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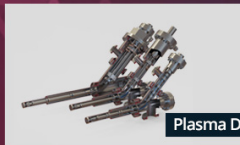
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DBD-Corona Discharge for Degradation of Toxic Gases

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Abstract The non-thermal plasma technology is a promising technique to treat SO₂ and NO_x. Chemical radicals produced with this technology can remove several pollutants at atmospheric pressure in a very short period of time simultaneously. Both theoretical and experimental study on SO₂ and NO_x removal, by a dielectric barrier discharge (DBD) with corona effect, is presented.

Keywords: DBD-corona, de-NO_x process, de-SO₂ process

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1 Introduction

Diesel exhaust gases are one of the sources of atmospheric pollution. Selective catalytic reduction of NO_x, which is widely adopted for gasoline engines, is very difficult to apply to diesel exhaust gases, because the gases contain considerable amount of oxygen and suspended particulates matter. Moreover the sulfur compounds from gasoline could not be entirely removed and they contribute to the catalysts (e.g. BaO around Pt sites) deactivation^[1].

Non-thermal plasma technologies have been very attractive to remove toxic gases^[2~10] because most of the electrical energy input is transferred into electron kinetic energy, rather into heating up the gas, forming highly chemically active compounds responsible to remove the harmful components in gases. Furthermore, this remediation technique can operate at atmospheric pressure rendering it attractive for application on mobile pollution sources.

The plasma used in the reactor proposed is formed by a dielectric barrier discharge with a cylindrical configuration. A coaxial filament plays the role of central electrode to augment the electric field. It has been showed that high electric fields favour the toxic gas removal^[11].

In this paper results obtained by simulation considering the experimental conditions, such as flux gas, volume of the reactor and frequency of microdischarges, on the de-NO_x and de-SO₂ processes, are presented. Some experimental results tested in a DBD-corona reactor are also discussed and compared with simulation results obtained from the model.

2 Chemical kinetic model

A better understanding of the species role and their influence in the SO₂ and NO_x removal processes can

be achieved using a chemical kinetics model. In the DBD-corona discharge, the free electrons gain energy from the applied electric field and lose part of this energy through collisions with neutral species. These energetic electrons transfer their energy to neutral gas resulting in quench, attachment, dissociation or ionisation. Other species like free radicals and ions would then be formed.

In general, the discharge is supposed to be established in two steps. First, a streamer head is formed, followed by the generation of the streamer channel. Theoretical results, reinforced with experimentals by KIM et al^[12] propose the streamer head formation at approximately 9 ns. Due to the nonuniform electrode configuration of the wire-cylinder electrode arrangement, a glow corona is initiated following by the transformation of nonuniform perturbation of charged particles into a microfilament-like structure known as microdischarge.

In our simulation, we suppose the formation of the streamer head at 9 ns and, to simulate the high field occurring locally in the streamer head, a reduced electrical field strength (E/N with E the electric field strength and N the gas number density) of 150 Td was taken into account^[11].

An initial density of 1 electron/cc is considered. This electron is responsibly to form an avalanche and to propagate a streamer.

After 9 ns, when microdischarge is established, the electric field decreases by maintaining itself almost constant until the dielectric wall^[12]. We suppose an E/N of 40 Td (1 Td is 10^{-17} Vcm²).

In general the kinetic model used takes into account the following scenario, namely during first few nanoseconds, the energetic electrons generated collide with gas molecules (in this case H₂O, N₂, O₂) appearing some primary radicals (OH•, O•, N•) and ions. Excited molecules, like excited oxygen (O¹(D)), form radicals by rapid quenching. The radicals formed will be the

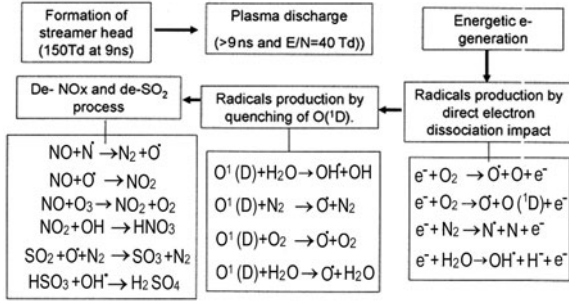


Fig.1 NO_x and SO₂ removal process

principal responsibly of de-NO_x and de-SO₂ process (Fig. 1).

