Modeling of a DBD Reactor for the Treatment of VOC

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Abstract:
Non-thermal plasma, generated in atmospheric pressure discharges (DBD), has been investigated in our laboratory in order to treat highly diluted (300 ppm to 1000 ppm) volatile pollutant. The collision of electrons created in the discharge with atmospheric air, leads to the formation of reactive species (O_3, O, singlet O, ions..) that can totally or partially oxidise the pollutants at near ambient temperature. The purpose of the present paper is to show that this process can be successfully modelled using COMSOL® code. Pressure and velocity fields are obtained with the Navier Stokes incompressible (*ns*) model. Concentrations of the species are obtained using the convection and diffusion (*chcd*) model. The calculations are in good agreement with experimental observations and results.

Keywords: electrical discharge, treatment of VOC, 3D reactor simulation.

1. Introduction

The industrialization of our society led to a massive increase of atmospheric pollution. The main atmospheric pollutants are light gases (SO_2, NO_x, CO_2, CO…) or volatile organic compounds (VOC). Most frequent VOC are organic solvents, hydrocarbons, (CFC), sulfured organic compounds (mercaptans or thiols RSH, thiophenes RSR…) or oxygen-containing organic compounds (alcohols, ketones, aldehydes, carboxylic acids) and Polycyclic Aromatic Hydrocarbons (PAH). Conventional techniques, for the elimination of VOC, such as activated carbon adsorption, thermal or catalytic oxidation combustion, require a lot of energy considering the high temperature conditions.

The treatment of organic pollutants via dielectric barrier discharge, is a low energy consumption process. Indeed, the collision of electrons accelerated by the electrical field created in the discharge area with atmospheric air, leads to the formation of active and reactive species (O3, O, singlet O, ions..). These species can totally or partially oxidise the VOC at near ambient temperature.

Plasma treatment in our laboratory is operated in the DBD reactor presented figure 1.

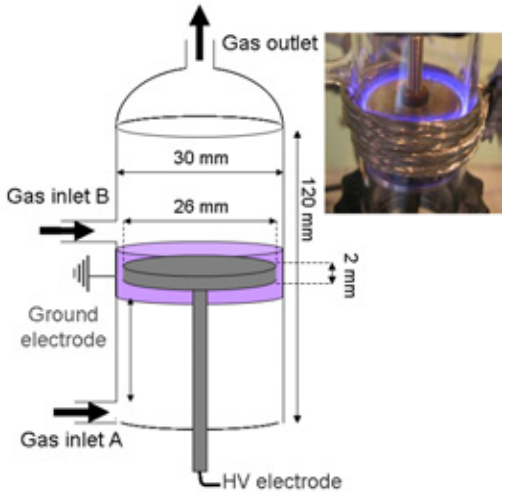

Figure 1. The DBD reactor.

The reactor is constituted of a 120 mm long and 2 mm thick glass tube with a diameter of 30 mm. The stainless steel high voltage electrode is a 2 mm thick and 26 mm diameter disc. The space between high voltage electrode and the glass tube used as dielectric material is 2 mm. A wire sheet (20 mm width and 2 mm thick) wrapped around the tube constitutes the ground electrode. A high voltage generator supplies from 5 to 30kV peak to peak (U_{pkpk}) alternative voltage. In the conditions of the experiments, the discharge is filamentary. Pure air is injected in the gas inlet A while the air charged with the pollutant is introduced in the gas inlet B at 10 mm from the electrode. The active species (O3, O, singlet O, ions..) produced in discharge area of the DBD react in the post region area with the pollutant, leading to its depletion. The first system studied in this reactor was the removal of beta-pinene used as model molecule of a VOC

pollutant in air [1]. Currently we study the removal of the thiols introduced in the post-discharge at concentrations in the range of 300 - 1000 ppm in the air. The results show a removal of thiol depending of the energy density. Its depletion varies from 60% to 100% but the main problem is the formation of a thin film due to the polymerization of the organic pollutant on the discharge zone. In order to explain this back diffusion in the reactor we have developed a CFD model using COMSOL. Due to the lack of symmetry, as the pollutant is introduced tangentially in the post discharge region, a 3D model is used.

