Modelling of the Removal of Nitric Monoxide from Exhausts by Dielectric Barrier Discharges

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The reduction of nitric oxide concentrations in gaseous exhausts of engines and power stations by use of dielectric barrier discharges (DBD) has become the object of extensive research over the last few years. A computer model capable of describing the main processes of a DBD under atmospheric pressure is introduced and applied to discharges in mixtures containing nitrogen, oxygen and water as main constituents and nitric oxide as toxic impurity. Results are compared with experimental data and reasonable agreement is found. Finally the influence of ammonia as additive is investigated. According to our calculations 500ppm ammonia increases the reduction of NO_x by a factor 2.

1. Introduction and Description of the Model

Since limits of allowable concentrations of toxic products in exhausts of car engines and other combustion engines have been decreased steadily over the last decade, the search for new means of efficient and economic exhaust gas treatment has gained wide interest. Cleaning by irradiation with electrons of several keV kinetic energy [1] has been investigated as well as corona and surface discharges [2]. Another promising method seems to be dielectric barrier discharges (DBD), which are operated AC or pulsed and where at least one electrode is covered by an dielectric.

In order to quantitatively describe the removal of NO and NO_2 (NO_x) by a dielectric barrier discharge, a physical model of individual discharge filaments is used, which was originally developed for dielectric barrier excimer lamps [3]. This model ("filament model") describes filaments as short lived, transient cylindrical plasma channels bridging the discharge gap and being attached to the dielectric electrode (or electrodes) via so-called "filament foot-prints". Filament ignition (t=0) is modeled as a streamer breakdown and quenching of the filament is a result of surface charges accumulating at the foot-prints. Subsequently (t > 5 - 10ns) a reaction phase follows, which includes ion- and radical chemistry followed by neutral chemistry (up to the millisecond range). This model includes Boltzmann electron kinetics [4] (time resolved solution of the stationary Boltzmann equation) during the discharge phase and heavy particle kinetics during the subsequent chemical reaction phase. These calculations yield rate coefficients for electron collisions. Data for collision cross-sections and rate coefficients for ion-, radical-, and other neutral particle reactions are taken from [5,6]. Typical input parameters are gas composition, gap spacing, dielectric thickness and permittivity, foot-print radius and filament repetition rate (i.e. reaction time between two successive filament ignitions). Ignition voltage and filament channel radius are calculated self-consistently using a simple streamer model.

For some of the calculations a simpler model ("primitive model") is used which assumes a spatially homogeneous discharge plasma and a constant electric field during the filament current pulse phase that was set to 10ns.

2. Results

The results presented are for a gas pressure of 1bar at a constant gas temperature of 373K. The initial NO-concentration is 500ppm for all cases. Reactor parameters for the "filament model" are 1.6mm gap width, 1.3mm thickness for both dielectrics (ε_{rel}=4.7) and an inter pulse duration T=0.87ms.

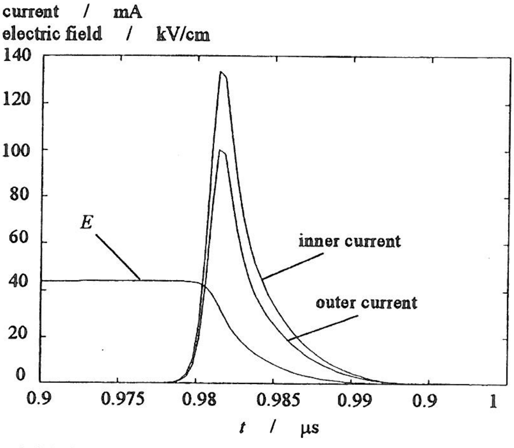

Figure 1: Electric Field, inner Current (i.e. Current in the Plasma) and outer Current (i.e. Current in outer Circuit) versus Time

Fig. 1 shows the time evolution of a typical filament current pulse together with the electric field in the gap for a gas mixture of following composition: $N_2/O_2/H_2O/NO$=79/1/20/0.0005. Fig. 2 shows results for NO_x-removal as calculated from the "filament model" for the same gas composition as used in Fig. 1. Each subsequent filament pulse leads to a net reduction of the NO-concentration during the interpulse reaction phase, despite the fact that [NO] increases during the pulse.

