

# NO- and HC- Removal by Non-Thermal Plasmas

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## Abstract

A promising method of exhaust-gas cleaning is the use of pulsed corona discharges. In these devices, short pulses at high frequency produce radicals for a subsequent transformation of toxic pollutants ( $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{C}_x\text{H}_y$  etc.).

For a better understanding and optimization of possible applications of this technique it is necessary to develop models for the underlying physical and chemical processes which are responsible for the removal of pollutants.

In this work, we have theoretically investigated the removal of NO and the effect of ethane and ethene on NO removal by non-thermal plasma discharges at low temperature (373 K) and at atmospheric pressure.

The model takes into account production of radicals in every discharge pulse and subsequent removal of NO and HC by radicals. For this purpose, a detailed chemical model has been developed consisting of 96 species and 1187 elementary reactions. The results of our numerical simulations show good agreement with experimental data published in the literature.

## Introduction

Nitric oxides (including NO and  $\text{NO}_2$ ) emissions are a major environmental problem because of their negative influence on human health and vegetation [8]. The transportation industry, mostly motor vehicles, contributes about 40 % of the total  $\text{NO}_x$  load. Here, first of all, diesel engines are a major source for those pollutants [5]. The catalytic converters used with great success in spark-ignited gasoline engines (the reduction rates are typically up to 90 %) can not be well used on diesel engines because of the excessive amount of oxygen in the exhaust gas.

Therefore, new federal regulations on limiting  $\text{NO}_x$  emissions from diesel vehicles enhanced the need to study alternative cleaning technologies. One possibility, which has been investigated intensely in the past two decades is the treatment of the exhaust gases with non-thermal corona discharges. In the discharge, the electrons are highly accelerated while the gas molecules remain at approximately ambient temperature. The collisions of energetic electrons with neutral gas molecules cause different processes such as ionization, dissociation or excitation of the carrier gas molecules [4].

The key for the usage of plasmas as method for gas purification are the different radicals: They react slowly with the carrier gas and are available for the degradation of the trace components.

The aim of this work is to explain the main chemical processes responsible for the removal of NO and HC by pulsed corona discharges in the gas phase using a detailed chemical mechanism and to validate the proposed model by a comparison with experimental data. The results for two different gas mixtures are presented here: (1) NO and ethane in humid air and (2) NO and ethene in humid air.

The effect of pulsed discharges is included in the model by considering the (re-)production of radicals after every pulse and consecutive removal of NO by the radicals. The production of O, OH, H, N, O( $^1D$ ), O<sub>2</sub>( $a^1\Delta_g$ ), and N<sub>2</sub>( $A^3\Sigma_u^+$ ) in the discharge is taken into account. The results of our simulations are in good agreement with experimental data published in the literature.

## Radical Production and Reaction Scheme

The overall process of gas purification can be separated into three phases: (1) the discharge phase corresponds to the formation of primary radicals and electronically excited species by electron-molecule interactions, (2) a post-discharge metastable-quenching phase and (3) a post-discharge radical utilization phase, in which the “secondary radicals” (O<sub>3</sub>, HO<sub>2</sub>) are formed and NO- and HC-reactions occur. For typical operating conditions, the discharge phase is of order of few nanoseconds, the metastable-quenching phase is of order of tens of nanoseconds, and the radical utilization phase is of order of microseconds or longer [3]. The fact that those processes occur on different time scales allow us to treat the radical production and radical utilization as two independent processes.

In our model, we include electron reactions with the carrier gas molecules (N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O) only. Since the mole fractions of NO and unburnt hydrocarbons are in the order of few hundred of ppm, the fraction of discharge power deposited in those species will be small in any case. We do not include ionization processes in our model. Since the mean electron energy used for calculation of the radical concentrations was approx. 5 eV, the fraction of input power consumed for ionization of the molecules of the carrier gas is negligible [7].

The detailed reaction mechanism used in this work is built in a hierarchical manner. The core of the mechanism represents the H<sub>2</sub>/O<sub>2</sub>-submechanism, which was extended by adding further reactions for C-species (up to butane) and N-species. The whole reaction scheme consists of two main parts: (1) The hydrocarbon mechanism, which was originally developed and validated for flame conditions is based on the work of Baulch *et al.* [1]. (2) A reaction mechanism, describing the formation of NO<sub>x</sub> at high temperature conditions, developed and validated by Klaus [6].