The simulation of the reactor is performed in three steps. In the first step the hydrodynamics and the diffusion of the pollutant in the discharge region is simulated in 3D. In the second step is simulated the discharge region. In this domain very strong gradients of pressure and concentrations occur, however as this domain is axisymmetric a 2D model is used. Electrons react with air, forming the active species (O3, O, singlet O, ions…). Their concentration is calculated by solving their equations of conservation in a kinetic model of 5 species and 6 reactions. The concentrations of the species obtained in this 2D model are used as inlet conditions in the 3rd step, in the post discharge region where the active species formed in the discharge region react with the pollutant. Here, as in the first step, the interaction of the active species with the pollutant is simulated in 3D.

2. 3D modeling of the non-reactive flow (1st step)

2.1 3D reactor and *ns* model

The 3D model used for the simulation of the non-reactive flow, subdomains, boundaries and mesh are shown in fig. 2. Pure air enters in the bottom of the reactor, passes through the annular space between the electrode high voltage and the wall of the reactor. This air flow containing the active species is then "mixed" with the polluted flow introduced at 1cm above the high voltage electrode in the post discharge region. The outlet of the gases is in the top of the reactor. The flow rate of pure air in the bottom of the reactor is 1 L/min corresponding to a velocity of 1.3 m/s and that one of polluted air is 1L/mn corresponding to a velocity (normal to the boundary) of 1m/s. The velocity and the pressure fields in the reactor are calculated by the model "Navier Stokes incompressible" (*ns*).

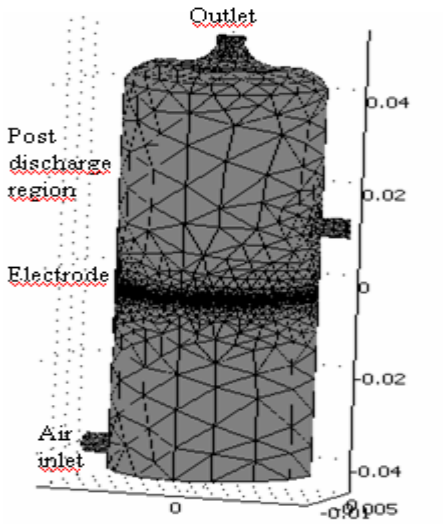

Figure 2: 3D simulation domain and unstructured mesh.

The velocity in the discharge region (mainly in x direction) is about 0.021 m/s, fig. 3.

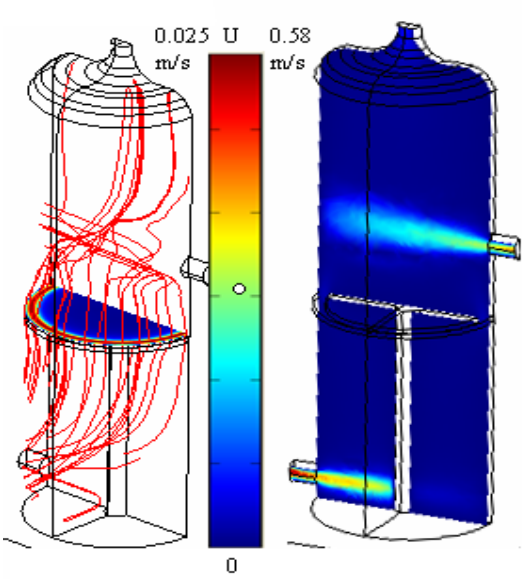

Figure 3: Velocity field & Streamlines**.**

This velocity is stable on all the perimeter of annular space (discharge region), whereas in the other parts of the reactor, as it is indicated by the streamlines, these velocities vary notably, due to the side injection of gases.

