

The effect of CO₂ on the plasma remediation of N_xO_y

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Plasma remediation is being investigated for the removal of oxides of nitrogen (N_xO_y) from atmospheric pressure gas streams. In previous works we have investigated the plasma remediation of N_xO_y from N₂/O₂/H₂O mixtures using repetitively pulsed dielectric barrier discharges. As combustion effluents contain large percentages of CO₂, in this paper we discuss the consequences of CO₂ in the gas mixture on the efficiency of remediation and on the end products. We find that there is a small increase in the efficiency of total N_xO_y remediation (molecules/eV) with increasing CO₂ fraction, however the efficiency of NO remediation alone generally decreases with increasing CO₂. This differential is more pronounced at low energy deposition per pulse. More remediation occurs through the reduction channel with increasing CO₂ while less NO₂ and HNO_x are produced through the oxidation channel. CO is produced by electron impact of CO₂ though negligible amounts of cyanides are generated. © 1996 American Institute of Physics.

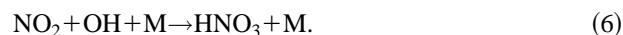
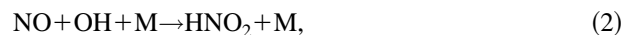
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Oxides of nitrogen (N_xO_y), in the emissions of coal fired electric power plants and diesel engines are deleterious to the environment and human health.¹ In order to meet new emission standards, a number of new technologies are being investigated for the removal of N_xO_y from such emissions. Among the plasma-based remediation techniques being considered,² dielectric barrier discharge (DBD) processing is a potentially effective method due to its efficiency for producing gas phase radicals that assist in remediation. A number of previous studies have investigated the plasma chemistry of humid air streams with 100s ppm of N_xO_y. They found that remediation of NO_x occurs through reduction and oxidation channels, producing N₂ and HNO_x respectively as products. In actual combustion effluent, additional species such as CO₂ and unburned hydrocarbons are present. These species may impact both the efficiency of remediation of N_xO_y and the by products which are generated. In previous works^{3,4} we presented the results from computational studies of the plasma remediation of N_xO_y from N₂/O₂/H₂O mixtures using repetitively pulsed DBDs. Here we discuss the additional effects of CO₂ in the gas mixture on the production of radicals, end products, and on the efficiency of remediation.

The general formulation of the model we have used in this study has been discussed in detail in Refs. 3–6 and therefore is only briefly summarized here. The one-dimensional simulation consists of a circuit model, a solution of Boltzmann's equation for the electron energy distribution, a plasma chemistry model, and a transport model. The circuit model provides E/N (electric field/gas number density) in the plasma. Boltzmann's equation is solved using a two term spherical harmonic expansion to determine the electron energy distributions which are then used to generate electron impact rate coefficients. The plasma chemistry model uses

both electron impact and temperature dependent heavy particle reaction rate coefficients to produce species densities as a function of time. There are 56 electron impact processes, 218 reactions, and 53 species used. The transport model further updates the species densities due to both diffusion and advection. Diffusion coefficients were estimated based on Lennard-Jones potentials as described in Ref. 7. A single advective velocity is used for all species and is determined from an iterative solution of the Navier-Stokes equations. After the species updates, the plasma conductivity is calculated for use in the circuit model. A complete list of reactions, rates, and species is available upon request from the authors. In this computational study we consider a DBD in which the microstreamers are radially symmetric and equally spaced. The initial streamer radius is 30 μm while the area density of the microstreamer streamers was chosen sufficiently small (1.5 cm⁻²) to resolve the advective motion without complications of interfering streamers.

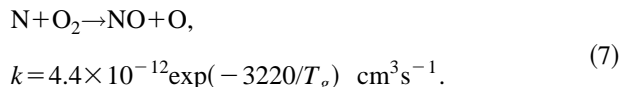
The dominant reaction pathways and time scales in the remediation of NO for mixtures without CO₂ were discussed in Refs. 3–4. Those reactions which are pertinent to this work are reviewed here. N, O, and OH radicals are produced by electron impact collisions on N₂, O₂, and H₂O during the short (<10 ns) current pulse. NO and N_xO_y are then dominantly remediated shortly after the pulse ($t < 10^{-4}$ s) by reactions with those radicals. Remediation of NO at longer times (10^{-3} s $< t < 10^{-1}$ s) occurs dominantly by reaction with O₃. The major products, N₂, NO₂, HNO₂, and HNO₃, are generated by



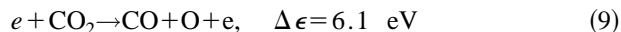
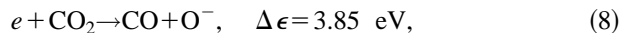
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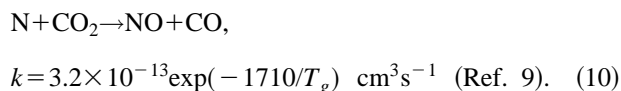
In addition, high localized radical densities and high gas temperatures, T_g , in the streamer region can lead to production of NO by large activation energy processes, such as⁸



In mixtures containing CO_2 , the major additional significant reactions are electron impact dissociation of CO_2 ,¹⁰



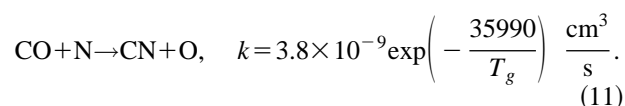
(where $\Delta\epsilon$ is the threshold energy) and the analogue to Eq. (7)



The only new major end product is CO.