Additionally, radicals produced are supposed to be well mixed with reactants and uniformly distributed within the whole volume (i.e. a zero-dimensional model).

Radical production takes place during a short period between two microdischarges pulses. In our case, the radical concentration does not decay because the time delay between two microdischarges (0.06 μs) is lower than the radical decay time (about 10 μs to 100 μs) [13]. So, for the radical production, we do not consider the radical decay time and will use the mass conservation equations concerning only the radical production by electron impact and quenching of excited states in function of time.

After the formation of radicals the expression used for the de-NO_x and de-SO₂ processes, is:

$$\frac{d[X_i]}{dE_D} = \frac{V \sum_j k_{ij}[X_i][X_j]}{E_p f}, \quad (1)$$

with $[X_{ij}]$ the species concentration in cm³/(mol·s), E_D the energy density in J/cm³, V the reaction volume in cm³, k_{ij} the reaction rate coefficient in cm³/mol·s, E_p the energy per pulse of the microdischarge in J/pulse and f the pulse repetition of the microdischarge in pulse/s.

Species that take part in material balance of NO_x and SO₂ removal process are: e⁻, O₂, O₂⁻, O⁻, O₂(a¹Δg), O₂⁺, H⁻, H⁺, N⁺, O⁺, OH⁺, H₂O, NO, NO₂, NO₃, N₂O₅, N₂O, N₂, N₂(A³Σ_u⁺), HNO₂, HNO₃, H₂O₂, SO₂, SO₃, HSO₃ and H₂SO₄.

The gas composition in this model is Air/H₂O=99/1 mixed with 50 ppm of NO, 50 ppm of NO₂ and 50 ppm of SO₂. The reaction set used in this study includes electron impact with the background gases generating ions, electrons and free radicals reacting with SO₂ and NO_x. A total of 26 species and 81 reactions are considered and the rate coefficients were taken from Ref. [14~16].

3 Experimental setup

The schematic of the DBD-corona plasma reactor is shown in Fig. 2. It consists in a tube of pyrex glass with an internal radius of 11.1 mm, a length of 75 mm and a thickness of 1.2 mm. A stainless steel concentric

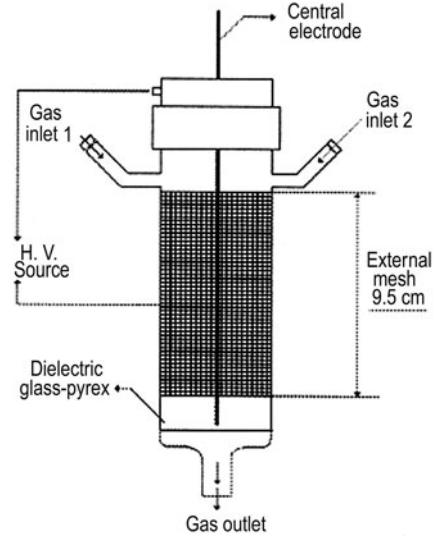


Fig.2 DBD-Corona reactor

central electrode of radius of 2.54 mm is set inside the pyrex tube. A metallic mesh wrapping the pyrex tube, as the external electrode.

Flow of NO in 50 ppm balanced with air, SO₂ in 50 ppm balanced with air and water vapor are incorporated into the reactor with flow controllers. Outlet gases were measured with a PG250 analyzer and a SEN-SONIC 2000. A study of electrical characteristics of the reactor here described is detailed in Ref. [17].

