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13. ABSTRACT *(Maximum 200 Words)*

Electrical energy coupled into an NTP can be used to create highly reactive species, e.g., oxygen atoms O(3P), OH radicals, N radicals, electrons, and other free radicals, ions, and active species in gaseous media at near-ambient temperatures and pressures. These active species subsequently react with entrained pollutants in the gas, converting them to non-hazardous compounds. Because NTP processing shows promis for simultaneously removing different types of pollutants (e.g., NOx/SOx and VOCs), it is particularly attractive for many present and future environmental applications.

In a thermal process thousands of electron volts of energy are typically required to decompose one pollutant molecule, because it is a non-selective process. Compared to a thermal process, non-thermal plasmas typicall require energies of order 10's-100's eV per decomposed pollutant molecule, thus showing the benefits of selective chemistry.

It has been decided that the primary targets for our work on NTP technology will be jet engine test cells (JETCs) and cruise missile test cells (CMTCs), which are stationary sources of air emissions. Therefore, we can exercise the option of converting the emitted NOx to HNO3 (or related acids) and scrub out the acid. In this white paper, we will show the primary paths of such conversions.

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NATIONAL LABORATORY

Reactions of Oxides of Nitrogen (NO_x) Leading to the Formation of Nitric Acid (HNO_3) in Non-Thermal Plasmas (NTPs)

White Paper for the Strategic Environmental Research and Development Program (SERDP) (Compliance Project CP-1038: "Development of Non-Thermal Plasma Reactor Technology for Control of Atmospheric Emissions")

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Reactions of Oxides of Nitrogen (NO_x) Leading to the Formation of Nitric Acid (HNO_3) in Non-Thermal Plasmas (NTPs)

Abstract

SERDP Compliance Project CP-1038 ("Development of Non-Thermal Plasma Reactor Technology for Control of Atmospheric Emissions") has been commissioned to evaluate and develop non-thermal plasma (NTP) reactor technology, a form of low-temperature plasma chemical processing, for Department of Defense (DoD) applications. The primary emphasis is on the control of emissions of oxides of nitrogen (NO_x), with a secondary emphasis on hazardous air pollutant (HAP) emission control (primarily volatile organic compounds - VOCs). In this white paper, as a SERDP-requested deliverable, we will verify the NO_x removal reactions in NTPs, especially those converging on nitric acid (HNO_3) as a primary reaction product. The benefit of making HNO_3 as a primary terminal de-NO_x product is that it can be easily neutralized by relatively simple caustic (base) scrubbers - although the economics of scrubber systems needs to be compared with the conversion to particles that can be filtered or precipitated.

Jet engines also emit a significant amount of SO_x in their exhaust; NTPs alos remove SO_x and actually do it more effectively in combination with NO_x. This will not be dealt with in this particular white paper.

Background

Free radicals, energetic electrons, and other active species are strongly reactive in decomposing many air pollutants (e.g. NO_x/SO_x - oxides of nitrogen and sulfur, VOCs - volatile organic compounds). The reaction rates of free radicals with organic compounds can be orders of magnitude larger than a strong oxidizer like ozone. Highly reactive species, such as free radicals, can be generated with plasmas.

A plasma (in electrical terminology) is an ionized state of matter (sometimes called the *fourth state of matter*) containing electrons and ions. A plasma behaves much like an *electrical gas*, where the individual charged particles which compose the plasma interact collectively with applied and self-generated electromagnetic fields. Plasmas can be created thermally by heating ordinary matter to a temperature greater than about 2,000 C. In such a *thermal plasma*, all the species - electrons, ions, neutral atoms and molecules - are in thermal equilibrium (i.e., at the same temperature). Considerable heat energy (enthalpy) must be added to the gas to achieve such an equilibrium. In contrast to a thermal plasma, a *non-thermal plasma* (or non-equilibrium plasma) is characterized by electrons which are not in thermal equilibrium with the other gas species. The electrons are *hot* (few to tens of eV temperature), while the ions and neutral gas species are *cold* (near-ambient temperature for neutrals and order tenths of eV for ions). The key idea in NTP processing is to direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas. Two common ways of creating an NTP are by an electrical discharge in a gas or the injection of energetic electrons (e.g., 100 keV - 1 MeV) into a gas. Both processes create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature).

Electrical energy coupled into an NTP can be used to create highly reactive species, e.g., oxygen atoms $O(^3P)$, OH-radicals, N-radicals, electrons, and other free radicals, ions, and active species in gaseous media at near-ambient temperatures and pressures. These active species subsequently react with entrained pollutants in the gas, converting them to non-hazardous mineralized compounds (CO_2, H_2O, and acids) or other more-easily managed compounds. Because NTP processing shows promise for simultaneously removing different types of pollutants (e.g., NO_x/ SO_x and VOCs), it is particularly attractive for many present and future environmental applications.

In a thermal process (like incineration or equilibrium plasma), thousands of electron volts of energy are typically required to decompose one pollutant molecule, because it is a non-selective process. Compared to a thermal process, non-thermal plasmas typically require energies of order 10's - 100's eV per decomposed pollutant molecule, thus showing the benefits of selective chemistry.

Atmospheric emissions reduction is a pervasive DoD environmental objective. the DoD has identified environmental initiatives for NO_x, HAP, and VOC emissions reduction as driven by environmental, safety, and health concerns, regulatory concerns, and concerns over the ability to maintain future missions and operations. JETC (jet engine test cell) and CMTC (Cruise Missile test cell) NO_x control and the control of NO_x emissions from industrial boilers, mobile power carts, and internal combustion engines are near-term targets for NTP technology. The de-NOx paths which lead to nitric acid are more attractive for stationary sources but not mobile sources (where it is preferable to reduce the NO_x to N_2 and O_2 instead).

