

Influence of water vapour on acetaldehyde removal efficiency by DBD

A. S. CHIPER^{a*}, N. B.-SIMIAND^b, F. JORAND^b, S. PASQUIERS^b, G. POPA^a, C. POSTEL^b

^aPlasma Physics Department, Faculty of Physics, "Al. I. Cuza" University, Bd. Carol I, No. 11, 700506 Iasi, Romania

^bLaboratoire de Physique des Gaz et des Plasmas, Université Paris XI, Bât. 210, 91405 Orsay Cedex, France

A dielectric barrier discharge (DBD) in cylindrical geometry working in air at atmospheric pressure and operating in the filamentary mode has been used for Volatile Organic Compounds (VOC) decomposition (namely, acetaldehyde). The DBD has been characterised by discharge voltage, transferred electrical charge and specific energy deposited into the gas. Efficiency of the DBD for the acetaldehyde decomposition has been determined for different types of the applied voltage (AC and pulsed) to the DBD reactor in dry air and humid air, by chromatographic measurements.

(Received October 14, 2005; accepted January 26, 2006)

Keywords: DBD, Acetaldehyde removal, Dry and humid air

1. Introduction

The DBD generates a non-equilibrium plasma at atmospheric pressure following application of a high voltage, of AC or pulsed type, to special system of electrodes [1,2]. Briefly described, the DBD consists of plasma microfilaments which are established following the propagation of ionization fronts, usually called streamers, in multiple places in the gas volume. These filaments have a very short lifetime, in the order of a few tens of nanoseconds. Each one is a narrow cylindrical channel (radius of the order of 100 μm). The exchange of energy between electrons and molecules takes place mainly during the phase of discharge development, namely during the propagation of the streamers. Electrons (average energy of some eV) excite the molecules and then transform a share of their kinetic energy into energy stored by excited species and free radicals (by dissociation of molecules). Therefore, like other type of transient discharges, non-thermal plasmas of DBDs have the advantage of decreasing the energy necessary for the elimination of the pollutants in air compared to more traditional techniques like thermal decomposition.

The capacities of a DBD to break up Volatile Organic Compounds (VOCs) were already shown [3-5], but much of work remains to be made to achieve a full understanding of the physico-chemical mechanisms responsible for this decomposition. For some VOCs like aliphatic hydrocarbons, alcohols, or aldehydes, it seems clear that production of oxygen atoms and hydroxyl radicals in the plasma leads to the removal of the undesirable molecule through oxidation processes. The higher the specific electrical energy deposited in the gas mixture (in Joule/litre), the higher the radical production and removal efficiency of those molecules. However, following recently published investigations on the removal of NO in air [6], one can expect that the removal

efficiency of the above mentioned VOCs should not only depend upon the specific energy value, but also upon other discharge parameters such as the number of streamers per unit volume and the energy deposited in each micro-discharges. At the same time, the presence of the additives into the gas discharge reactors increases removal efficiency of the VOCs [7]. As additives we have choose one of the most widely used additives, namely water vapour.

2. Experimental set-up and experimental conditions

The whole experimental set-up (Fig. 1), which was constructed for evaluate the removal of acetaldehyde from air, is composed of three different parts: (i) a continuous gas flow generating system, (ii) a DBD reactor, and (iii) a gas sampling analysis and detection system.

The acetaldehyde was vaporized by flowing part of the air (2.5 sccm) above liquid acetaldehyde, kept at a constant temperature ($-35\text{ }^{\circ}\text{C} \pm 0,5\text{ }^{\circ}\text{C}$) in a cooled alcohol - water mixture. The gas flow rates of each component, as air with acetaldehyde and air with or without water vapour, were kept constant using mass flow controllers. The value of the total gas flow rate was 602.5 sccm and the residence time was 0.97 s. All experiments were performed at atmospheric pressure and room temperature.

The DBD reactor was made of a pyrex tube (relative permittivity $\epsilon_r=4.6$). The inner diameter of this tube was 11 mm and the wall thickness was 1.6 mm. The high voltage electrode was the central electrode, which was made of stainless steel screw rod with 3 mm diameter. The grounded outer electrode was made of stainless steel wire mesh and covered up the outside of the dielectric.

