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EFFECT OF OXYGEN CONTENT ON VOC ABATEMENT IN DC-DRIVEN DISCHARGES

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Summary: We investigate the effect of oxygen content in the carrier air on the VOC (toluene) abatement induced by DC-driven discharges in atmospheric pressure air and nitrogen. The discharges used are a glow discharge and a transient spark, both generating non-thermal plasmas with gas temperatures of 1000-2000 K. The discharge properties, as well as the VOC abatement process are sensitive to the oxygen content. The removal efficiency related to the energy density increases with the increasing oxygen content, leading to oxidation products such as CO_x, H₂O and NO_x. However, the VOC abatement is feasible at the reduced oxygen content, or even in nitrogen. In such atmospheres, less oxidation products are formed, thus promoting the formation of unsaturated hydrocarbons, and condensed products. Water vapours in the carrier gas optimize the process by slightly increasing the efficiency and significantly reducing the noxious outlet gases due to the effect of OH radicals.

Key words: atmospheric non-thermal plasma, DC discharges, VOCs, oxygen, nitrogen

1 Introduction

Non-thermal atmospheric pressure air plasmas present considerable interest for a wide range of applications, including air pollution control. Many works deal with the abatement of volatile organic compounds (VOCs) by means of various electric discharges generating such non-thermal plasmas. Our research is focused on direct current (DC) driven discharges in atmospheric pressure air. We have been extensively studying the physical properties of two new types of streamer-induced electric discharges operating in the non-uniform electric field: a DC glow discharge and a transient spark. Both these discharges generate non-thermal plasmas with the gas temperature in the range of 1000 to 2000 K. A detailed description of these discharges can be found in [1-4].

The discharges have been successfully tested for the abatement of VOCs, as described in our previous works [1, 3-4]. The objective here is to investigate the effect of oxygen content in the carrier air on the behaviour of the studied DC-driven discharges, and consequently on the VOC abatement (deVOC) process. These investigations were in part motivated by interesting results of Falkenstein and Snyder et al. who found out that the deVOC process is the most effective in air with the oxygen content reduced to 2 % and 0.3 % for toluene and TCE (C₂HCl₃), respectively [5], or 2-3 % for chlorobenzene [6], both in dielectric barrier discharges. They explain these results by an optimal radical utilisation for VOC decomposition, which occurs at low O₂ concentration, rather than the ozone production. O₂ is a donor of atomic oxygen that reacts quickly with the VOCs. However, the excess of O leads to the dominant formation of ozone that reacts with the VOCs slowly. Furthermore, Hensel et al. [7] reported the removal of formaldehyde by DC corona discharge more effective in air but in the spark discharge more effective in nitrogen.

2 Experiment and Results

The experimental setups, the electric circuits, the discharge reactors, the gas flow system, and the FTIR absorption spectroscopic analysis are in details described in our previous works [1-4]. The experiments described here were performed in a glass tube reactor with 5 parallel rhodium points opposite to the common plane copper electrode, depicted in [4].

Toluene was chosen as a VOC representative in this study, in concentrations of about 2000 ppm. DeVOC experiments were carried out in the flowing dry or humid air with varying oxygen content: oxygen rich atmosphere ($30\pm 2\%$ O₂, $70\pm 2\%$ N₂), normal air (21% O₂, 78% N₂), oxygen poor atmosphere ($5\pm 2\%$ O₂, $95\pm 2\%$ N₂), and pure N₂. Humid atmospheres contained water vapour at its saturated vapour pressure.

Discharge properties with respect to the oxygen content

The DC glow discharge and the transient spark in atmospheric pressure air have been extensively studied in our previous works [1-4]. The DC glow discharge typically operates at several kV with currents above 2 mA. The transient spark is typical for ~ 100 ns short current pulses, mean currents below 1 mA, and frequency in kHz range. Both discharges generate non-thermal plasma with the gas temperature depending on the dissipated energy; in the glow discharge starting from 1600 K, and in transient spark from 1000 K. Both discharges in air emit UV-VIS radiation with the dominant N₂ 2nd positive system (C-B).

With reducing O₂ content the discharges become more stable and allow operating at lower currents. The glow discharge in pure N₂ is very stable even at currents below 1 mA; the gas temperature is consequently lowered to 600-1200 K. In N₂, besides N₂ 2nd positive system we observed a strong emission of N₂ 1st positive system (B-A), thereby leading to a large population of the N₂ (A) metastable state, which then acts as the energy supply (~ 6 eV) in the deVOC process.

The discharge properties in air with VOC admixture and/or water vapours do not substantially differ from pure dry air. With the reduced O₂ content and especially in N₂, however, humidity or even a small VOC admixture significantly affects the discharges. They become less stable and require larger currents for normal functioning. Strong CN violet emission indicates the formation of CN radicals. Similarly, OH emission indicates the presence of OH radicals in humid N₂.