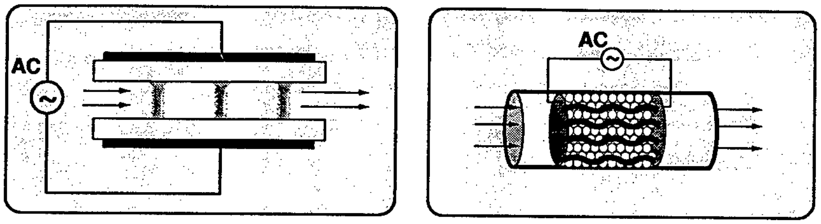
It has been decided that the primary targets for our work on NTP technology will be JETCs and CMTCs, which are stationary sources of air emissions. Therefore, we can exercise the option of converting the emitted NO_x to HNO_3 (or related acids) and scrub out the acid. In this white paper, we will show the primary paths of such conversions.

Non-Thermal Plasma Reactors

NTPs for gas-phase pollutant processing are normally created in one of two ways: by an electrical discharge (where a high voltage is applied across electrodes in a gas or along a surface adjacent to a gas) or by the injection of a beam of energetic electrons (e.g., 100 keV - 1 MeV) into a gas. The key idea of both methods is to direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas (i.e., add enthalpy). The energetic plasma electrons are sometimes themselves dominant in the process of pollutant decomposition, while under other conditions, the electrons create free radicals that attack the pollutants.

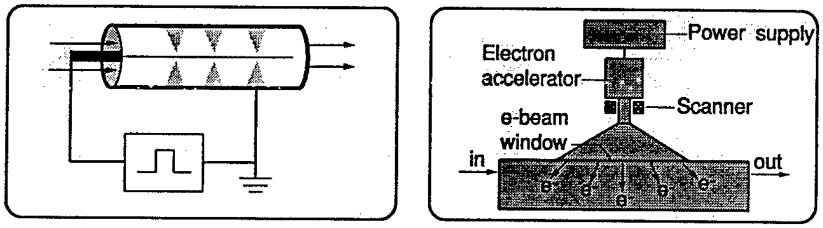
Figure 1 shows four plasma reactor configurations commonly employed for NTP processing **[1, 2]**. These four reactors - silent discharge (dielectric barrier), corona, electrified packed bed, and electron beam - are the subject of several international investigations for the abatement of hazardous, toxic, and undesirable-odor air emissions. All of them require electricity as a power source and may also require peripheral equipment, such as scrubbers and particulate filters, in a complete system.

The operational basis of the reactors will only be briefly discussed here. The reader is referred to the literature for more detailed descriptions of each reactor.



Silent discharge (dielectric-barrier discharge)

Electrified packed bed



Pulsed or DC corona

Electron beam

Figure 1: Commonly-employed NTP reactors.

In corona, there are three ways to stabilize the discharge and prevent thermal spark formation: a non-homogeneous electric field, a pulsed field, or a high-speed gas flow. Silent discharges use charge buildup on a capacitive barrier to achieve a similar end result. The electrified packed bed (and a similar surface discharge reactor) are closely related to a barrier discharge. All three of these methods create transient electrical-discharge streamers in the gas. The streamer is the source of energetic electrons and other active species. A relatively high voltage (determined by the reactor geometry, gas composition, and gas pressure) is required to cause electrical breakdown in the gas. The necessary voltage is supplied by an electrical drive circuit connected to the reactor.

An electron-beam reactor requires an electron accelerator to produce the beam that is injected into the process gas. The source of electrons (the cathode) can be separate from the accelerating-field section (as in thermionic-cathode and plasma-cathode devices) or integrated with the accelerating-field section (as in a field-emission-cathode electron gun). Electron-beam reactors must use a foil or window to separate the vacuum section of the accelerator from the process gas. The electron beam penetrates the foil, depositing energy in the process gas by collisions and molecular excitation processes coupled to the creation of a large-volume non-thermal plasma.

A novel corona reactor called the Corona Radical Shower (CRS), or radical injector, has been demonstrated by (Kanazawa et al 1997 [3] and Chang et al 1998 [4]). This device is more fully described in an earlier-report (M. Matsuoka et al 1997 [5]). Here, a brief summary of the system will be presented.

In the CRS system (see Figure 2), arrays of small nozzles or showers, each with a small bleed-gas flow, are introduced into a wire-plate DC corona reactor. The purpose of the nozzles is to create desirable active species and inject them into the larger main corona treatment region, which enhances the overall pollutant-removal effectiveness. The injected active species can be tailored to the particular pollutant stream being treated by selecting the shower-injector bleed-gas so that it produces active species that are particularly effective in decomposing the target pollutant.

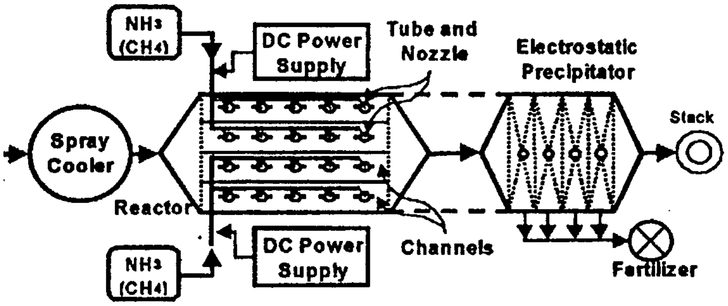


Figure 2: Schematic diagram of CRS reactor. Ammonia (NH_3) or methane (CH_4) are added to generate radicals that drive reactions leading to the formation particulates; these particulates are then captured by the electrostatic precipitator. Some of the captured products are useful for agricultural fertilizer (e.g., ammonium nitrate, NH_4NO_3).

Experiments by our collaborators at McMaster University have shown that, for NO removal, ammonia (NH_3) and a hydrocarbon like methane (CH_4) are useful injector-gas additives. It is interesting to note that McMaster has also shown that, for JETC de-NO_x, normally-present hydrocarbons in the exhaust stream can enhance the de-NO_x process. In this case, air or a slipstream of the JETC exhaust itself is effective as a shower-injector gas, without requiring additional external additives (like NH_3).