This electrode was 10.7 cm long, while the inner one and the pyrex tube were 40 cm long.

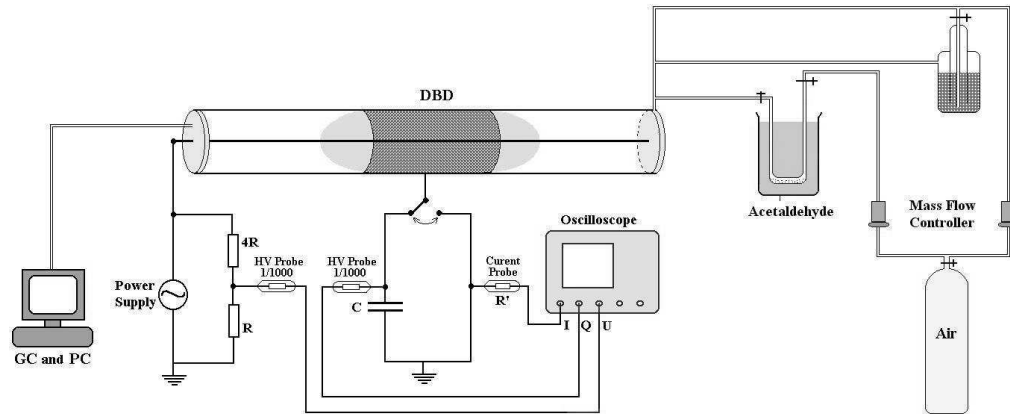


Fig. 1. Experimental set-up.

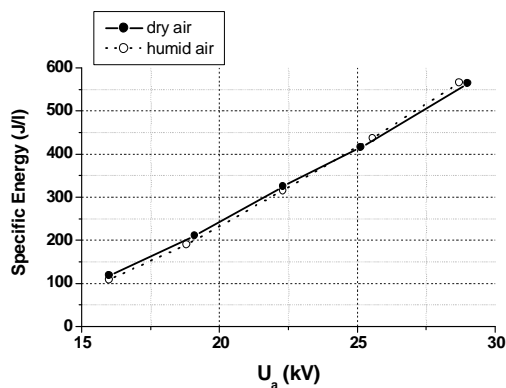


Fig. 2. Specific energy versus applied voltage, for AC generator, in dry air and humid air.

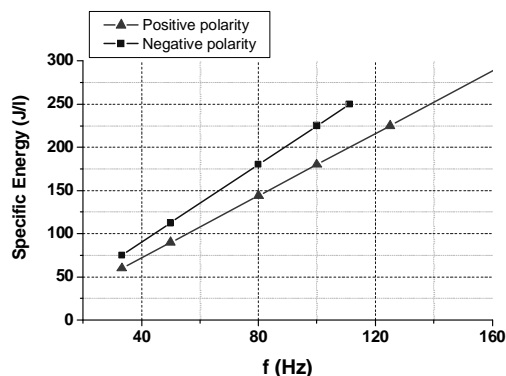


Fig. 3. Specific energy versus frequency, for pulsed generator, in dry air.

The treated gas mixture was flowing from the DBD reactor to the gas analysis apparatus (Micro Gas Chromatograph VARIAN CP-4900) equipped with a thermal conductivity detector. The Micro GC has three columns. Two of them are identical, molsieve, but with different carrier gases (He and N_2 respectively). The third chromatographic column is a CP-PoraPLOT Q and the carrier gas is He. Using the Micro GC by-products such

as: CO , CO_2 , H_2O , $HCHO$ have identified and their concentration measured after appropriate calibration of the apparatus.

The electrical energy was supplied by a high voltage AC generator (peak voltage value up to 30 kV, working at a frequency of 50 Hz) or by a pulsed high voltage generator (peak voltage value up to 30 kV, voltage pulse duration 2 μs , working at a frequency between 10 Hz and 10 kHz).