VOC abatement with respect to the oxygen content

The studied DC-driven discharges of both polarities were applied for the abatement of toluene in dry and humid air, as well as in the atmospheres with increased and reduced oxygen content (0-30 % O₂). We characterise the VOC abatement (deVOC) process by these fundamental parameters: (a) removal efficiency (removal rate) η [%], (b) energy density (specific energy input; i.e. power divided by gas flow rate) w [J/l], and (c) products.

In normal air, the achieved removal efficiencies η of toluene varies from 13 to 77 %. The η increases with the increasing energy density w in both polarities, and in dry as well as humid air. This increase is not linear; we observe a saturation effect. Humid air and the negative polarity yield slightly higher efficiency for the same w . These results are described in detail in [4].

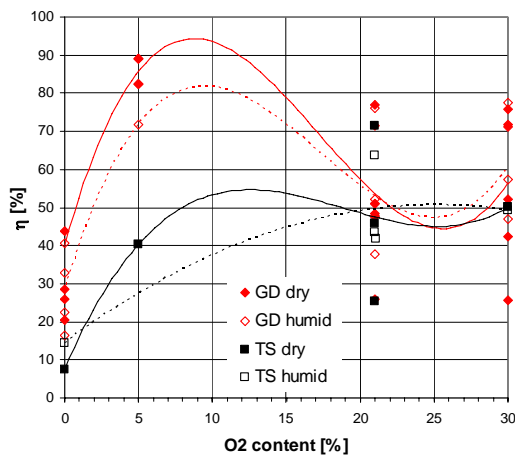


Figure 1. Removal efficiency as a function of O_2 content for glow discharge and transient spark in dry and humid atmospheres.

The removal efficiency η as a function of the O_2 content is shown in Figure 1. Experimental points are rather scattered to draw any straightforward conclusions, however, some trends may be observed. The glow discharge in both dry and humid atmosphere demonstrates the maximum efficiency at the reduced O_2 content. The dry transient spark behaves similarly, but in the humid case displays a monotonic increasing trend for η .

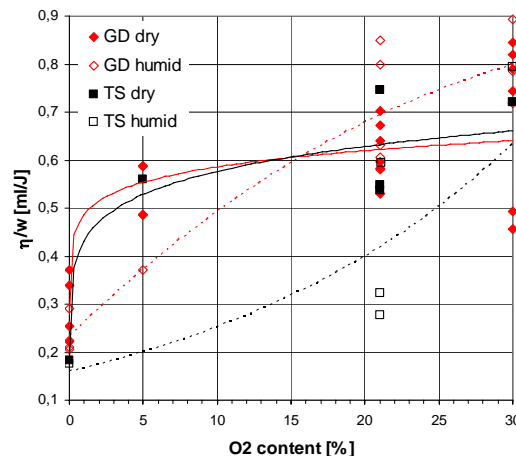


Figure 2. Removal efficiency normalized by energy density as a function of O_2 content for glow discharge and transient spark in dry and humid atmospheres.

When depicting η vs. O_2 content curves we must take into account that η is primarily governed by the energy density w . We therefore normalized η by w , as shown in Figure 2. With both discharges in dry atmospheres, the normalized efficiency η/w increases with O_2 content in a logarithmic trend and no more maxima at the reduced O_2 are observed. In humid atmospheres, η/w increases with the O_2 content more steeply.

Since the typical gas products from the deVOC process in air (CO_2 , CO , H_2O , NO_2 , NO) contain oxygen, the O_2 content strongly influences their character. The more oxygen is present, the more CO_x , H_2O , and NO_x are produced. On the other hand, lower concentrations of noxious products such as CO and NO_x are produced in humid atmospheres.

In nitrogen, obviously no oxygen-containing products were formed but hydrogen cyanide (HCN) and acetylene (C_2H_2) were detected. In the humid N_2 , HCN formation was suppressed and C_2H_2 formation enhanced. Some CO_2 , CO and NO were found in low concentrations, obtaining the necessary oxygen from the dissociated H_2O vapours. The typical IR spectra of the gas products from toluene abatement in dry and humid N_2 are shown in Figure 3 and Figure 4.