Active Species Generation and Pollutant Decomposition

In the decomposition process, plasma physics and plasma chemistry are interconnected. The NTP is created by the electrical discharge or electron beam and the active species are generated in the pollutant-containing gas by plasma-initiated processes (starting from energetic electrons). The active species then react with and decompose the chemical pollutants. In the sections below, we will present brief discussions of active species (i.e., radicals) generation and decomposition chemistry. Example radical formation mechanisms and radical yields for an air-like mixture will be presented. Following this, the decomposition chemistry of NO_x (primarily nitric oxide NO and nitrogen dioxide NO_2) will be discussed.

Radical Production

Active species can be formed in a variety of ways in non-thermal plasmas. Table 1 below shows the main processes for an air-like carrier gas **[1, 6]**. Ammonia (NH_3) is also included in the example because it is sometimes employed as an additive in flue-gas (NO_x/SO_x) processing.

Table 1
Example Radical Formation Mechanisms

Electron Impact

$e + O_2 \rightarrow O + O^* + e$

$e + N_2 \rightarrow N + N + e$

$e + N_2 \rightarrow N + N^* + e$

$e + NO \rightarrow N + O + e$

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

$e + O_2 \rightarrow O_2\,(^1\Delta_g) + e$

$e + O_2\,(^1\Delta_g) \rightarrow O + O + e$

$e + O_2\,(^1\Delta_g) \rightarrow O + O\,(^1D) + e$

$e + NH_3 \rightarrow NH + H_2 + e$

$e + NH_3 \rightarrow NH_2 + H + e$

Quenching

$O^* + H_2O \rightarrow 2OH$

$N_2^* + O_2 \rightarrow N_2 + O + O$

$N^* + H_2O \rightarrow NH + OH$

Ionization/Clusters, Recombination

$e + O_2 \rightarrow O_2^+ + 2e$

$e + N_2 \rightarrow N_2^+ + 2e$

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

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

$O_2^+ + H_2O \rightarrow O_2^+\,(H_2O)$

$O_2^+\,(H_2O) + H_2O \rightarrow HO_3^+ + O_2 + OH$

$O_2^+\,(H_2O) + H_2O \rightarrow HO_3^+\,(OH) + O_2$

$HO_3^+\,(OH) + H_2O \rightarrow HO_3^+ + H_2O + OH$

$e + O_2^+ \rightarrow O + O^*$

$e + N_2^+ \rightarrow N + N^*$

Others

$H + O_3 \rightarrow OH + O_2$

$HO_2 + NO \rightarrow OH + NO_2$

$H + O_2 + M \rightarrow HO_2 + M$

Selected Abbreviations

O: $O(^3P)$, O^*: $O(^1D)$, N: $N(^4S)$, N^*: $N(^2D)$,
O_2^*: $O_2\,(^1\Delta_g)$
N_2: $(A^3\Sigma_u^+)$, N_2^*: $N_2\,(A^3\Sigma_u^+)$ or $N_2(A)$

The yield of a particular radical species (i.e., the number of radicals produced per unit deposited plasma energy) will depend on factors such as the gas composition, the gas pressure, and the average electron temperature **[1, 2, 6]**. Consider a humid, atmospheric pressure, air-like mixture. For commonly-used electric-discharge reactors, the yields of $O(^3P)$, OH, and N radicals are of order 10, 1, and 1 per 100 eV of deposited energy, respectively. For electron-beam reactors, the $O(^3P)$ yield is about one-third less, the yield of OH is roughly twice as large, and the yield of N is nearly 20 times larger than in discharge reactors. Another way of stating the difference between discharge reactors and electron-beam reactors is that discharge reactors are very efficient producers of oxygen atoms, while electron-beam reactors are very efficient producers of hydroxyl radicals and nitrogen atoms. This means that oxidation reactions with O-atoms have the highest efficiency in discharges, while electron beams can more efficiently promote N-atom-driven reductive reactions in addition to OH-radical-driven oxidation reactions.

Leverage in increasing the effective radical yields is obtained by increasing the electron temperature. More active species (radicals, electrons, ions, excited states, etc.) can be created with higher efficiency at higher electron temperatures T_e (or reduced electric field strength E/N). Electron beam reactors normally produce more energetic electron temperatures, but they are not presently the simplest or most economical system. If the electron temperature of an electrical-discharge reactor can be significantly increased (e.g., through a novel electrical drive), significant improvements in efficiency and associated economics may be possible.

Decomposition Chemistry of Oxides of Nitrogen

The use of NTPs for the removal of NOx and SOx from flue gases was pioneered by Japanese researchers in the 1970's and focused on electron-beam reactors. The scrubbing of flue gases with electron-beam systems was initiated in 1970 in Japan by the Ebara Corporation (Frank & Hirano 1993 **[7]**) and extensively studied during that decade by Japanese scientists (Kawamura et al. 1978 **[8]**, Tokunaga & Suzuki 1978 **[9]** and others (Willis & Boyd 1976 **[10]**, Pearson & Ham 1988 **[11]**).

Out of that work came the essential chemical reactions for NO_x removal in both dry and moist gas mixtures (Tokunaga and Suzuki, Pearson & Ham). Pearson and Ham used a rather complicated reaction scheme that employed more than 150 chemical reactions to describe NO_x removal alone. These mechanisms were refined and expanded to include hundreds of chemical reactions by (Chang 1986 **[12]** and Matzing 1991 **[13]**). Recently, the role of hydrocarbons (in particular, propene in gasoline-engine exhaust) in the removal of nitric oxide NO has been proposed by (Penetrante et al 1997 **[14]**, Chang et al 1998 **[4]**). This will be discussed further below in considering the eventual fate of NO in various gas mixtures.

The removal of SO_x and NO_x from gaseous media was also investigated at laboratory scale using electrical-discharge reactors (pulsed corona) in the 1980s - with pioneering experimental work performed for NO_x by (Masuda & Nakao 1990 **[15]**) and for SO_x by [Mizuno et al. 1986 **[16]**; and modeling work performed by (Gallimberti 1988 **[17]**). Following these basic investigations, scale-up of the pulsed corona process for flue gases emitted from a coal-burning electrical power plant was carried out at pilot-plant and demonstration levels (Dinelli et al. 1990 **[18]**, Civitano et al 1993 **[19]** and Song et al 1997 **[20]**). An excellent review of electric-discharge work can be found in (Chang et al 1991 **[21]**). The role of microhydrodynamics in de-NOx by electrical-discharge streamers has recently been elucidated by (Gentile & Kushner 1995 **[22]** and Xu & Kushner 1997 **[23]**).

