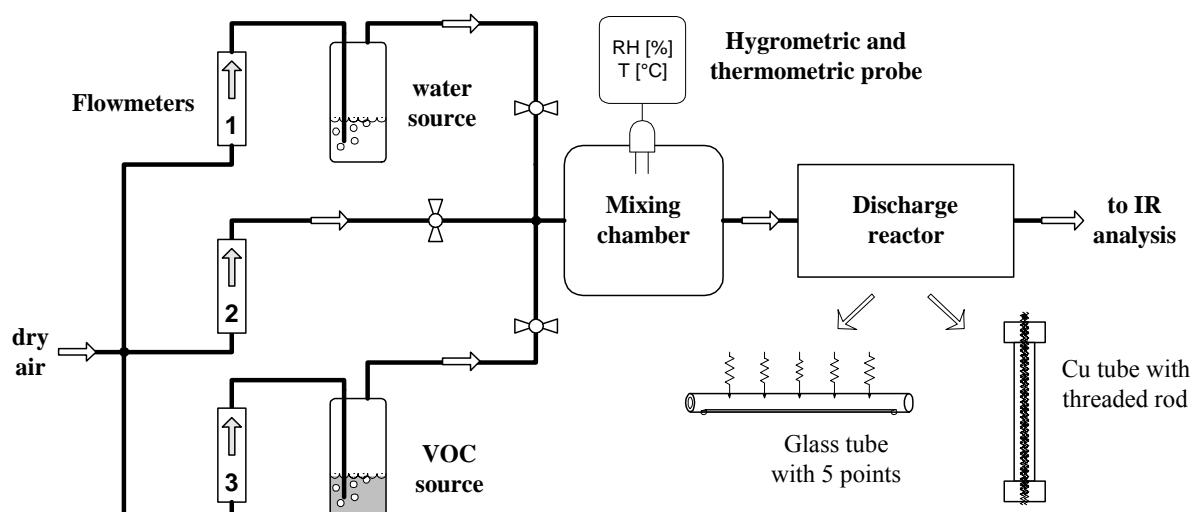


Figure 4 Schematic of the gas flow system.

DC GLOW DISCHARGE

The DC atmospheric pressure air discharge under study is a stable continuous discharge regime with no pulses. It operates with DC currents from 1.6 to several hundreds of mA, and DC voltages from a few kilovolts to a few hundred volts. The interelectrode distance can be varied from 1 mm to a few cm, depending on the gas flow conditions and the current. The voltage-current characteristic of the discharge in ambient air is descending, as shown in Figure 5 (left). In contrast, the discharge power increases with the current, as shown in Figure 5 (right).

The discharge is ignited by a streamer-to-spark transition, but the ballast resistor immediately limits the spark current. However, the ballast resistor is chosen experimentally so that the limiting current is large enough that the discharge, after extinction of the initial spark phase, enters a state of permanent conduction. The ballast-limited current then controls this pulseless discharge regime. The electrode material is not crucial for the discharge mechanism. The electrodes with small radius of curvature (pins) permit easier discharge ignition. The point polarity also does not significantly influence the discharge properties.

Figure 6 shows a photograph of a typical DC glow discharge in ambient air at atmospheric pressure operating at low flow velocity (about 0.2 m/s) and a current of 5 mA, with the interelectrode distance of 7 mm.

We recorded the spectra emitted by the DC air discharge in the UV-VIS region for various discharge parameters. The N₂ (C³Π_u-B³Π_g) spectral system was then used to measure the rotational and vibrational temperatures, T_r and T_v , by comparison with simulated spectra. In atmospheric pressure plasmas, the rotational temperature is close to the gas temperature ($T_r \approx T_g$) owing to fast collisional relaxation. The gas temperature T_g , measured at the centerline of the discharge column, varies typically in the range of 1500-2500 K. The current and the gas flow velocity control the power density deposited in the discharge, and thus the gas heating. At a given low flow velocity of ambient air through the discharge, T_g increases and T_v decreases with increasing current, as shown in Figure 7. The measured vibrational temperatures T_v of the excited states are around 4000 K. These temperatures are higher than the gas temperature and therefore suggest that the plasma is in a state of thermal nonequilibrium.