In our previous works, we found that remediation of NO proceeded mainly by the reduction reaction, Eq. (1), since the gas mixture contained low percentages of O_2 (5%). In this work we consider gas mixtures of $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2 = 77/15 - x/8/x$, $0 \leq x \leq 12$ with 500 ppm NO (400 K, 1 atm). These mixtures keep the proportions of N and O approximately those of air. N and OH are created primarily during the current pulse by electron-impact reactions with N_2 , and H_2O , respectively. O is created by both electron-impact reaction with O_2 during the current pulse and to a lesser extent during remediation by reduction of NO [Eq. (1)]. As a result, much of the NO remediation by N and O occurs in and near the streamer region where the local N and O densities greatly exceed the volume averaged density. O_3 is created at later times (peak density at $t \sim 2 \times 10^{-4}$ s) by reactions of O with O_2 . O_3 is created on a longer time scale after O has transported outward from the streamer region by diffusion and advection. Therefore O_3 is produced over a larger radius in the discharge and, hence, is more diffuse when it reacts with NO to produce NO_2 . For example, in the cases studied here, at the end of the current pulse the O atom density is largely confined and reacts over a radius of $< 100 \mu\text{m}$. By the time reactions with O_3 [Eq. (5)] are the principal remediation mechanism of NO (at $t \approx 10^{-3}$ s), remediation occurs over a radius of ~ 0.04 cm. For these conditions we found that the reaction of NO with O_3 [Eq. (5)] accounts for roughly 1/2–2/3 of the remediation due to the larger concentrations of O and O_3 .

The presence of CO_2 in the gas stream can result in the production of CO and cyanides, and can affect the efficiency of remediation of N_xO_y . In all cases investigated, the production of cyanides (CN, HCN, and NCCN) was negligible. The most direct pathway to CN, and hence HCN, is the reaction⁹



Due to the large activation energy of this reaction, little CN is produced at the temperatures of interest (< 500 K). Cya-

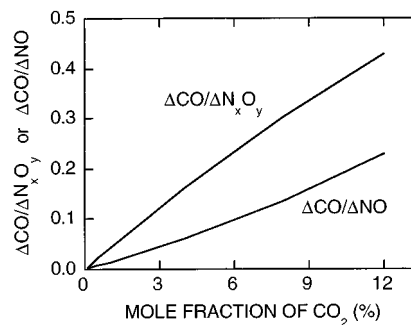
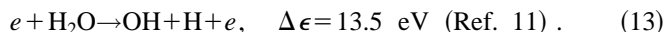
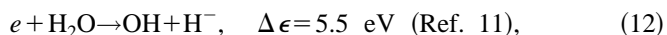


FIG. 1. Production of CO as a function of CO_2 mole fraction after 0.1 s following the current pulse. Production is expressed as a ratio of the CO generated divided by the NO or N_xO_y remediated. At large CO_2 fractions, generation of CO is comparable to the removal of N_xO_y .

nides may also be generated by the reaction of N with unburned hydrocarbons, processes not addressed here.

The generation of carbon monoxide is of greater importance. CO is generated by the electron impact reactions in Eqs. (8) and (9). Due to the small Arrhenius factor for reoxidation of CO to CO_2 by O, and the large rate of reaction of O atoms with other species, CO tends to persist in the gas stream. A measure of the relative importance of the production of CO is $\Delta[\text{CO}]/\Delta[\text{NO}]$ or $\Delta[\text{CO}]/\Delta[\text{N}_x\text{O}_y]$, which are the ratios of the total amount of CO generated compared to the amount of NO or N_xO_y remediated. These ratios are shown in Fig. 1 as a function of initial mole fraction of CO_2 . At large fractions of CO_2 , the amount of CO generated is approximately half of the N_xO_y removed.

The presence of CO_2 affects the radical production in at least two ways. First, the low energy threshold for CO_2 dissociation and vibrational excitation lowers the high energy portion of the electron energy distribution, thereby decreasing the frequency of high energy processes for a given power deposition. This is most important for the production of OH since the H_2O dissociation thresholds are higher than those for O_2 (4.5 eV),



The production of OH decreases by factors of 3–4 when the CO_2 concentration increases to 12%. Second, when CO_2 is in the gas stream, the production of O and O_3 are also lower due to the decrease in the initial mole fraction of O_2 . Although production of both O and O_3 also decrease by 3–4 as the CO_2 concentration increases to 12%, the decrease in the O_3 density has more severe consequences. The O atom densities typically peak at short times after the current pulse at small radii about the microstreamer. The peak density is many times that of the initial NO density, and so the described decrease still leaves a critical amount of reactant. The diffuse distribution of O_3 which occurs 100s μs after the pulse produces a low density ($\approx 1/10$ of the initial NO density). A decrease in this already small density has a more severe impact on remediation.