That means, it is possible to use this velocity of 0.021 m/s as inlet boundary limit in the 2D model reactor (2nd step) and the 3D post discharge reactor (3rd step).

2.1 3D reactor and *chcd* model

After the development of the *ns* model and the calculation of the velocity field, we introduced the model of convection-diffusion *chcd* in order to calculate the concentration field. To this end in the bottom of the reactor the oxygen was introduced with inlet concentration c1=10 mol/m^3 and thiol with inlet concentration c2=0.67 mol/m^3. The resolution of convection-diffusion equation for oxygen shows a concentration gradient from the bottom to the top of the reactor (10 to 8.4 mol/m^3) but the more important result is the diffusion of thiol in discharge region, fig.4.

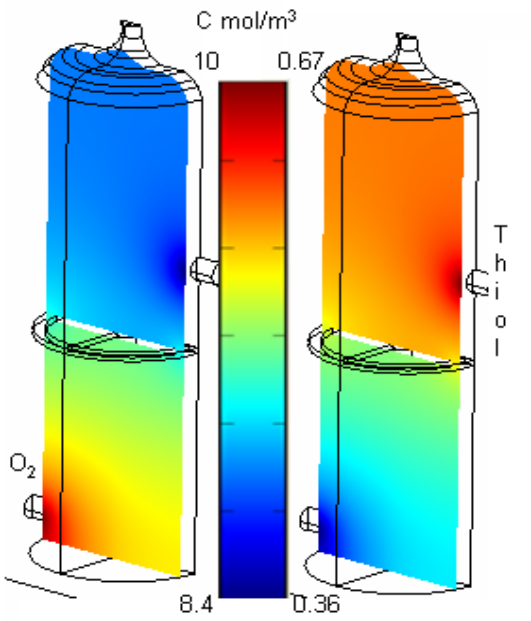

Figure 4. Concentration field for oxygen and thiol

This diffusion of thiol is observed experimentally by the formation of a polymeric deposit that changes the electrical parameters of the discharge. So it is necessary to change the design of the reactor.

3. 2D modeling of the discharge region (2nd step)

Due to the strong gradients of pressure and velocity in the discharge region, it was impossible to run the 3D model in our computer, with the kinetic model implemented. Fortunately thanks to axial symmetry in this domain, it was possible to work with a 2D simulation domain fig. 5.

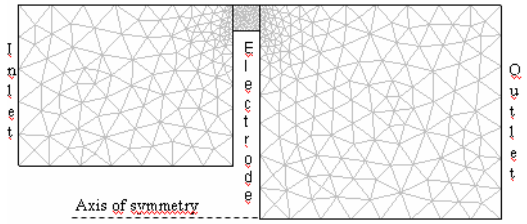

Figure 5. 2D simulation domain, unstructured mesh

Here also the velocity field is calculated using the *ns* model. As already mentioned the velocity in the discharge region (mainly in x direction) is uniform on all the perimeter of annular space (discharge region), thus it is possible to use this velocity, of 0.021 m/s, as inlet boundary limit in the 2D model reactor. However the inlet of the 3D model is different from that of the 2D model. Therefore it was necessary to adjust the velocity at the inlet of the 2D model in order to obtain in the discharge region, the velocity of 0.021 m/s fig. 6.

3.1 Kinetic model for the formation of the active species.

The kinetic model implemented here includes 4 species (e-, O, O_2, O_3) and 3 reactions.

	Chemical Reactions	Rate Constants (cm^3/s)or(cm^6/s)
1	$e+O_2 \rightarrow 2O+e$	1.95e-9
2	$O+ O_2+O_2 \rightarrow O_3+O_2$	$6.4e^{-34}$
3	$e+O_3 \rightarrow O+O_2+e$	2.5e-8

This simplified model is part of a more complex one (including 15 species and 24 reactions) developed in our laboratory and implemented in 0D codes. [2]

The electron concentration is an important parameter in DBD reactors as electrons are simultaneously reactants and energy carriers, initiate and perform activation, dissociation or ionization reactions at ambient temperature.