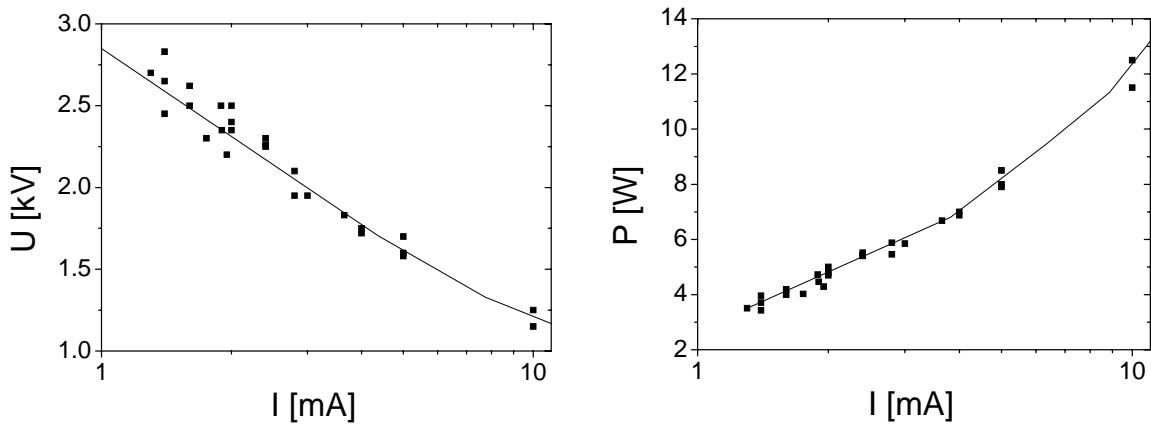


Figure 5. Voltage-current characteristic (left) and the discharge power as a function of current (right) of a DC glow discharge in ambient air. Interelectrode distance $d = 7$ mm.

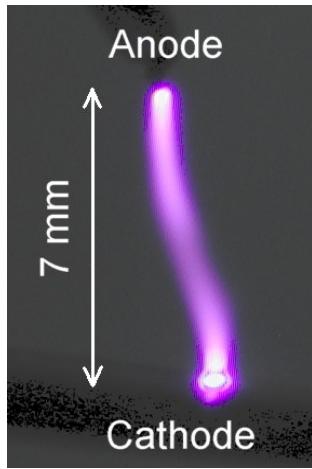


Figure 6. DC glow discharge in ambient atmospheric pressure air, $I = 5$ mA, $U = 1.7$ kV, $d = 7$ mm.

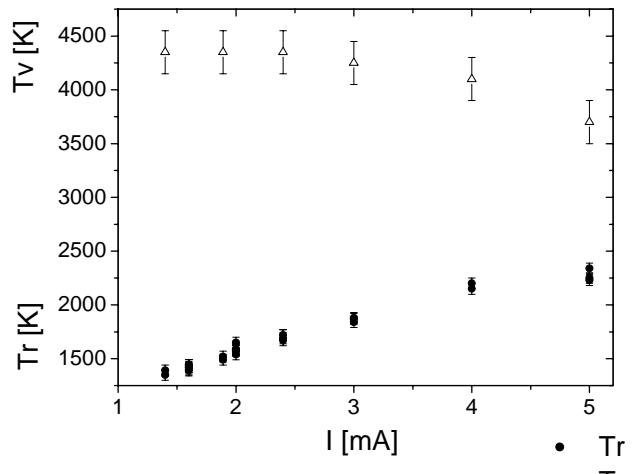


Figure 7. Rotational and vibrational temperatures as functions of the discharge current in ambient air at low flow velocity $v \approx 0.2$ m/s, $d = 7$ mm.

Besides temperature measurements, optical emission spectroscopy diagnostics also provides the spatial distributions of emission intensity. The axial emission intensity profiles indicate the stratification into dark and bright layers, typical of low pressure glow discharges [10]. The bright and dark regions near the cathode are reminiscent of the negative glow and the Faraday dark space, although their dimensions seem quite large to identify them without further analysis. Nevertheless, the positive column occupies most of the interelectrode space. The electric field strength E is approximately uniform in the positive column. It decreases from 3000 to 300 V/cm as the current is increased, thus leading to a falling voltage-current characteristic (Figure 2). The voltage drop across the very thin region next to the cathode is close to 370 V, a typical cathode fall of glow discharges in air with Cu cathode [7].