In this white paper, we will not attempt to describe NO_x removal with the more-complicated chemical models because it is not necessary to do so. We will describe essential aspects of the reaction chemistry with a focus on the paths leading to nitric acid HNO_3 formation. We will discuss three categories of NO_x removal (primarily NO) by NTPs: dry gases without the presence of hydrocarbons, moist gases without hydrocarbons, and moist gases with the presence of hydrocarbons (the usual case for engine emissions).

Dry Gas Mixtures

The decomposition chemistry for NO in dry gas (e.g., air) is tractable and can be largely described as follows **[1, 9, 11, 13, 21, 24]**:

$O + NO + M \rightarrow NO_2 + M$
$O + NO_2 \rightarrow NO + O_2$
$O + N_2 \rightarrow NO + N$
$O + O_2 + M \rightarrow O_3 + M$
$O_3 + NO \rightarrow NO_2 + O_2$
$O_3 + NO_2 \rightarrow NO_3 + O_2$
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
$N(^2D) + O_2 \rightarrow NO + O$
$N + NO \rightarrow N_2 + O$

$N(^2D) + NO \rightarrow N_2 + O(^1D)$
$N + NO_2 \rightarrow N_2O + O$
$N + NO_2 \rightarrow 2NO$
$N + NO_2 \rightarrow N_2 + O_2$
$N + N_2O \rightarrow NO + N_2$
$O(^1D) + NO_2 \rightarrow NO + O_2$
$O(^1D) + N_2O \rightarrow 2NO \text{ or } N_2 + O_2$
$N_2(A) + O_2 \rightarrow N_2 + 2O$
$N_2(A) + N_2O \rightarrow N_2 + N + NO.$

The main objective of a de-NO_x process is to reduce the NO_x to benign molecular nitrogen and oxygen or to convert it to compounds that that can be more easily removed by conventional technologies. From the above reaction scheme, one observes that oxidative-mode reactions involving O-atoms can trap total NO_x as NO and NO_2. Reductive-mode reactions involving N-atoms drive more NO_x to N_2 and O_2. This reduces the scrubber requirements, but depends on higher average energy electrons (a condition presently favored by electron-beam reactors).

With oxidative de-NO_x processes driven by O-atoms and O_3, NO_2 is the the most probable reaction intermediate. It is somewhat more soluble in water than NO_x, which facilitates its removal by conventional wet-scrubbing techniques. However, for higher flow rates, the scrubber is usually impractically large. The chemistry can be favorably influenced by multiple excitation, in which two or more NTP reactors are placed in series with scrubbers. Here the NO_2 reaction intermediate is scrubbed out at a low concentration before the gas is treated by the next reactor, thus reducing the conversion back to NO. NO_2 is also more easily adsorbed by some sorbents, which can make the oxidative conversion of NO to NO_2 attractive in practical systems (the NO_2 can be captured and later treated).

Moist Gas Mixtures without the Presence of Hydrocarbons

Oxidative-mode reactions involving OH-radicals produce nitric acid HNO_3, which can be easily removed by a caustic scrubber.

In wet gas (most representative of practical off-gas conditions), conversion to caustic-scrubbable nitric acid (HNO_3) is probably the most practical de-NO_x pathway. Here the key reactions are the same as those operative in dry-gas mixtures but with the addition of OH, $N(^2D)$, NH, H, and HO_2-radical and O_3 reactions (Chang 1989 **[25]** and Penetrante et al 1995 **[26]**):

$O + NO + M \rightarrow NO_2 + M$
$O + NO_2 \rightarrow NO + O_2$
$O + N_2 \rightarrow NO + N$
$O + O_2 + M \rightarrow O_3 + M$
$O_3 + NO \rightarrow NO_2 + O_2$
$O_3 + NO_2 \rightarrow NO_3 + O_2$
$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$N(^2D) + H_2O \rightarrow NH + OH$
$NH + NO \rightarrow N_2 + OH$
$NH + O_2 \rightarrow NO + OH$
$NO + NO_3 \rightarrow 2NO_2$
$NO + OH + M \rightarrow HNO_2 + M$
$OH + HNO_2 \rightarrow NO_2 + H_2O$
$OH + NO_2 + M \rightarrow HNO_3 + M$

$$N(^2D) + O_2 \rightarrow NO + O$$
$$N + NO \rightarrow N_2 + O$$
$$N(^2D) + NO \rightarrow N_2 + O(^1D)$$
$$N + NO_2 \rightarrow N_2O + O$$
$$N + NO_2 \rightarrow 2NO$$

$$N + NO_2 \rightarrow N_2 + O_2$$
$$N + N_2O \rightarrow NO + N_2$$
$$O(^1D) + NO_2 \rightarrow NO + O_2$$
$$O(^1D) + N_2O \rightarrow 2NO \text{ or } N_2 + O_2$$
$$N_2(A) + O_2 \rightarrow N_2 + 2O$$
$$N_2(A) + N_2O \rightarrow N_2 + N + NO$$

In a scrubber, nitric acid can also be converted to potentially useful byproducts, such as ammonium nitrate NH_4NO_3 agricultural fertilizer, by adding ammonia NH_3. With humid gas, nitrous acid HNO_2 is also a significant reaction intermediate, which may decompose into NO and NO_2. Multiple excitation, accompanied by intermediate filtration can probably also reduce such undesirable reformation of NO_x.

The addition of ammonia can also be used to advantage is further promoting reductive chemistry **[1]**, as exemplified by the following reactions:

$$OH + NH_3 \rightarrow NH_2 + H_2O$$
$$NH_2 + NO \rightarrow N_2 + H_2O$$
$$NO_2 + NH_2 \rightarrow N_2O + H_2O$$
$$NO_2 + H \rightarrow NO + OH,$$

where the oxidative radical OH is replaced by the reductive radical NH_2.

