

Experimental Investigations of the Removal of Toxic Exhaust Gas Components by Dielectric Barrier Discharges

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Abstract: Experimental investigations of the removal of toxic components (NO, NO₂, CO) from different synthetic exhaust gases (N₂, O₂, H₂O, CO₂, CO, NO) by DBD have been conducted in plane and coaxial reactor configuration. The concentration of NO_x could be reduced significantly from 500 vpm to below 100 vpm. NO could be removed completely from the exhaust gas. The decomposition efficiency is between 90 and 200 eV per converted NO_x molecule.

Introduction

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 flue gas treatment has gained wide interest, in addition to the improvement of the combustion process. Particularly the reduction of nitric oxides concentration [N_xO_y] in exhaust gases has become focus of world-wide research. Amongst established methods for the removal of NO_x in flue gas like selective and nonselective catalytic reduction (SCR, SNCR) other techniques are investigated as well, e.g. plasmachemical conversion. Examples for this are exhaust gas treatment by corona [1, 2], surface [3] and dielectric barrier discharges (DBD) [2 - 5] as well as irradiation with electrons of several keV energy (e-beam technique [2, 6, 7]). All these methods have in common that energetic electrons will be produced which induce plasma processes.

The object of our investigations is the DBD - discharges which are operated under a.c. or pulsed and where at least one of the electrodes is covered with an insulator. If exhaust gas at atmospheric pressure is subjected to a DBD which is operated at typically 0.5 to 3 mm gap spacing, a frequency of a few hundreds of Hz to a few kHz and a voltage of several kV, discharge channels (filaments) develop where ions and radicals like N, OH and O are created. The radicals react with nitric oxide (NO) either directly or via other chemical reactions. Thus NO can either be reduced to N₂ and O₂ or oxidised to form other nitric oxides (mainly NO₂) or nitric acid (HNO₃). Both optimisation of decomposition efficiency and decomposition rates and detailed analysis of discharge by-products are objects of our experimental investigations.

Experimental Set-up

A schematic of the experimental apparatus is shown in Fig. 1. The discharge reactor is operated at a continuous gas flow at atmospheric pressure. In order to control the gas mixture quantitatively (flow rates 1 - 15 l_n/min) electronic mass flow controllers (MFC) are used to adjust N₂-, O₂-, NO-, CO- and CO₂-flow rates. The rates of additives (A. in Fig. 1), the concentrations of which lie between 100 and 2000 vpm, are adjusted by flowmeters. Before adding toxic gas components and additives, the gas (N₂ / O₂ / CO₂) is humidified in a washing bottle. By varying the water temperature, the H₂O concentration can be adjusted between 0 and 30 %. The whole system can be heated up to 250 °C (H. C. in Fig. 1).

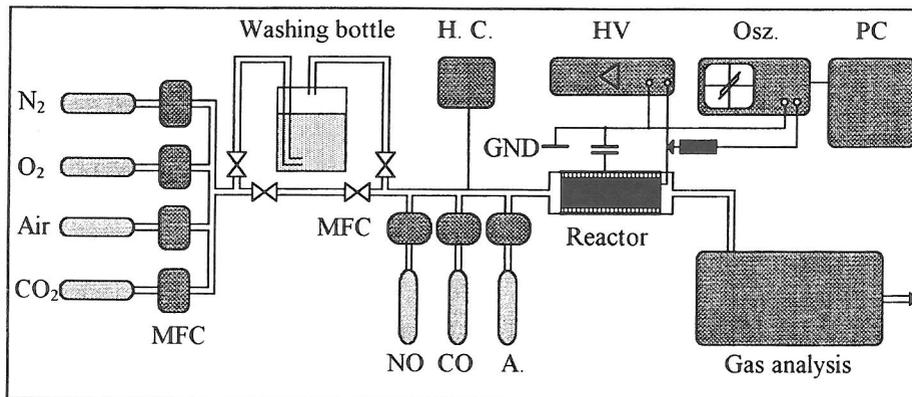


Fig. 1: Schematic of the experimental Apparatus

Experimental investigations have been conducted in coaxial - both symmetric (dielectric/dielectric) and unsymmetric (metal/dielectric) - and in plane plasma reactor configurations. Fig. 2 shows a schematic of symmetric coaxial plasma reactor set-up whereby the range of used gap spacing d , plasma length l_{plasma} and dielectric thickness x are included in it. The dielectrics are Duran tubes or Tempax plates (in each case $\epsilon_r = 4.7$)

Electrical input energy per a.c. cycle into the reactor for a.c. discharges is measured by the familiar Lissajous figure technique (voltage-charge-diagram for each discharge cycle). This method is very advantageous because the detailed shape of the Lissajous figure reveals valuable information about discharge behaviour and changes thereof.

The composition of the gas is quantitatively analysed by different methods: Electrochemical sensors (O₂, NO, NO₂, CO₂), UV-absorption spectrometry (NO, NO₂, HNO₃, O₃, ...) and infrared absorption spectrometry using a variable path length (0.8 - 8 m) FT-IR spectrometer (NO, NO₂, N₂O, ...).