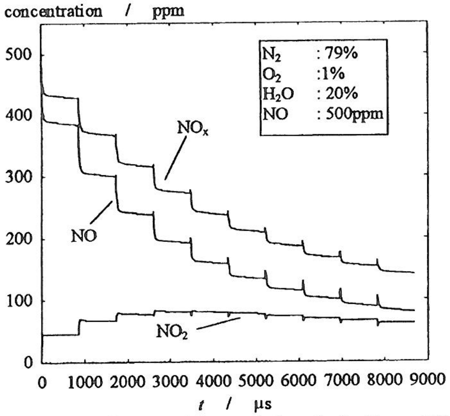

Figure 2: Concentrations of NO, NO_2 and the their Sum (NO_x) versus Time.

Figs. 3 and 4 show NO-, NO_2- and NO_x-concentrations versus discharge energy per unit volume as calculated from the "primitive model" at E=4.65kV/mm (≈ 236.5Td) and T=0.87 ms. The modelling results are compared with experimental data by Wolf et al. [7] from our laboratory. The experimental parameters are given in figures. Experimental and modelling data show similar dependencies on energy input per unit volume. In order to obtain such a reasonable agreement the post discharge phase of several seconds (i.e. the duration between the instant when the treated gas leaves the discharge reactor and the time when it reaches the NO_x-detector) must be taken into account. Specific NO_x- removal energies are 90eV/NO_x-molecule for the first 100ppm NO_x removed. Increasing the oxygen content from 1% to 16% improves the calculated specific energy to about 75eV/NO_x.

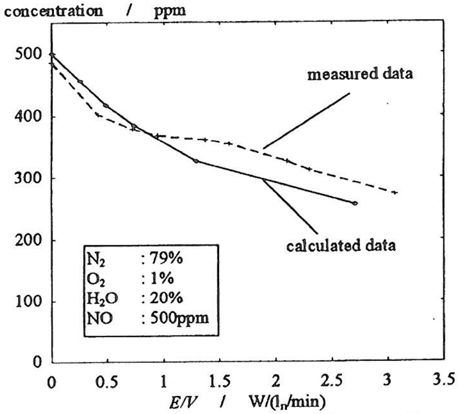

Figure 3: Calculated and Measured NO_x-Concentrations as Function of the Discharge Energy per Volume. 1W/(l_n/min) is 60J per 1 litre at 1.013bar and 0°C.

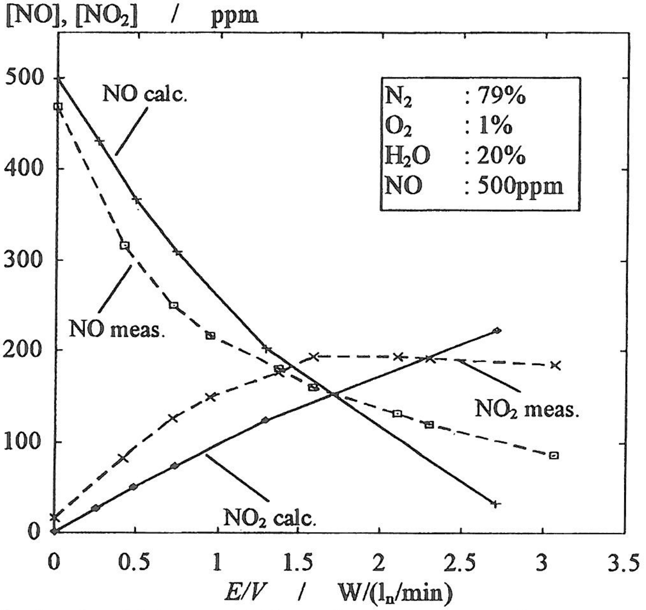

Figure 4: Calculated and Measured NO- and NO_2-Concentrations as Function of the Discharge Energy per Volume.

A scrutiny of the host of different electron and chemical reactions shows that NO is mainly converted into HNO_2 and NO_2 by oxidation:

$NO + OH \rightarrow HNO_2$

$NO + HO_2 \rightarrow NO_2 + OH$

$NO + O \rightarrow NO_2$

$NO + O_3 \rightarrow NO_2 + O_2$.

NO_2 is partly further oxidised to HNO_3 by

$NO_2 + OH \rightarrow HNO_3$.

The only significant reaction by which NO is reduced is

$NO + N \rightarrow N_2 + O$.