Effect of Hydrocarbons on NO Removal in Moist Gas Mixtures

There is some evidence in the literature to suggest that hydrocarbon additives can improve the efficiency of NO_x removal by regenerating OH-radicals. This is illustrated by the following reaction scheme using methane (CH_4) as a representative hydrocarbon.

$$OH + CH_4 \rightarrow H_2O + CH_3$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2\bullet + M$$
$$CH_3O_2\bullet + NO \rightarrow CH_3O\bullet + NO_2$$
$$CH_3O\bullet + O_2 \rightarrow HCHO + HO_2$$
$$HO_2 + NO \rightarrow NO_2 + OH.$$

Experiments on pulsed corona performed at the Lawrence Livermore National Laboratory have shown that the addition of n-octane (C_8H_{18}) improves the efficiency of NO removal **[27]**. Even more recent work has reported an increased NO removal efficiency with the addition of other hydrocarbons **[28]** besides CH_4. However, the NO removal is driven toward the oxidative channel of NO_2 as a final product, not reduction to N_2.

As recently proposed by (Penetrante et al 1997 **[14]**), in gasoline engines, in which propene (C_3H_6) is a major hydrocarbon component of the exhaust, oxidation of NO to NO_2 dominates. If the exhaust gas is moist (which is the usual case), HNO_3 production would be expected to be a dominant de-NO_x pathway. However, competition between the scavenging of OH-radicals by C_3H_6

and the formation of acids by reactions of OH with NO and NO_2 results in a lower yield of acids. These mechanisms **[14]** are illustrated in more detail by the following reactions:

Initially, propene mostly reacts with O-atoms

$C_3H_6 + O \rightarrow C_2H_5 + HCO$
$C_3H_6 + O \rightarrow CH_2CO + CH_3 + H$
$C_3H_6 + O \rightarrow CH_3CHCO + 2H$.

After this stage, the OH-radical becomes dominant at reacting with propene (because significant amounts of OH are now being produced via the reaction $NO + HO_2 \rightarrow NO_2 + OH$)

$C_3H_6 + OH \rightarrow C_3H_6OH$
$C_3H_6 + OH \rightarrow C_3H_5 + H_2O$.

HO_2-radicals are also produced in the oxidation of hydrocarbon intermediates arising from propene oxidation reactions

$CH_2OH + O_2 \rightarrow CH_2O + HO_2$
$CH_3 + O_2 \rightarrow CH_2O + HO_2$
$HCO + O_2 \rightarrow CO + HO_2$
$H + O_2 \rightarrow HO_2$.

Acid production is mainly governed by the following two reactions:

$NO + OH \rightarrow HNO_2$
$NO_2 + OH \rightarrow HNO_3$.

As mentioned before, there is a competition between these reactions and the scavenging of OH by propene. Temperature has an effect of the this competition. For example, at 300 C, only about 6% of the OH reacts with NO and NO_2, while the rest reacts with propene and its aldehydic decomposition products; at 100 C 15% of the OH reacts with NO and NO_2, rather than propene and its aldehydic intermediate products.)

However, diesel engines (of which turbojets are a subset) do not contain considerable gas-phase hydrocarbons in their exhaust **[14]**, rather they contain liquid-phase hydrocarbons attached to particulate emissions. So the arguments concerning gasoline-engine emissions probably do not apply to jet-engine emissions (unless a sizable fraction of the hydrocarbons are volatilized). Therefore, we can probably count on producing significant amount of HNO_3 as a NO_x-removal product in moist, jet-engine exhaust.

Further Modeling of de-NO_x in Moist Air Containing Hydrocarbons - Chemical Kinetics

We are continuing to understand and study the main de-NO_x processes in moist air in the presence of hydrocarbons. Our NIST contractor, Herron & Associates, has modeled the processing of such mixtures using the dielectric barrier as an example NTP reactor (corona is similar, because it is also based on electric-discharge streamers). Through this modeling, the temporal profiles of [NO] and other species are obtained, the rates of loss and formation of NO have been derived for specific reactions, and we can now propose with a relatively high degree of certainty which reactions lead to NO loss in which time regimes. An understanding of the role of water and of added propene (an example hydrocarbon) has also been elucidated. A summary of this work appears below.

Chemistry in Pulsed Barrier Air Discharges: Prospects for Removal of NO

Pulsed barrier discharges are one of several approaches to removing NO from combustion device exhaust streams. Although the general nature of the chemistry following the pulse seems reasonably well established, there is little quantitative data as to which reactions are important in which time regimes, and what are the principal routes to the destruction of NO. The role of water is critical as it is always present in combustion streams. The role of organic compounds either as steam impurities or as additives also need clarification.

In order to address some of these concerns, detailed chemical kinetics modeling studies of the chemistry subsequent to a pulsed discharge in dry air and in air containing water and a "generic" alkene were undertaken (the reaction mechanisms appear in Tables 2 - 4 in the Appendix). The goal was to identify the mechanisms of NO destruction and NO formation, and to determine the nature of the "final" products for different starting gas compositions.

The pulsed discharge was modeled as a two step process. The first part consisted of a simplified model of the chemistry during the pulse, the second a model of the chemistry in the post-pulse regime. The discharge parameters used for all model calculations were: pulse width 10 ns, E/N=150 Td , T=300 K, and p=1 bar (1 atmosphere). Ion reactions were not included. The electron concentration was set at 10^{14} cm^{-3} during the pulse, which is typical of the average observed under these conditions. The pulse was treated as a square wave such that the electron concentration went to its full value at t=0, and fell to zero at 10 ns. All systems contained 100 ppm NO at t = 0.

Modeling was by means of the Acuchem program. This program is limited in the size of calculation that can be handled so that in some cases it was not possible to extend the calculations to very long times. However, the calculations cover the time range over which more than 99% of the NO is lost. And this permits an identification of the dominant loss channels under all conditions used here.