Their concentration depends on the electrode gap, the nature of the gas or the dielectric, thus their density must be calculated continuously as for the other species (O, O2, O3...). Currently a 1D model for the calculation of electron, positive and negative ions, is developed in our laboratory, by solving, using Matlab, a system of 4 non linear equations, including the equation of Poisson for the electric potential and the three equations of conservation for the three species (e^-, A^+ and A^-). The aim in the near future is to implement this model in our 3D COMSOL model. These calculations, in the working conditions of our reactors, show average electron densities of about 10^{14} cm^{-3}, in agreement with the literature [3].

3.2 Concentration of the active species in the discharge region.

As previously the concentration field is calculated by using the convection-diffusion *chcd* model. In order to obtain an electron density of 10^{14} cm^{-3}, we introduced in the subdomain settings a constant source term before the sink terms due to the above reactions.

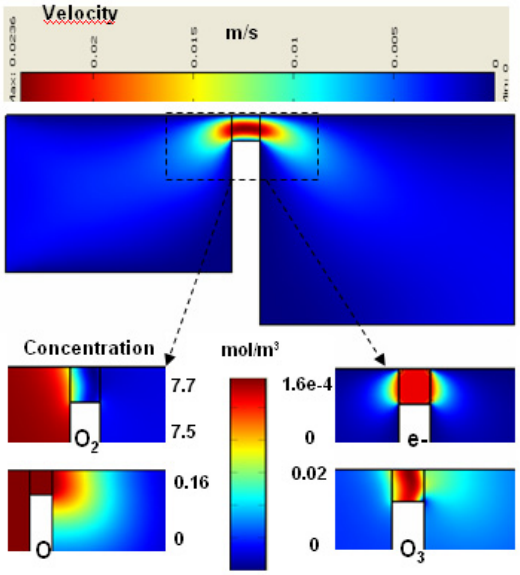

Figure 6. Velocity and concentration of the species in the discharge region

The concentrations calculated (fig. 6) in the 2D model by the convection-diffusion equations show a good agreement with the order of magnitude. The more important species here are oxygen (0.16 mol/m^3) and ozone (0.02 mol/m^3) because they can react with the pollutant (thiol). This is explained by the few species and reactions taken into account in this model. However it is possible to use these concentrations as inlet boundary limit in the post discharge reactor for the treatment of the pollutant.

4. 3D modeling of the post discharge region (3rd step)

The 3D model used for the simulation of the interaction of active species created in discharge region and the pollutant, subdomains, boundaries and mesh are shown in fig. 7. This model reactor corresponds to the upper half of the real reactor, downstream from the high voltage electrode. Thus the discharge region for this reactor corresponds to the inlet boundary limit for the velocity (0.021 m/s) and the concentrations (O_2: 7.7 mol/m^3, O: 0.16 mol/m^3 and O_3: 0.02 mol/m^3) of the active species.

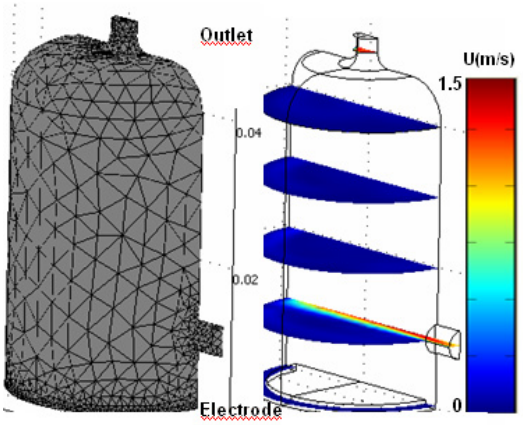

Figure 7. Post discharge reactor. 3D simulation domain, unstructured mesh and velocity field.