In our reaction scheme, we adopted the Arrhenius parameters for the low temperature range according to literature values and added new reaction paths and new chemical species which are important at given conditions (temperature of the exhaust gas). Essential new chemical species are partially oxidated species and electronically excited species: O( $^1D$ ), O<sub>2</sub>( $a^1\Delta_g$ ) and N<sub>2</sub>( $A^3\Sigma_u^+$ ). Those species can not be neglected because they have a direct influence on both the evolution of certain radicals and the NO- and HC-transformation. The rate coefficients used in this work are compiled from different

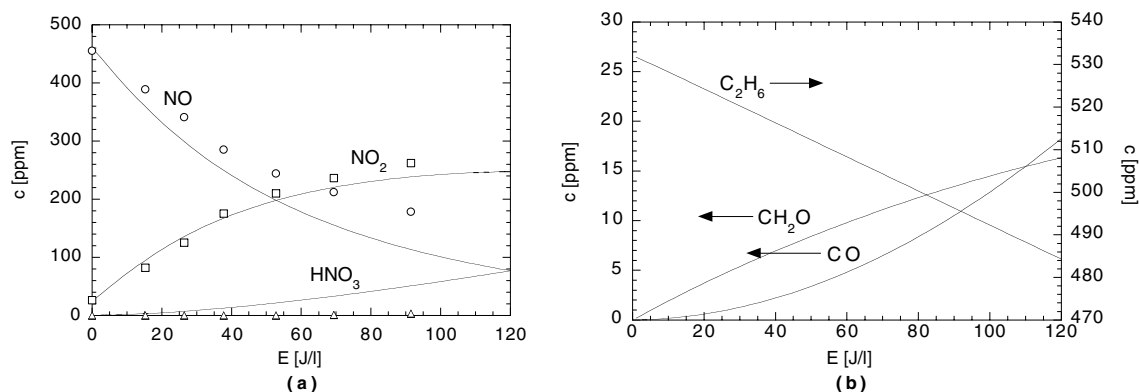


Figure 1: Removal of NO and C<sub>2</sub>H<sub>6</sub> in a pulsed plasma reactor as a function of transferred energy. Carrier gas: 72 % N<sub>2</sub>, 18 % O<sub>2</sub>, 10 % H<sub>2</sub>O Additive: 500 ppm NO, 500 ppm C<sub>2</sub>H<sub>6</sub>,  $T = 373$  K,  $p = 1$  bar. (a) Comparison between experiments [2] (points) and simulations (lines) for N-species. (b) Results of simulations for C-species.

sources and they are applicable over the temperature and pressure range encompassed by the experiments.

## Rate Equation Model and Two-Dimensional Model

In a volume-averaged approach (well-stirred reactor), the state of the system is completely specified by the mass fractions of each species in the system. The temperature and the pressure are constant under typical operating conditions of non-thermal plasmas. The simulations are performed with the well-stirred reactor code 'HOMRUN'

The two-dimensional simulations in a multi-point-to-plane plasma-reactor are performed with the computer-code 'CHEMFLOW' described in detail in [9] A dual-time-stepping technique has been implemented to solve unsteady reacting flow problems.

## Results

Our simulations are compared against the experiments of Bröer [2]. Here, the carrier gas is composed of 72 % N<sub>2</sub>, 18 % O<sub>2</sub> and 10 % H<sub>2</sub>O. Initial concentrations of NO and unburnt hydrocarbons are 500 ppm. The temperature and pressure are 373 K and 1 bar respectively. The author measures the concentration of different species as the function of energy transferred from the supply source to the gas per unit volume.

In the discharge, O- and O(<sup>1</sup>D)-radicals are formed rather than N-radicals. Additionally, NO-conversion is facilitated by the presence of unburnt hydrocarbons. Thus, oxidation products (NO<sub>2</sub>, HNO<sub>2</sub> and HNO<sub>3</sub>) are governing the removal of NO. We also investigated the evolution of C-species by plasma processing. In the experiment of Bröer [2]), the hydrocarbons are not fully oxidated to CO<sub>2</sub> and H<sub>2</sub>O. The main products are carbon monoxide and formaldehyde, consistent with the experiments.