4 Results

Preliminary results obtained in the simulation of de-NO_x and de-SO_x processes throw the importance to add water into the process. Even 1% of water vapour added, can remove, theoretically, the 100% of SO₂ [18].

Results obtained from simulation show the radical concentration such as O[•], OH[•], N[•], H[•], and excited species as O(¹D) formed at 1×10⁻⁸s. These species are key species in the degradation of NO_x and SO₂.

Fig. 3 shows the density of active radicals in the de-NO_x and de-SO_x processes. It can be observed that densities of the O[•], OH[•] and N[•] radicals are close to 10¹⁵ particles/cm³ at about 1 ns and, after that, an exceptionally fast diminution of their concentrations is observed (less of 0.1 μs). Therefore, the formation of radicals occurs on short time scales compared with the subsequent chemical reactions responsible for NO removal. In Fig. 4, de-NO_x and de-SO_x processes can be observed in parts per million (ppm).

For NO_x removal (Fig. 4(a)) an extremely rapid conversion of NO to NO₂ (less than 0.1 ms) is obtained, while the diminution of NO_x (NO+NO₂+N₂O₅+N₂O) is slower (40 s). For the conditions studied the NO_x removal reaches the 92% at 50 s.

For the de-SO₂ process (Fig. 4(b)) the degradation is even more rapid than the de-NO_x process, 98% of removal is obtained at 0.4 s.

Results of NO_x and SO_x removal expressed in a function of the energy density can be appreciated in Fig. 5.

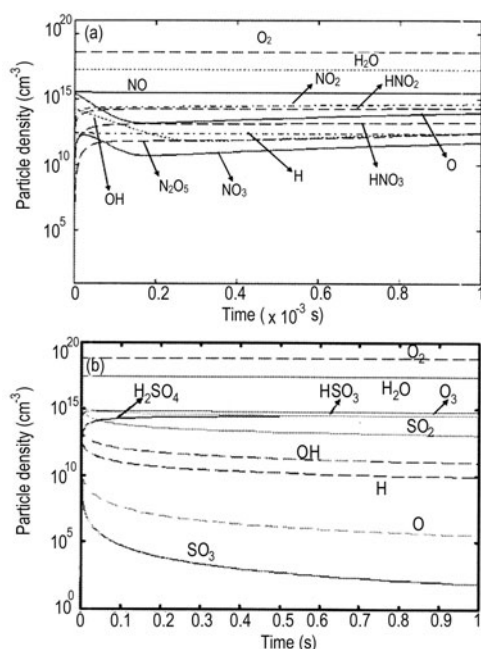


Fig.3 Species density. (a) NO_x removal, (b) SO_x removal

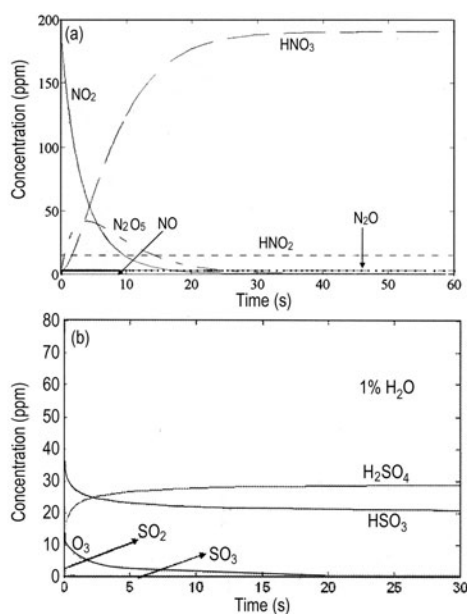


Fig.4 (a) NO_x removal in ppm (b) SO_x removal in ppm

From this figure the concentration is deduced that 0.8 J/cm³ should be applied to obtain more than 99% of NO_x and SO₂ removal.