We have used two different modes of excitation for DBD reactor: a high voltage AC generator and a pulsed high voltage generator; in this way we have obtained an AC DBD discharge and a pulsed DBD discharge. We have measured the electrical power deposited into the discharge and then we have calculated the specific energy (E_s) as ratio between the electrical power deposited into the discharge and the volume flow rate. We have observed that, for the AC generator, the specific energy increases linearly when the peak voltage value increases from 14 kV up to 30 kV (Fig. 2). For the pulsed high voltage generator, the electrical energy per pulse is almost constant for a frequency varying between 20 Hz and 200 Hz, therefore the energy increases linearly with the frequency (Fig. 3).

For AC DBD discharge (Fig. 2) the electrical power was determined using the well-known Manley's method of Lissajous figures [9]. At the same time, it can be observed that the specific energy increases when the applied voltage increases, and that it does not depend on the relative humidity value (0 or 40 %). The maximum value is 600 J/l at 30 kV peak voltage, for a constant mass flow rate.

3. Results and discussions

It is well know that the additives are introduced into the gas discharge reactors in order to enhance the VOC removal. As additives we have choose one of the most widely used additives, namely H_2O .

The acetaldehyde removal by DBD has been studied as function of the presence of the water vapour (45 % RH) in air. Initial acetaldehyde concentration (before the discharge) was 343 ppm. Results are plotted in Fig 5. It can be observed on this figure that acetaldehyde removal by DBD in humid air is higher than that in dry air (Fig. 4), for the same value of the specific energy. The presence of water vapour increases the CH₃CHO removal in the whole range of specific energy value studied, for any generator used.

For conditions of the experiment, it has been found that the removal of acetaldehyde is more efficient when we have energised the DBD reactor with a pulsed generator by comparison with the case of the AC power supply. This is probably due to the fact that the discharge current pulses are very different, i.e. one very short intense current in the pulsed case, and a great number of much less intense current pulses in the AC case. Streamers are probably more intense in the pulsed case, or more numerous per unit volume, leading to a higher production of oxygen atoms which leads to a higher oxidation rate of acetaldehyde for a given value of the specific deposited electrical energy. This result is similar with those obtained for other VOCs [7,10].

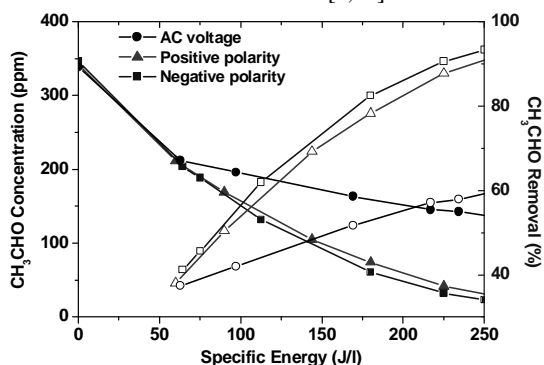


Fig. 4. CH₃CHO concentration and CH₃CHO removal at the exit of the DBD reactor, in dry air.

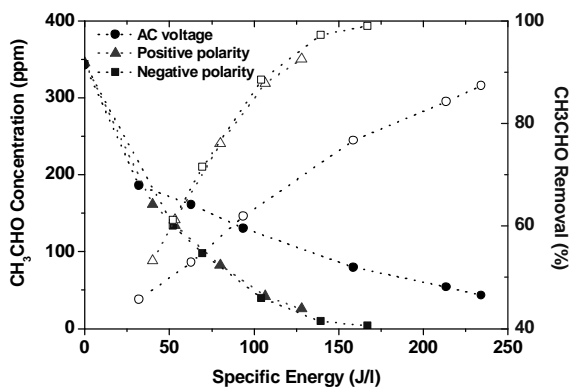


Fig. 5. CH₃CHO concentration and CH₃CHO removal at the exit of the DBD reactor, in humid air.

When we increase the water percentage in air, we observe a small decrease of the electrical charge. This is emphasised in Fig. 6 on which are plotted the time evolution of the charge at different values of humidity together with the applied voltage. Thus the number of electrical charges in the discharge volume decreases. It should be explained by electron attachment on water molecules, i.e.



Moreover, the breakdown voltage increases when water vapour is added to air and that should lead to an increase of the average electron energy from DBD in humid air compared to that in dry air.