These changes in radical production affect the proportions of end products and the remediation efficiency. The energy efficiency for remediation of NO and N_xO_y for streamer energy depositions of 225 and 1130 mJ/cm^3 are

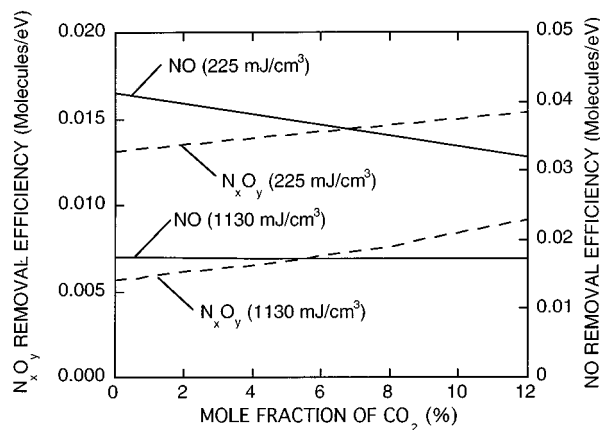


FIG. 2. Energy efficiency for remediation of NO and N_xO_y as a function of initial CO_2 fraction for energy depositions of 225 and 1130 mJ/cm^3 in the streamer. Higher values indicate more efficient removal. Remediation is more efficient at lower energy deposition due to more efficient utilization of radicals. NO removal efficiency generally decreases with increasing CO_2 due to decreasing conversion of NO to NO_2 by O_3 [Eq. (5)] and generation of NO. The generation of NO by CO_2 is proportionally smaller at the higher energy deposition and temperature.

shown in Fig. 2. Efficiency is evaluated in terms of NO or N_xO_y molecules removed per eV deposited so that higher values indicate more efficient removal. The relative production of the major products are shown in Fig. 3. Concentrations of HNO_x products decrease with increasing CO_2 due to the decreasing production of OH. NO_2 production [Eq. (5)] decreases due to the diminishing production of O_3 and the resulting decrease in NO remediation. There is a decrease in radicals which consume N atoms and in species which compete with N to react with NO. These conditions allow more N to react with NO, resulting in greater reduction of NO [Eq. (1)] and greater total N_xO_y remediation. The energy efficiency for remediation of all N_xO_y improves by some 10s % with increasing CO_2 due to the more efficient utilization of the N atoms.

These trends remain generally the same at higher energy deposition. The energy efficiencies, however, are generally lower. This results from an increase in radical production which enhances the rate of radical-radical reassociation reactions, such as $N+N+M \rightarrow N_2+M$. These processes are non-linear in radical density relative to the remediation reactions [Eqs. (1)–(6)] and thus radicals are used less efficiently. At low energy depositions and temperatures, reactions of N with CO_2 [Eq. (10)] which produce NO are faster than reactions with O_2 [Eq. (7)]. At low energy depositions, then, increasing the CO_2 mole fraction can increase regeneration of NO, and complements the decrease in O_3 production to decrease net remediation. However, as the energy deposition and temperature increase, the rate of $N+O_2 \rightarrow NO+N$ [Eq. (7)] can surpass that of the analogous reaction with CO_2 [Eq. (10)]. Therefore, at high energy deposition, increasing the CO_2 fraction can actually lower the amount of NO regeneration. The decrease in NO remediation efficiency with increasing CO_2 is therefore not as severe as at the lower energy deposition. Additionally, the lower rate of consumption of N atoms by Eq. (7) leaves more N atoms available for the reduc-

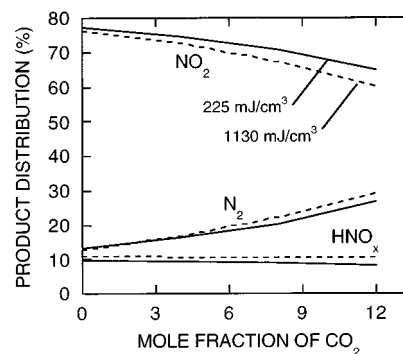


FIG. 3. Relative proportions of the major products for remediation of NO. The solid line is for an energy deposition of 225 mJ/cm^3 . The dashed line is for an energy deposition of 1130 mJ/cm^3 . Less oxidation occurs at large CO_2 fraction due to the lower rate of generation of O and O_3 .

tion reaction, thereby increasing the amount of reduction with increasing CO_2 concentration.

In conclusion, the presence of CO_2 in gas streams in mixtures affects the plasma remediation of NO through decreased production of O_3 and OH. Total N_xO_y remediation efficiency increases with increasing CO_2 while the remediation of NO alone decreases with increasing CO_2 . The reaction products also are a function of CO_2 fraction. More N_2 , less HNO_x , and less NO_2 are produced with increasing CO_2 . This is particularly advantageous for mobile sources, such as diesel exhaust, since the acidic waste product would have to be collected. CO is also a significant end product; however, negligible quantities of cyanides are produced.

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