From simulation it is deduced that the principal channel for the removal of SO₂ is via its combination with the OH• radical and its oxidation with O• radical. Whereas for the de-NO_x process the principal mean for their removal is through its reduction by N atoms and the reaction with hydroxyl molecules. These results are in accord with the previous results^[11].

An efficiency of 98% in the de-SO_x process is obtained experimentally at 5 s and at 0.2 J/cm³ of energy density, as shown in Fig. 6(a). At this time and energy density, a removal of 100% of SO_x (i.e. SO₂ + SO₃) is

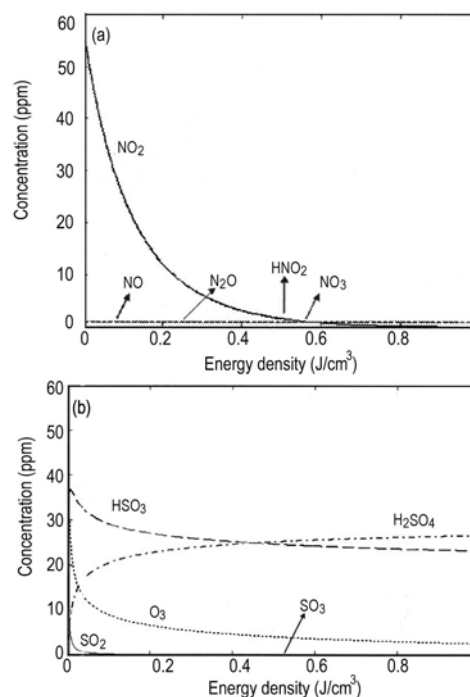


Fig.5 Toxic gas removal in function of applied energy (a) de-NO_x process, and (b) de-SO₂ process

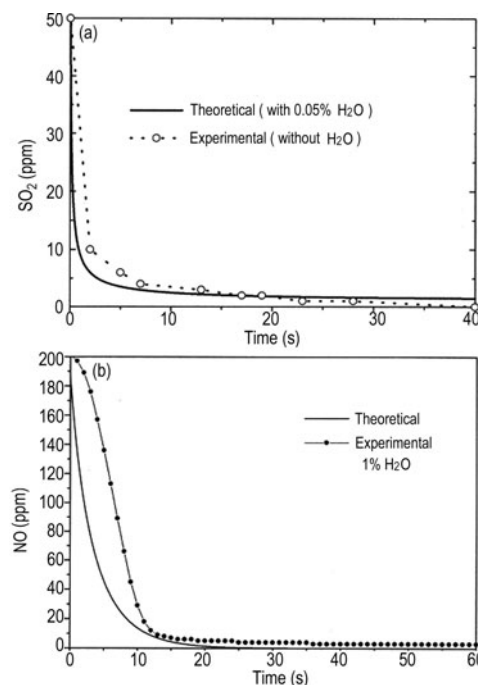


Fig.6 Experimental vs. theoretical results. (a) SO₂ removal, (b) NO_x removal

found in the simulation, the SO_x are then supposed to be completely converted into acids (H₂SO₄ and HSO₃).

For the de-NO_x process a removal of 85% of NO_x (i.e. NO+NO₂) is obtained experimentally (Fig. 6(b)).

Measured electric fields of 100 kV in dielectric barriers were founded by KIM and FILIMONOVA and co-workers^[12,19], so additional simulation work must be conducted in order to corroborate the experimental and theoretical results under this condition of electric field.

5 Conclusions

$O^\bullet$ and $OH^\bullet$ radicals generated by O_2 and H_2O molecules play an important role in NO_x and SO_2 removal. $O^\bullet$ radicals are principal precursors of oxidation reactions of SO_2 and $OH^\bullet$ radicals convert the NO_x and SO_2 into acids which could be removed easier, with ammoniac, for example.

Removal percentage in experimental results, reaches 98% and 85% for de- SO_x and de- NO_x processes respectively, at 5 s and 0.2 J/cm^3 of energy density.

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