The kinetics data are taken from the review of (Herron and Green 1998 **[29]**). That review relies heavily on evaluations of data for atmospheric chemistry for the reactions of unexcited neutral species and an examination of the primary literature in the case of data for excited state reactions of neutral species. The rate constants are all adjusted as necessary for the conditions of 298 K (298 and 300 K are used interchangeably) and 1 bar (1 atmosphere). Rate constants for initiating reactions involving the excitation and dissociation of N_2 and O_2 by electrons are from (Lowke and Morrow 1995 **[24]**). There is some disagreement in the literature as to the correct values to be used for these rate constants, but where comparisons were possible, the work of these authors appears to be reliable.

For the discussions that follow, the reader should refer to Figures 3 and 4 which appear further below.

Discharge in dry air: Because the main purpose of this White Paper is to examine the production of nitric acid from nitric oxide and, because HNO_3 is only produced in the presence of H_2O, the dry air case will not be discussed here - although some of the calculated results for dry air are shown on the species-profile plots.

Discharge in air with 3% water: The addition of 3% water to dry air has a major impact on the chemistry. There is an increase in the NO level at short time followed by a decay. Also, the time scale for reduction of the initial NO level by 90% is extended from about 10^{-3} to 10^{-2} s. At a reaction time of about 10^{-2} s, the major products are NO_2, N_2, HONO, HNO_3, and N_2O_5, the latter increasing rapidly as the NO_2 now reacts with excess O_3.
Again, one can understand the process more clearly by examining the rates of the various processes. The N + NO reaction, although still a major loss process, is no longer the most important one, O + NO is the fastest loss process. The OH + NO and HO_2 + NO reactions are also important. The reductive path is now about 35% and oxidative 65% based on the distribution of final products.

There are several reasons for the changes induced by adding water. The first has to do with the scavenging effect of OH. OH + N is very fast (as is HO_2 + N), so that the concentration of N is effectively reduced, and the oxidation channel is now favored. In addition, if we examine the rates of formation of NO, we see that the same reactions, OH + N and HO_2 + N, both lead to the formation of NO, so that there is a significant source term for NO which is seen as a peaking in the NO concentration at about 10^{-6} s.

Discharge in air with 3% water and 1000 ppm alkene: Because of the size limitations of the modeling program used in this work, a very simplified model was used to address the effect of added alkene (equivalent to propene). However, it should be adequate to obtain a qualitative picture of the important reactions in this system, particularly at short reaction times. The major products are NO_2, N_2, HO_2NO_2, HONO and HNO_3. Inasmuch as the mechanism does not include reactions such as $RO_2 + NO_2 \rightarrow$ products, the final distribution will be somewhat different. N_2O_5 is a relatively minor product, although with excess O_3 present, it will continue to increase with time. The reductive path is now about 17% and oxidative 83% based on the distribution of final products. The scavenging effect of alkene on HO means that HONO is no longer the main HNO_x product as is seen in the system with just the 3% water, but is now HO_2NO_2.

If we look at the rates of NO loss, it can be seen that at all times greater than about 10^{-6} s, RO_2 + NO is the dominant reaction. NO loss is much more rapid then in the other two cases. Except at very short times, N + NO is always at least a factor of 10 less effective.

These observations can be summarized as follows:

1. In air with 3% water, NO is lost about 65% through oxidation and 35% through reduction. Addition of water, because it leads to formation of OH radicals, reduces the concentration of N

atoms and effectively suppresses the reductive path. At the same time it enhances the formation of NO. The major final products are still NO_2 and N_2 with contributions to the product mix from other oxides of nitrogen, and HNO_x acids, most of which can be removed by wet scrubbing.

2. In air with 3% water and 1000 ppm of propene, NO is lost about 83% through oxidation and 17% through reduction. Addition of alkene, which scavenges both O and OH, might appear to lesson the scavenging effect of OH on the N concentration. However, this effect is overwhelmed by the effect of the RO_2 radicals arising from the alkene reactions, which rapidly convert NO to NO_2. In effect the time available for N to react with NO is reduced. The time for NO_2 to reach a plateau value is reduced correspondingly. The major final product are NO_2, N_2, and HO_2NO_2 (and/or RO_2NO_2) with contributions to the product mix from other oxides of nitrogen, and HNO_x acids, most of which can be removed by wet scrubbing.

The economics of using a wet scrubber/neutralizer to remove the HNO_x acids is an important economics consideration and will be treated in future economic/cost-benefit analyses and associated reports.

Plotted data from the modeling calculations is shown in Figures 3 and 4 below. One should note that the detailed reaction sets for d-NO_x are evolving and that the calculated results presented below are subject to evolution as more experimental data is compared with model calculations.