Because the electrical charge decreases weakly when the percentage of water in air increases (Fig. 6), and the power deposited in the DBD is approximately the same in dry and humid air (see [8]), we presume that the difference in acetaldehyde removal in wet air by comparison with the DBD in dry air is only due to different oxidation pathways of the CH₃CHO molecule in the two gas mixtures.

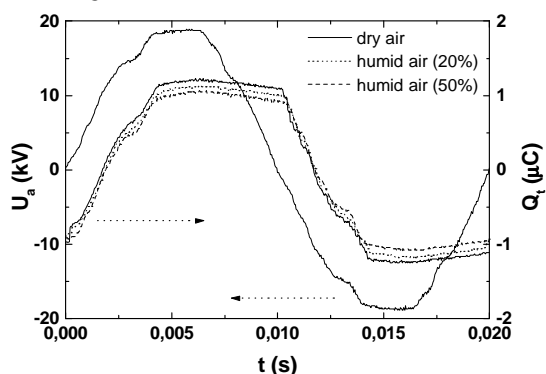
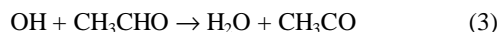


Fig. 6. Time evolution of electrical charge, for different humidity of air.

The two following reactions contribute to oxidise the acetaldehyde molecule [8]:



In absence of water in the mixture, the hydroxyl radical is produced by reaction (2) and also by others, which involve various chemical species, produced in the afterglow. However, for wet air, OH is of course also produced by dissociative electron collisions on H₂O (eq. 1). This is probably the reason why the decomposition of acetaldehyde in humid air is more efficient as compared to the decomposition in dry air. Works are in progress in order to validate this kinetic explanation.

In humid air, by-products identified by chromatographic measurements, at the exit of the DBD reactor, are approximately the same as those from DBD in dry air, namely: CO₂, CO, H₂O, HCHO. Amongst by-products following the VOC oxidation, only

concentrations of CO₂ and CO are significant (for details, see [11]).

In Fig. 7 are plotted the CO and CO₂ concentration values at the exit of the reactor for the two types of gas mixture. The concentration of by-products following the VOC oxidation by the DBD in humid air is approximately double comparatively to that in dry air. On the other hand, these two figures show that the ratio between CO₂ and CO concentrations is approximately 1.2:1 both for dry air and for humid air, except the AC DBD reactor where this ratio increases slowly from 1.6:1 in dry air to 2:1 in humid air (see Table 1).

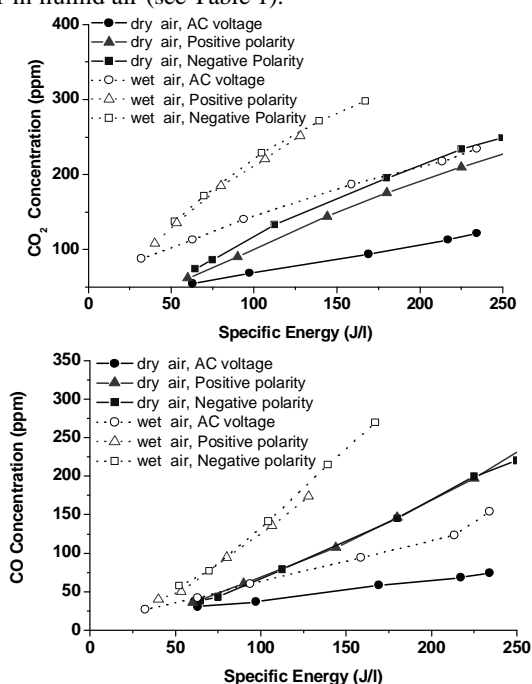


Fig. 7. CO₂ and CO concentrations at the exit of the DBD reactor, in dry and humid air, for 343 ppm initial concentration value of CH₃CHO.