In the preceding 2D model one can see that electrons diffuse post discharge in the area and can react with the pollutant. To simplify the model, in this region, we did not take into account these reactions. Moreover in the 3D model of the 1st step calculations and the experimental results it is known that the pollutant diffuses in discharge region, interacts with electrons, and reaction products form a thin film on the reactor wall. In this model it is impossible to take into account the interaction electron-pollutant. For the kinetic model in the

post-discharge region are considered 5 species (O, O_2, O_3, thiol and prod) and 3 reactions:

	Chemical Reactions	Rate Constants (cm^3/s)
1	thiol+O_3→prod	1.2e-12
2	thiol+O→prod	9.6e-12
3	O+O_3→2O_2+e	8.0e-15

As in the two preceding steps, the velocity field was calculated using the Navier-Stokes incompressible model *ns* (fig. 7) while the concentrations were obtained using the model convection-diffusion *chcd* (fig. 8 and 9).

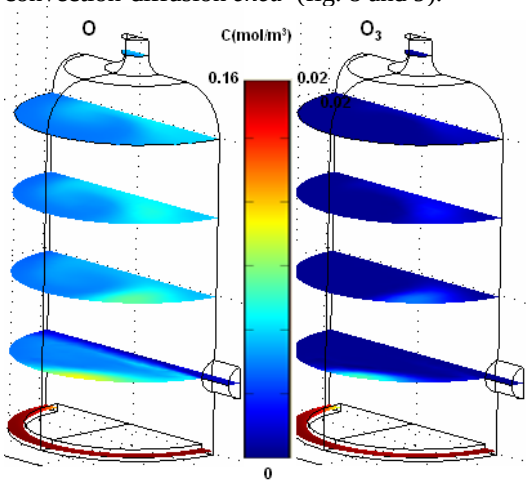

Figure 8. Concentrations of atomic oxygen and ozone in the post discharge 3D reactor.

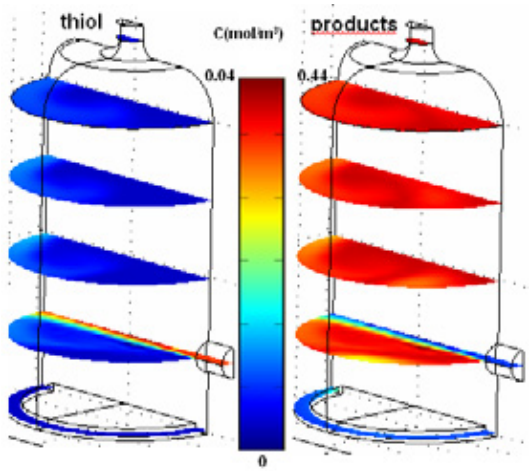

Figure 9. Concentrations pollutant and products in the post discharge 3D reactor.

The concentration of thiol corresponds to 1000 ppm in air with a flow rate of 1l/mn. With a boundary integration of thiol in the side inlet and the outlet one can deduce the depletion of the pollutant, that is quite complete. However as in the case of the 2D model, in order to have accurate and representative results, it would be necessary to take into account more reactions.

5. Conclusion

The depletion of a pollutant in a DBD reactor can be successfully simulated with a 3D model reactor using COMSOL® code. Obtaining accurate and representative results depends on the performance of the computer as it is necessary to use complex kinetic schemes including several species and reactions.

With the convection-diffusion model we demonstrated the diffusion of the pollutant in the discharge region. This diffusion is responsible for the formation of the polymeric film observed experimentally.

Nevertheless the challenge is the implementation of model solving the system of 4 non linear equations, including the equation of Poisson for the electric potential and the three equations of conservation for the three species (e^-, A^+ and A^-). The aim in the near future is to implement this model in our 3D COMSOL model.

8. References

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