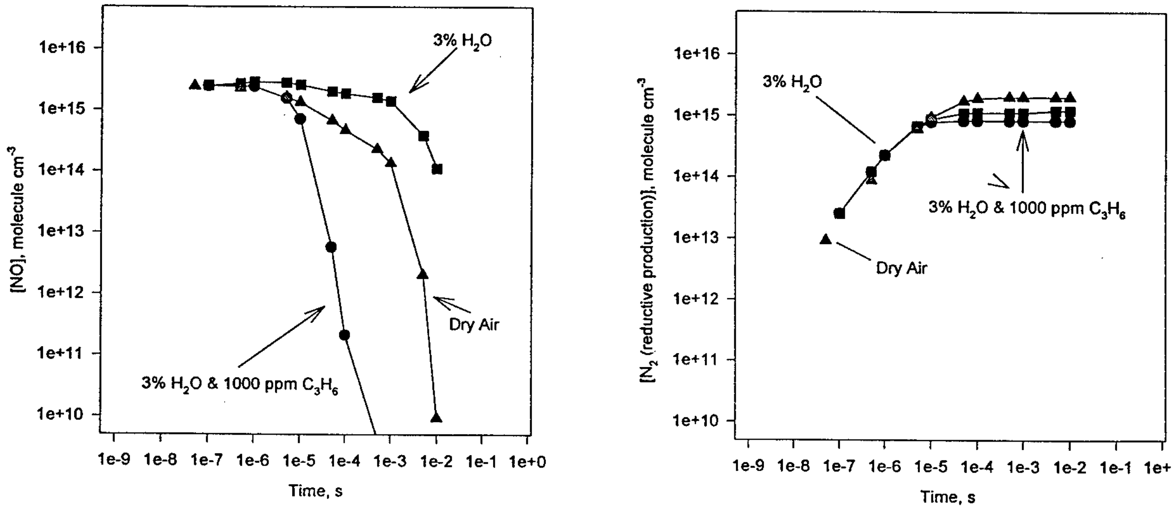


Figure 3: (Left) - Model results for NO removal under various gas conditions (dry air, moist air, and moist air with added propene; all at a temperature of 300 K and a pressure of 1 atm). (Right) - Model results showing only the portion of NO removal arising only from the chemical reduction to N_2 (reductive pathway).

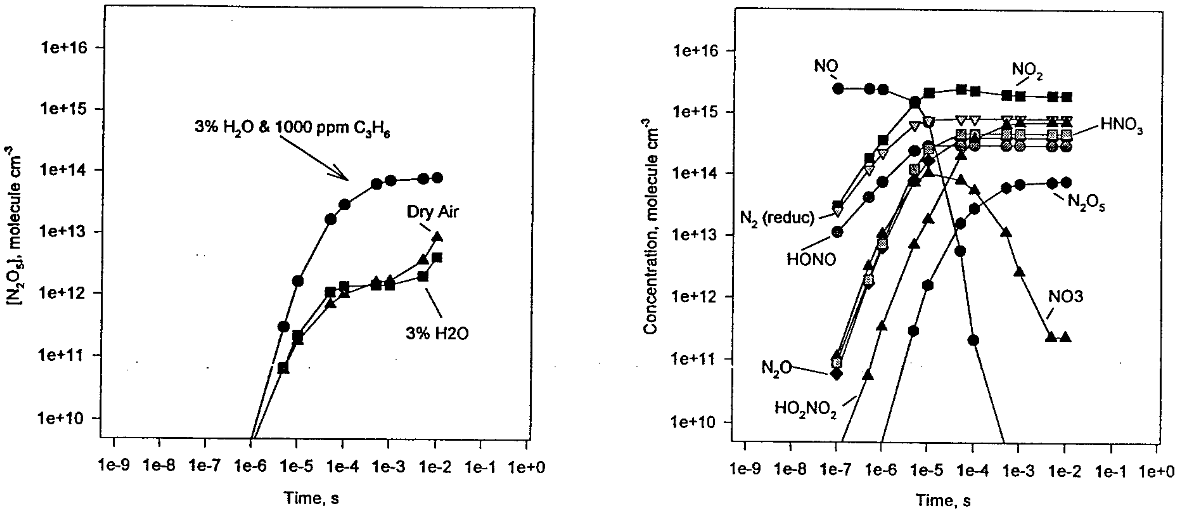


Figure 4: (Left) - Calculated temporal profiles of N_2O_5 under different gas conditions (dry air, moist air, and air with added propene; all at a temperature of 300 K and a pressure of 1 atm); (Right) - Calculated reaction-products temporal profiles for a moist (3% H_2O) gas mixture containing 100 ppm NO and 1,000 ppm C_3H_6 (propene).

Further Modeling of de-NOx in Moist Air Containing Hydrocarbons - Combined CFD, Plasma, and Chemical-Kinetics Model Trail Run

The CFD model has been combined with the present chemical kinetics reaction set to carry out a preliminary calculation on the spatial and temporal profiles of HNO_3 production from NO in a moist gas mixture. The reactor modeled is a simple parallel plate dielectric-barrier discharge device. In Figure 5 below, on the top is a schematic diagramof the computational model of a simple NTP reactor and on the bottom is an HNO_3 vs. x (dimension along gas-flow axis) plot with several time traces. One should note that HNO_3 is formed by the first discharge and diffuses out in both directions. The contributiion of additional HNO_3 from flow-through discharges downstream is smaller than that of the first. Note that other species are in the flow as one progresses downstream and thus the reactions are different. For more information on these types of calculations se (Nusca et al 1997 **[30]**). More calculations are being carried out with more discharge sites and as the reaction sets evolve (Herron & Green 1998 **[29]**).

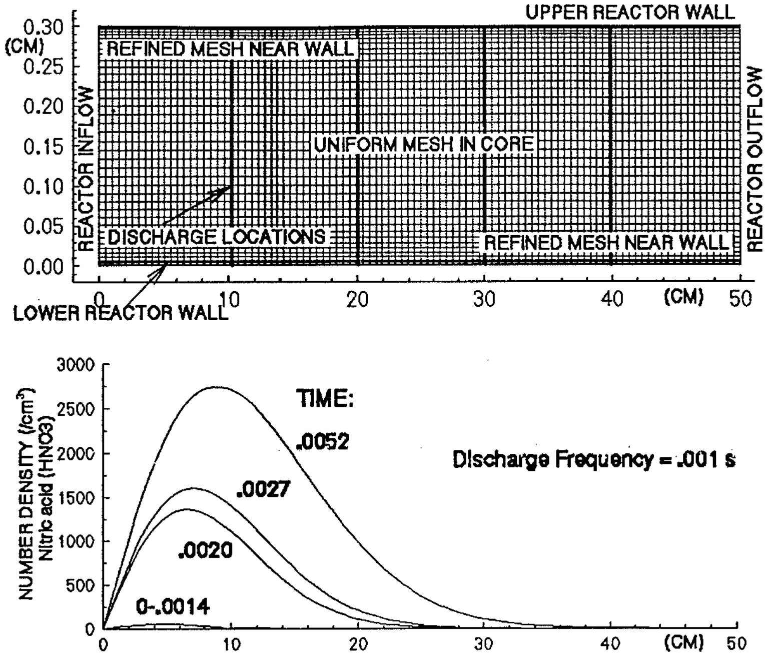


Figure 5: Results of coupled CFD and chemical-kinetics model calculation for dielectric-barrier discharge. Only four discharge sites are employed.