In Table 1 are given the ratio between CO₂ and CO concentration values at the exit of the DBD reactor in dry and humid air, for an initial acetaldehyde concentration of 343 ppm and for three types of electrical excitation: (i) AC, (ii) pulsed with a positive polarity and (iii) pulsed with a negative polarity. The carbon balance is determined as follows:

$$\%C = \frac{[\text{CO}_2] + [\text{CO}] + 2 * [\text{CH}_3\text{CHO}]_{\text{out}}}{2 * [\text{CH}_3\text{CHO}]_{\text{in}}} * 100 \quad (4)$$

where: [CH₃CHO]_{in} - the initial acetaldehyde concentration,

[CH₃CHO]_{out} - the acetaldehyde concentration after treatment by the discharge.

Table 1. Typical C balance at the exit of the DBD

reactor, for [CH₃CHO]_{in} = 343 ppm.

Type of excitation, (E _s =160 J/l=const.)		CO ₂ : CO	% C
AC generator	Dry air	1.64 : 1	69.83
Positive polarity		1.26 : 1	68.48
Negative Polarity		1.39 : 1	66.96
AC generator	Humid air	2.01 : 1	63.98
Positive polarity		1.15 : 1	80.74
Negative Polarity		1.15 : 1	80.74

In the carbon balance aspect (eq. 4), between ~67%-81% carbons of acetaldehyde are going to CO₂ and CO, for an initial acetaldehyde concentration value of 343 ppm and a specific energy of 160J/l. This value increases slightly up to 90 % with decrease of initial acetaldehyde concentration up to 195 ppm (for details, see [11]).

4. Conclusions

The removal of acetaldehyde by a DBD reactor in dry and humid air, at atmospheric pressure, energised by an AC 50 Hz voltage waveform or a pulsed voltage waveform has been investigated.

For conditions of the experiment, it has been found that removal efficiency achieved is in order of *pulsed DBD in humid air > AC DBD in humid air ≈ pulsed DBD in dry air > AC DBD in dry air*, for an initial acetaldehyde concentration of 343 ppm. Therefore, the acetaldehyde removal is more efficient using a DBD reactor in humid air than the DBD reactor in dry air and we presume that is due to different oxidation pathways of the CH₃CHO molecule in the two gas mixtures.

Acknowledgements

The first author acknowledges the *Laboratoire de Physique des Gaz et des Plasmas (Orsay, France)* for the opportunity of work in their laboratory and for financial support together with the *SOCRATES Scholarship*.

This work was partial supported by Romanian Ministry of Education and Research under grant CNCSIS, type A, no. 1344/2003-2005.

References

- [1] U. Kogelschatz, B. Eliasson, W. Egli - Pure Appl. Chem. **71**, 10 (1999)
- [2] U. Kogelschatz, B. Eliasson, W. Egli – ICPIG XXIII, Toulouse, France, 1997, p.1
- [3] Non-Thermal Plasma Techniques for Pollution Control. Penetrante B and Schultheis S (eds) 1993 NATO ASI Series Vol. G34, parts A and B, (Berlin: Springer-Verlag).
- [4] Electrical discharges for environmental purposes. Fundamentals and applications. Van Veldhuizen E-M (ed) 2000 NOVA Science Publishers.
- [5] K. Yan, E. van Heesch, A. Pemen, P. Huijbrechts – Plasma Chem. Plasma Proc. **21**, 107 (2001).
- [6] A. Khacef, J-M. Cormier, J-M. Povesle - XVIth

- International Symposium on Plasma Chemistry, Taormina, Italy, 2003.
- [7] R. Hackam, H. Akiyama – IEEE Transactions on Dielectrics and Electrical Insulation, **7**, 5, 654 (2000).
- [8] A. S. Chiper, N. Blin-Simiand, N. Dumitrascu, F. Jorand, S. Pasquiers, G. Popa, C. Postel - GD XV, Toulouse, France, 2004, p. 299.
- [9] Z. Falkenstein, J. Coogan, J. Phys. D **30**, 817 (1997).
- [10] J. Jarrige, N. Blin-Simiand, F. Jorand, L. Magne, S. Pasquiers, C. Postel – 17th ISPC, Toronto, Canada, August, 7, 2005.
- [11] A. S. Chiper, N. Blin-Simiand, F. Jorand, S. Pasquiers, G. Popa, C. Postel - 17th ISPC, Toronto, Canada, August, 2005.

*Corresponding author: alina.chiper@uaic.ro