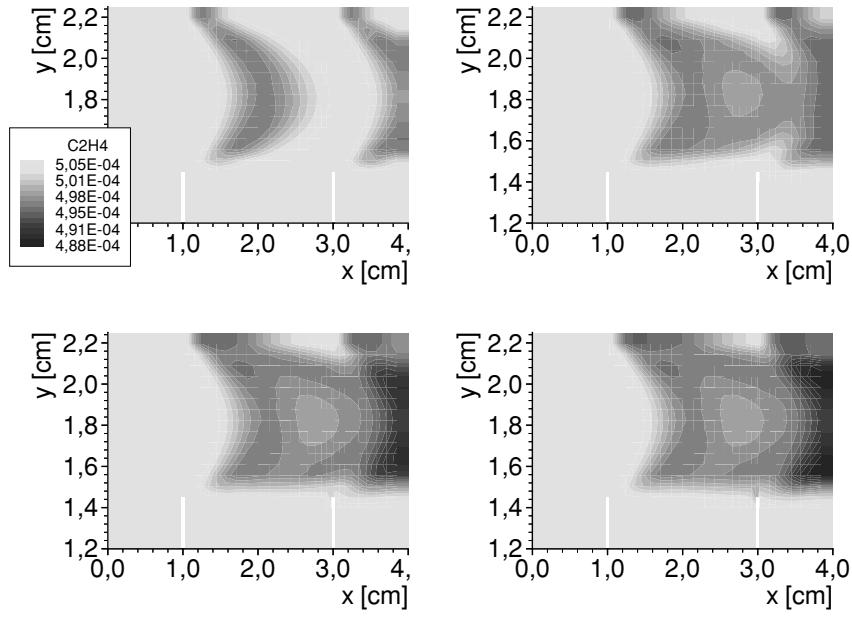


Figure 2: Consumption of  $C_2H_4$  in a multi-point-to-plane plasma-reactor  $t = 0,5$  ms (upper left),  $t = 1,0$  ms (upper right),  $t = 1,5$  ms (lower left) und  $t = 2,0$  ms (lower right). Electrodes shown in white, flow: Left to right. Temperature  $T = 473$  K, pressure  $p = 1$  bar.

Fig. 1 shows the species evolution by plasma processing of 500 ppm NO and 500 ppm  $C_2H_6$  in 72 %  $N_2$ , 18 %  $O_2$ , and 10 %  $H_2O$ . The results of our simulations are in good agreement with the experimental data. We can observe that the concentration of NO in both, experiment and calculation decreases almost proportionally with the growth of  $NO_2$ .

In a two-dimensional study a multi-point-to-plane co-axial plasma reactor is simulated to investigate fluid dynamic effects on the concentrations of NO and unburnt hydrocarbons. For a flow rate of 540 slm at a temperature of 473 K the flow through a typical section of the reactor is simulated. Due to the geometric complexity of the problem only a reduced reaction scheme consisting of 36 species and 210 reactions is implemented.

The two-dimensional calculations show an inhomogeneous consumption of  $C_2H_4$  perpendicular to the flow direction due to inhomogeneous initial concentrations of cleaning radicals in the discharge. The life-time of these cleaning radicals is too short to observe additional cleaning effects through enhanced mixing in the recirculation zone between the electrodes.

## Summary and Conclusion

In this paper, numerical simulations applying detailed chemical reaction schemes are used to explain the processes responsible for the removal of NO by plasma processing. For this purpose, a reaction mechanism consisting of 96 species among 1187 reactions

has been developed and validated by comparison with experimental data. Two different mixtures have been investigated: (1) NO and ethane in humid air (well-stirred reactor approach), and (2) NO and ethene in humid air (two-dimensional study). In systems containing oxygen, the main pathway for NO-removal is oxidation to NO<sub>2</sub>. Although the later can be converted to N<sub>2</sub> and O<sub>2</sub> using heterogeneous catalytic methods, the energy input for NO-oxidation needs to be optimized to reduce power consumption. A direct reduction of NO to N<sub>2</sub> is only feasible in system containing no oxygen (the detailed results for oxygen free systems are not shown here due to the lack of space).

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