Hydroxyl (OH) is mainly created during the short discharge phase by dissociation of H_2O through electron collision and by the reaction of H_2O with atomic oxygen:

$H_2O + e \rightarrow OH + H + e$

$H_2O + O \rightarrow 2\,OH$.

Electron collision is also the source of atomic oxygen:

$O_2 + e \rightarrow 2\,O + e$

$H_2O + e \rightarrow O + H_2 + e$.

and atomic nitrogen

$N_2 + e \rightarrow 2\,N + e$

While ozone and hydroperoxo (HO_2) are produced via

$O_2 + O \rightarrow O_3$

$O_2 + H \rightarrow HO_2$

in the post-pulse phase.

The removal of NO_x can be significantly improved by adding ammonia (NH_3) to the gas mixture. Fig. 5 shows calculated and measured results for NO_x-removal in a mixture containing 500ppm NO and 500ppm NH_3. Except for the ammonia added, this mixture would be typical for Diesel exhaust. Both experimental and modeled NO_x-removal are increased, however, the theoretical improvement far exceeds the experimental one. Specific removal energies are 30eV/NO_x (theoretical) versus 70eV/NO_x (exp.). The role of the post discharge phase – already mentioned above – is now even more important. A significant amount of NO_x is removed well after the last pulse (several 100 to 1000ms). The most important chemical reactions involving NH_3 are the following ones:

$NO_2 + NH_3 \rightarrow HNO_2 + NH_2$

$NO + NH_2 \rightarrow N_2 + H_2O.$

The latter reaction is especially desirable because it offers a reductive path for NO_x-removal. The large discrepancy of a factor of two between calculated and experimental values for NO_x-removal via NH_3-addition has not been resolved yet. Both experimental diagnostic problems and modelling uncertainties due to the NH_3-related chemistry have to be taken under consideration.

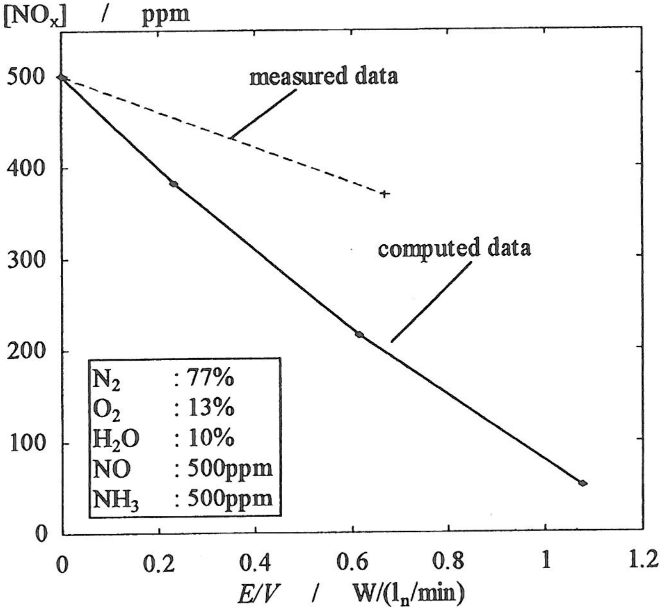

Figure 5: Calculated and Measured NO_x-Concentrations as Function of the Discharge Energy per Volume.

3. Summary and Conclusions

Removal of NO and NO_2 (referred to as NO_x) from exhaust gases by treatment in dielectric barrier discharges (DBD) has been investigated theoretically. Two different models, both treating the DBD-filaments as a series of current pulses were used. The "filament model" treats each DBD-filament in its full temporal evolution, whereas the "primitive model" assumes a spatially fully homogeneous discharge of given pulse width at constant electric field. Calculations with both models show that NO_x-removal from $/N_2/O_2/H_2O/NO/$-gas mixtures proceeds via oxidation of nitrogen oxides to form HNO_2 and HNO_3 mainly. The major oxidative species are OH-, HO_2-, and O-radicals. Modelling results for this regime agree reasonably well with experiments. Adding NH_3 to the gas to be treated the specific removal energy calculated by our model is improved considerably from 70 - 80eV/NO_x to 30 - 35eV/NO_x. This improvement is partly due to an additional NO_2-HNO_2 channel and partly to a new reductive path converting NO directly into N_2. An additional benefit of NH_3-addition would be the removal of HNO_3 by conversion into NH_4NO_3 (ammonium nitrate dust), also seen in our experiments [7].

Acknowledgment

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