The radial emission intensity profiles were used to measure the diameter of the positive column. The discharge diameter is then used to estimate the plasma volume and the current density j . Knowledge of E , j and the gas density (calculated from the measured T_g) enables us to estimate the plasma conductivity, hence the electron density n_e , using Ohm's law [1,7]. The measured discharge diameters range from 0.4 to 3.3 mm, depending on the current, the

gas flow velocity, and the gas temperature. The corresponding current densities j are between 0.1 and 10 A/cm² and the estimated electron densities n_e are in the range of 10¹²-10¹³ cm⁻³. The measured j is lower than the typical current densities of arcs. Also the measured cathode fall is typical of glow discharges. Moreover, the high values of n_e at gas temperatures between 1500 and 2500 K confirm the departure from thermal equilibrium, since the LTE values of n_e in atmospheric pressure air are about 10², 10⁶, and 10⁹ cm⁻³, for the temperatures of 1500, 2000, and 2500 K, respectively.

VOC ABATEMENT PROCESS

The studied DC discharge of both polarities was applied for the abatement of selected VOCs in dry and humid air. We characterise the process by these fundamental parameters:

- (a) Removal efficiency (or removal rate) η [%],
- (b) Energy density (or specific energy input) w [J/l],
- (c) Energy costs R_{mol} [eV/molecule or kWh/kg],
- (d) Character and concentration of products.

In the glass tube reactor with 5 discharges, the achieved removal efficiencies vary from 30 to 96 % for cyclohexanone and from 13 to 77 % for toluene. We observed almost no influence of the initial VOC concentration to the removal efficiency. The removal efficiency increases with increasing energy density w in a logarithmic trend for both studied compounds in any initial concentration, in dry as well as humid air, as shown in Figure 8 (left).

Discharge energy costs R_{mol} as a function of w for cyclohexanone treatment are shown in Figure 8 (right). These curves are very similar for toluene. With both VOCs, R_{mol} increases with w exponentially. Therefore, to decrease the energy costs it is better to work at low w , although η is lower. Figure 8 also shows little differences between the effects of positive or negative discharge polarity and the presence of moisture. However, the humid air and the negative polarity yield slightly higher efficiency and lower energy costs for the same w . This is probably caused by an enhanced formation of highly reactive OH radicals in the humid air.

VOCs treated by HPGD in the glass tube reactors were converted to some gaseous and some condensed products. Their character and concentrations depend on the discharge polarity, presence of moisture in the carrying air, VOC type and its initial concentration, and especially on the energy density dissipated in the reactor. The typical gaseous products were CO₂ and H₂O, as well as noxious by-products such as CO, NO₂ and NO. In trace amounts we also detected HCHO, HNO₂, N₂O, and alcohols (methanol, ethanol); in humid air sometimes HNO₃. A representative FTIR spectrum of 2000 ppm cyclohexanone air mixture before and after the negative HPGD treatment in the 5-point reactor is shown in Figure 9.

The produced CO₂ concentrations increase with the increasing w . CO₂ concentrations of 600-6000 ppm were formed from 2000 ppm cyclohexanone, and 800-15000 ppm from 2000 ppm toluene. CO production first increases with w , then reaches the maximum (at ~2500 J/l for cyclohexanone and ~1500 J/l for toluene) and finally decreases. Produced CO concentrations were 600-1600 ppm for cyclohexanone and 500-2500 ppm for toluene, slightly lower in the humid air. The CO/CO₂ ratio decreases with w for both compounds and discharge polarities, being lower in the humid air. For cyclohexanone, CO/CO₂ is from 1.5 to 0.1. In toluene treatment we get lower CO/CO₂: from 1.2 to 0.05. The lower is the CO/CO₂ ratio the closer to the perfect combustion is the process.

Production of NO_x is typical for combustion-like processes occurring in air, including plasmas. NO₂ and NO production in the studied discharge increase with w in both polarities and in dry as well as humid air. NO₂ production in the glass tube 5-point reactor was 100-400 ppm, NO was produced within 0-1200 ppm. The lowest NO_x production occurred in the negative HPGD and humid air, the presence of water vapours reduces the NO_x production.