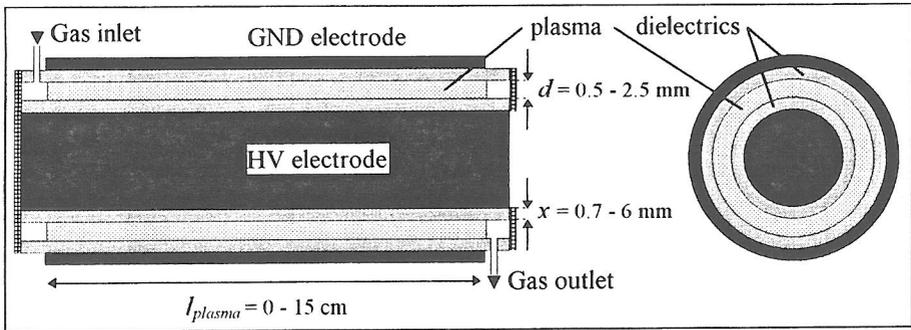


Fig. 2: Schematic of the coaxial Plasma Reactor

Results

Fig. 3 shows Lissajous figures of two different discharge states. The left-hand figure corresponds to a quasi-homogeneous plasma (both electrodes covered with dielectrics, gas flow 100 % N₂), the right-hand one to a non-homogeneous plasma with distinct filaments (only one electrode covered with a dielectric, gas flow 80% N₂, 20 % O₂). While in the former case the electric charge ΔQ transferred across the gap increases continuously during the discharge phase, in the latter case ΔQ grows stepwise which is caused by the creation of strong filaments.

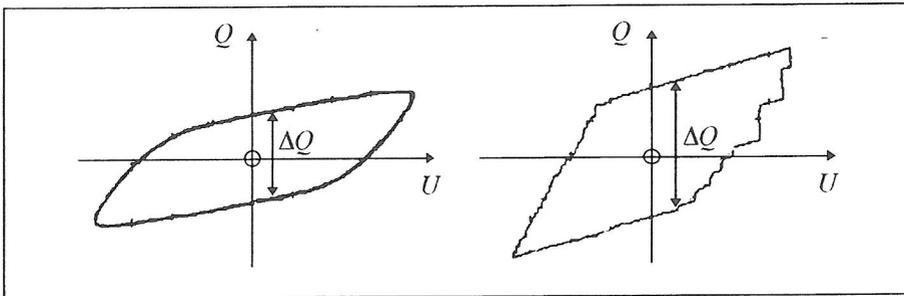


Fig. 3: Lissajous Figures

Concentrations of NO, NO₂ and NO_x of an exhaust gas subjected to a DBD are shown in Fig. 4 alongside the decomposition efficiency in eV per removed NO_x molecule (dotted line in Fig. 4) as function of energy density ($P/(dV/dt)$).

The geometric parameters in this and the following figures are: $d = 1.65$ mm, $x = 1.3$ mm, $l_{plasma} = 15$ cm. The unit of ($P/(dV/dt)$) is W/(l_v/min), which is equivalent to 60 J per litre at 0°C and 1013 hPa. The initial NO concentration [NO]₀ in all following experiments is adjusted to 500 vpm with the MFC. Regarding real applications, the

energy density should be below 2 W/(l_n/min) in order to guarantee efficiency and competitiveness to other cleaning methods.

Since in the presence of O₂, NO is converted to NO₂ even if the gas is not subjected to a discharge, [NO]₀ is 390 vpm and [NO₂]₀ is 110 vpm i.e. [NO_x]₀ is 500 vpm. [NO] decreases with increasing energy density (which is achieved by increasing the voltage which in turn leads to a higher filament density) accompanied by an increase of [NO₂] to a maximum value and a further decrease, leading to a steady decrease of [NO_x]. This trend can be seen in all discharges in humid mixtures. If water is absent, no decomposition can be observed. The decomposition efficiency lies below 100 eV/NO_x^{dec.} at low decomposition, deteriorates however with increasing energy density. O₃ and HNO₃ could be detected as by-products, O₃ however only if NO is almost completely removed. Its concentration is then always below 100 vpm. HNO₃ is created in detectable amounts even at low energy density and its concentration can grow up to a few 100 vpm.