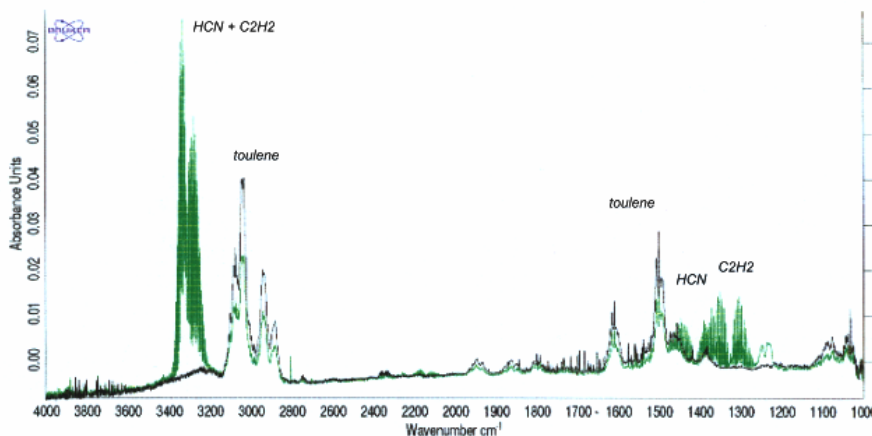


Figure 3. FTIR spectrum of toluene before (black) and after (green) the glow discharge treatment in dry N_2 .

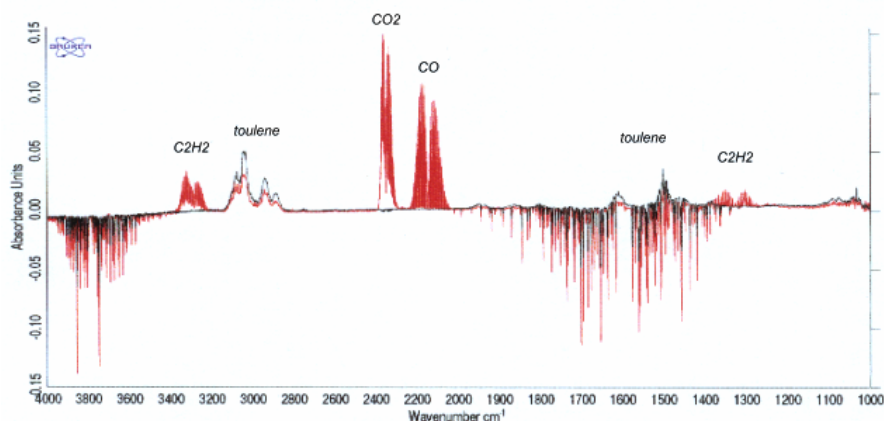


Figure 4. FTIR spectrum of toluene before (black) and after (red) the glow discharge treatment in humid N_2 .

Solid and liquid deposits of the deVOC process in normal air were described in more details in [4]. Similar condensed products were formed in oxygen rich and oxygen poor atmospheres. By FTIR absorption spectroscopy we detected amino acid and amide structures, aromatic rings and nitro-groups. In oxygen poor atmospheres and in nitrogen, the deposits contained also unsaturated CN structures ($N=C=N$ and $C\equiv N$). In N_2 and N_2+H_2O atmospheres, a solid black powder grew quickly on both electrodes. Infrared absorption analysis showed no bands of this powder in $4000-600\text{ cm}^{-1}$ region which indicates that the powder is a pure, probably amorphous carbon (symmetric C-C groups are inactive in IR). In humid N_2 , a black deposit layer covering the Cu electrodes contained besides carbon, amine (NH, NH_2), C-N, C-O, and amino acid groups.

3 Discussion and Conclusions

Our experiments with the DC glow discharge and the transient spark in atmospheres with varying oxygen content showed that the discharge properties change with the reducing O_2 content; the discharges become more stable. This effect is due to the reducing rate of electron attachment to oxygen atoms and molecules, which is the dominant loss mechanism of electrons.

The efficiency of the toluene abatement in the DC discharges, normalized by the energy density, increases with the increasing oxygen content. Thus, we did not confirm the favourable effect of the reduced O_2 content reported by Falkenstein [5] and Snyder et al. [6]. Our DC here generate plasmas with relatively high gas temperatures (up to 2000 K), so the oxidations dominate in the deVOC process. In addition, no ozone was detected due to these temperatures, and so the mechanism of ozone scavenging the O atoms in the excess of oxygen does not apply.

On the other hand, the reduced O_2 content results in reducing the concentrations of the noxious gas products such as NO_x , and promotes formation of the condensed products. Reduced oxygen and Cu electrode surfaces seem to be favourable for the formation of amino acid structures, in agreement with Hanic et al. [8]. The noxious gases can be substantially lowered by adding water vapours at any oxygen content. This is most likely due to the oxidation effect of OH radicals efficiently reacting with VOC molecules.

In nitrogen (0 % O_2), the achieved removal efficiency is low, yet VOCs are destroyed even without oxygen present. Both N radicals and energetic $N_2(A)$ metastables that are not quenched by oxygen species may be responsible for the attack of VOC molecules in nitrogen. Such a process leads to unsaturated products such as HCN and acetylene, and formation of the amorphous carbon, because it is similar to the carbonisation with the discharge as a thermal source.

In summary, the VOC abatement by the DC glow discharge and the transient spark is feasible in normal air, oxygen rich and oxygen poor atmospheres, and even in nitrogen. With respect to the removal efficiency and the products, the process is optimal in normal humid air.

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