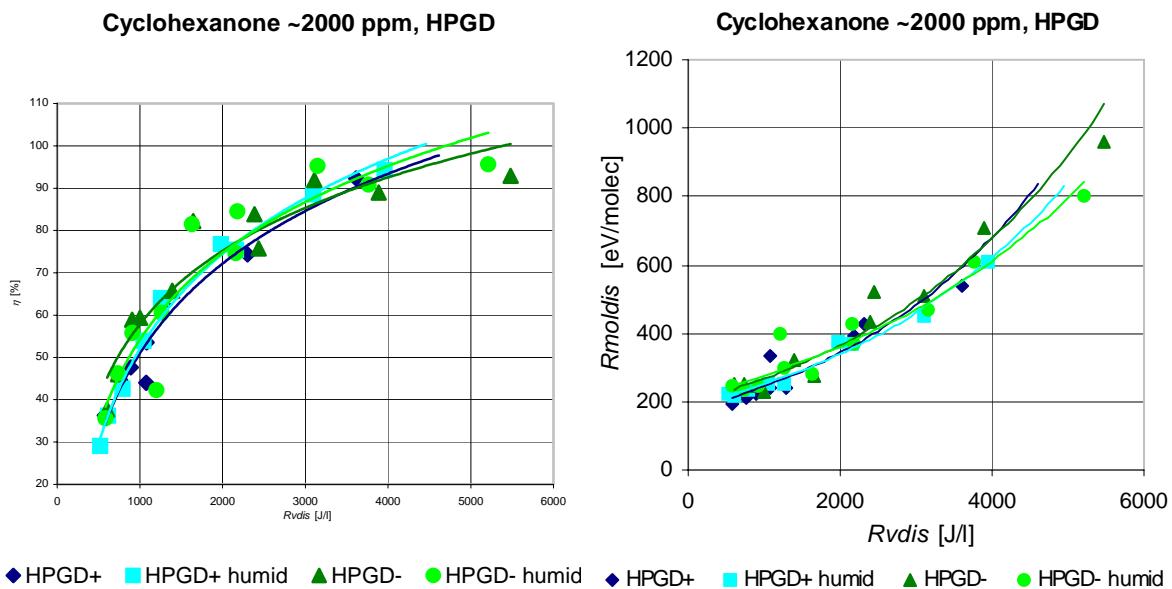


Figure 8 Removal efficiency η (left) and energy costs R_{moldis} (right) as functions of the energy density w . Both polarities of HPGD in the 5-points glass tube reactor in dry and humid air.