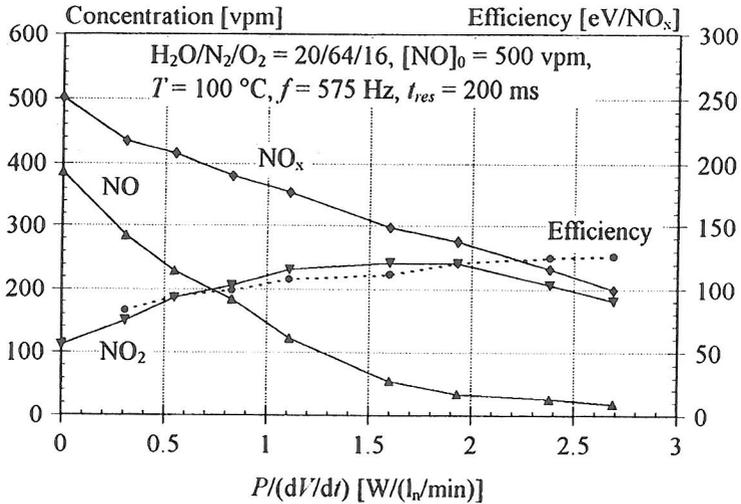


Fig. 4: Decomposition Rate and decomposition Efficiency

Fig. 5 shows the influence of H₂O vapour concentration in the exhaust gas on the NO_x decomposition and decomposition efficiency. Humidities of 10 %, 20 % and 30 % were investigated. An increase of [H₂O] from 10 to 20 % causes better decomposition and because of this better decomposition efficiency. A further increase of H₂O concentration to 30 % had no significant effect within the limits of the accuracy of the measurements.

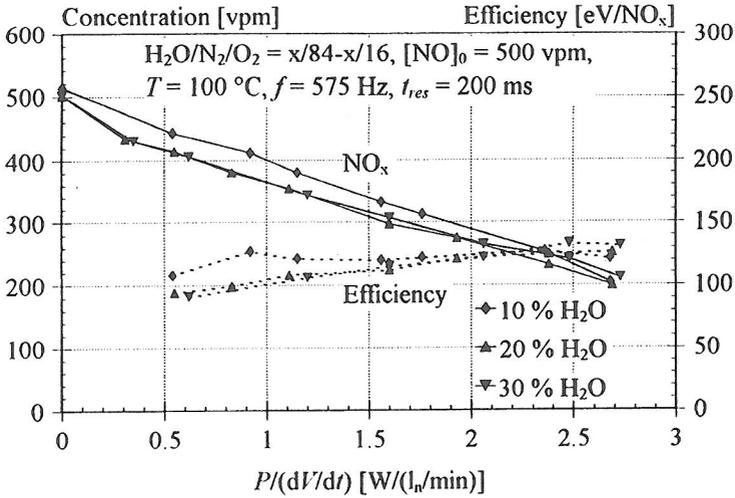


Fig. 5: Influence of [H₂O] on [NO_x]

The influence of O₂ concentration in the exhaust gas is shown in Fig. 6. Below 1 W/(l_r/min) no change of decomposition and decomposition efficiency could be observed. For low [O₂] and higher energy density the decomposition is worse and its efficiency deteriorates to 200 eV/NO_x^{dec.}.

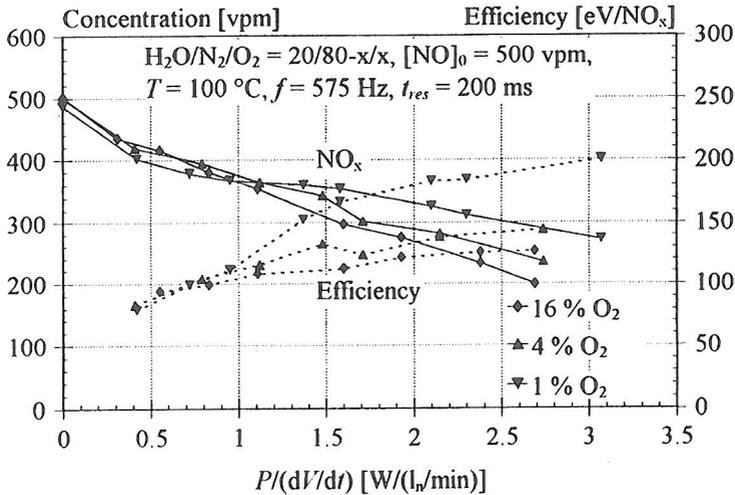


Fig. 6: Influence of [O₂] on [NO_x]

Conclusions and Outlook

Experimental investigations on the removal of toxic traces in synthetic exhaust gas mixtures (N_2 -, O_2 -, H_2O -, NO -, CO - and CO_2 -mixtures) using DBD were conducted. Apart from varying the composition of the gas different reactors were tested as well. A reduction of the NO_x concentration from 500 to below 100 vpm could be achieved at an efficiency of 150 eV per removed NO_x molecule. The best conditions for a good decomposition are 500 - 1000 Hz frequency, gap spacing 1 - 2 mm, residence time 200 ms, H_2O concentration at least 10 % and the oxygen concentration should be as high as possible. Up to now CO could not be removed and is even produced in the presence of CO_2 .

In order to improve the decomposition and its energy efficiency additives were also used (H_2 , CH_4 and NH_3 -solution) of which NH_3 -solution showed promising first results, which is also confirmed by theoretical investigations [8] which are carried out in conjunction with the experimental work. A further improvement is expected by using pulsed power supplies.

Acknowledgement

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