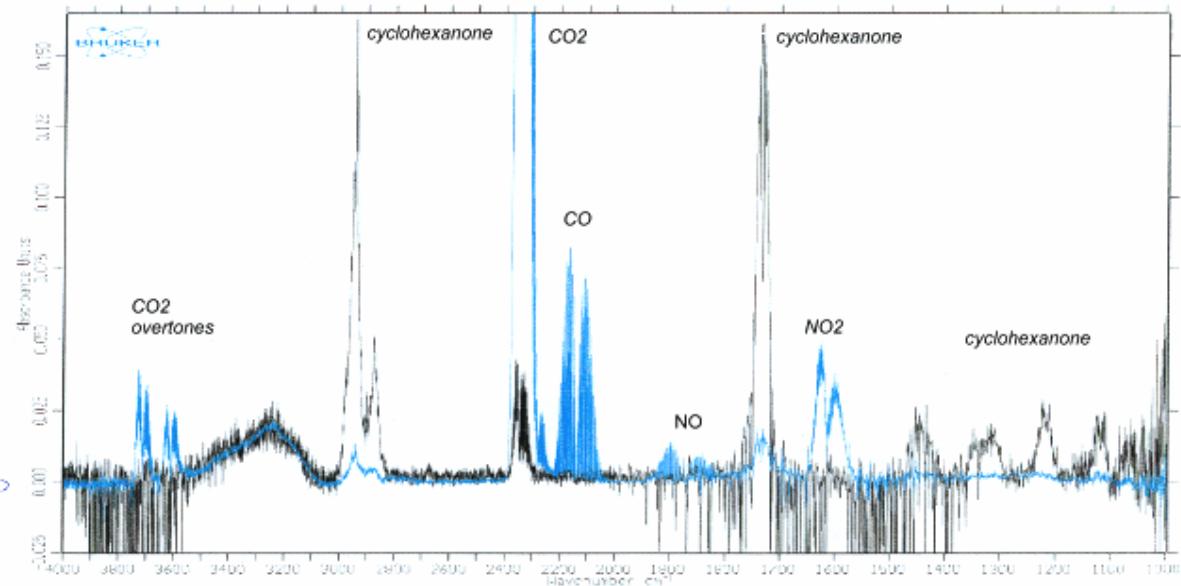


Figure 9 FTIR spectrum of cyclohexanone (2000 ppm) in humid air before (black) and after (blue) negative HPGD treatment in the 5-point reactor. Bands of the dominant gaseous products are identified.

The carbon balance, i.e. the ratio between the carbon converted to the gaseous products and the total treated carbon, varies from 40 % at low w to 80 % at high w , which corresponds to 20-60 % of the treated carbon being converted to non-gaseous products. In the negative polarity and at high w , this ratio approaches 100 %. The more thermal process leads to the greater formation of gaseous products, while at low w the process preferentially leads to the condensed products. In air pollution control, condensed products are generally avoided, while CO_2 and H_2O are the most desired. Nonetheless, the production of toxic CO and NO_x usually accompany VOC removal processes, and certain amounts of condensed products or aerosols are also unavoidable. Furthermore, regarding CO_2 as the main contributor to the Earth's enhanced greenhouse effect leads us to introduce a novel approach in the pollution control techniques: non-toxic condensed products may be more convenient than the gaseous products.

Besides gaseous products discussed above and aerosols, we detected liquid and solid deposits on the electrodes and reactor walls. They were extensively analyzed by the infrared absorption spectroscopy, electron and optical microscopy. Condensates of different composition were formed at various parts of the reactor, depending on the surface properties and the distance from the discharge channels. The deposits contain C=O, OH, COOH, NH, NH₂, -CO-NH- or -CO-N<, CH₂, COO⁻, C-O-C and -NO₂ groups. Their presence indicates that the deposits are complex organic structures, very probably containing amino acids. We observed that the amino acids are preferentially formed on the Cu electrode surfaces that seem to have certain catalytic effects in the process. These effects were confirmed in the Cu tube reactor where the surface of the Cu electrodes is considerably larger than in the glass tube reactors, thereby allowing better contact of the treated gas with the charged Cu surfaces. As a result, VOCs were destroyed at lower energy costs and we obtained lower concentrations of gaseous products and aerosols and larger amounts of condensates containing amino acids.

CONCLUSIONS

We presented a stable atmospheric pressure DC discharge in ambient air. The discharge properties are those of a glow discharge, with a distinct cathode layer and positive column. This type of discharge provides a source of highly ionized nonequilibrium air plasma with electron number densities of the order of 10^{12} - 10^{13} cm⁻³, and gas temperatures of 1500-2500 K. The ease of DC operation and convenient properties of the generated plasma make this discharge attractive for many applications, including pollution control.

The DC discharge was tested for the abatement of selected VOCs in glass and copper tube reactors. Removal efficiency increases logarithmically with the energy dissipated in the reactor, reaching as high as 95 %. The energy costs also increase with the energy density, reaching 200-1000 eV/molecule. Main gaseous products are CO₂, CO, H₂O, and NO_x. Their concentrations depend on the initial VOC concentration, presence of moisture, reactor properties, and the injected energy density. The VOC removal process is partially similar to the combustion characterised by a relatively low CO/CO₂ ratio. The negative discharge polarity and humid air result in the highest efficiencies, the lowest energy costs and the lowest concentrations of noxious outlet gases. A non-negligible part of the treated carbon from VOCs transforms to the condensed products. The DC glow discharge used for the pollution control is neither a typical low temperature plasma application, nor a thermal plasma process, but something between them. The thermal VOC decomposition is coupled with radical-induced volume reactions and heterogeneous surface reactions.

ACKNOWLEDGEMENTS

The original work at University Paris XI was conducted during the Ph.D. studies of Z. Machala and was funded by a scholarship of the French government. The work performed at Comenius University was funded by VEGA 1/0256/03 grant of the Slovak grant agency.

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