Outlook and Conclusions

Conventional de-NO_x technologies generally employ thermal-catalytic processes, scrubbing, and/or the addition of chemical additives (e.g., hydrocarbons, ammonia, urea compounds, isocyanic acid). The attractiveness of NTP-based technologies for jet-engine (diesel-engine) exhaust treatment is the ability to initiate NO_x-removal chemistry similar to that of conventional process by employing electricity-based, selective chemistry that might help produce products that can be easily neutralized or, in the case of reductive chemical pathways, even eliminate the need for large-scale chemical scrubbers.

We expect to use information gained from mechanisms and models like those described above and the results of lab-scale experiments in NTP de-NO_x reactor design and optimization for a small pilot-plant field demonstration.

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Appendix

Table 2. Mechanism for Dry Air Discharge[a]

No.	Reaction	k[b]	No.	Reaction	k[b]
1	$e + O_2 = O_2(^1\Delta_g) + e$	7.3e10	26	$NO + NO_2 = N_2O_3$	7.2e-15
2	$e + O_2(^1\Delta_g) = e + O_2$	7.3e-10	27	$NO_2 + NO_2 = N_2O_4$	2.5e-14
3	e + O2 = O + O + e	8.9e-10	28	$NO_2 + NO_3 = N_2O_5$	1.5e-12
4	$e + O_2(^1\Delta_g) = O + O + e$	8.9e-10	29	$O(^1D) + O_2 = O + O_2$	4.0e-11
5	$e + O_2 = O + O(^1D) + e$	2.7e-09	30	$O(^1D) + N_2 = O + N_2$	2.6e-11
6	$e + O_2(^1\Delta_g) = O + O(^1D) + e$	2.7e-09	31	$O(^1D) + O_3 = O + O$	1.2e-10
7	$e + N_2 = N + N + e$	9.4e-11	32	$O(^1D) + O_3 = O_2 + O_2$	1.2e-10
8	$e + N_2 = e + N_2(A)$	1.4e-09	33	$O(^1D) + NO = N + O_2$	4.0e-11
9	$e + N_2(A) = e +$ N2	1.0e-08	34	$N_2(A) + N_2 = N_2 + N_2$	2.6e-18
10	$O + O = O_2$	2.6e-14	35	$N_2(A) + O_2 = N_2 + O_2$	7.0e-13
11	$O + O_2 = O_3$	1.4e-14	36	$N_2(A) + O_2 = N_2 + O + O$	1.8e-12
12	$O + O_3 = O_2 + O_2$	8.0e-15	37	$N_2(A) + N_2(A) = N_2 + N_2(B)$	4.0e-10
13	$O + N = NO$	2.7e-13	38	$N_2(B) + N_2 = N_2 + N_2$	3.0e-11
14	$N + N = N_2$	1.1e-13	39	$N_2(B) + O_2 = N_2 + O_2$	2.0e-10
15	$O + NO = NO_2$	2.1e-12	40	$N_2(A) + O_2(^1\Delta_g) = N_2 + O + O$	2.0e-11
16	$O + NO_2 = O_2 + NO$	9.7e-12	41	$O_2 + O_2(^1\Delta_g) = O_2 + O_2$	2.2e-18
17	$O + NO_2 = NO_3$	1.7e-12	42	$O_2(^1\Delta_g) + O_2(^1\Delta_g) = O_2 + O_2$	2.0e-17
18	$O + NO_3 =$ O2 $+ NO_2$	1.0e-11	43	$N_2O_5 = NO_2 + NO_3$	5.3e-02
19	$N + O_2 = NO + O$	8.7e-17	44	$N_2O_4 = NO_2 + NO_2$	~~1.1e+5~~
20	$N + O_3 = NO + O_2$	1.0e-16	45	$N_2O_3 = NO + NO_2$	3.7e+5
20	$N + NO = N_2 + O$	2.9e-11	46	$N_2(A) + O_3 = N_2 + O + O_2$	3.4e-11
22	$N + NO_2 = N_2O + O$	1.2e-11	47	$N_2(A) + O_3 = 2NO + O$	8.4e-12
23	$NO + O_3 = NO_2 + O_2$	1.8e-14	48	$N_2(A) + O = N_2 + O$	2.8e-11
24	$NO + NO_3 = NO_2 + NO_2$	2.6e-11	49	$N_2(A) + N = N_2 + N$	5.0e-11
25	$NO_2 + O_3 = NO_3 + O_2$	3.2e-17	49a	$NO_3 + NO_3 = 2NO_2 + O_2$	2.3e-16

a. From Herron and Green **[30]**, except data for reactions 1-9 from Lowke and Morrow **[19]**.

b. All rate constants are in terms of equivalent two-body rate constants in units of cm^3/s (in three-body reactions, the concentration of the third reaction partner is taken as that of atmospheric-pressure, ambient-temperature air.

Table 3. Additional Reactions for Water

No.	Reaction	k	No.	Reaction	k
50	$O + HO = O_2 + O$	3.3e-11	65	$HO_2 + NO_2 = HO_2NO_2$	1.4e-12
51	$O + HO_2 = O_2 + HO$	5.7e-11	66	$HO_2 + HO_2 = H_2O_2$	7.4e-12
52	$O + H_2O_2 = HO_2 + HO$	1.7e-15	67	$N + HO_2 = NO + HO$	2.2e-11
53	$O + HNO = NO + HO$	6.0e-11	68	$H + O_3 = HO + O_2$	2.9e-11
54	$O + HONO = NO_2 + HO$	8.6e-16	69	$H + HNO = H_2 + NO$	5.6e-12
55	$N + HO = NO + H$	5.1e-11	70	$HO + NO_3 = HO_2 + NO_2$	2.0e-11
56	$HO + O_3 = HO_2 + O_2$	6.6e-14	71	$H + O_2 = HO_2$	1.2e-12
57	$HO + HO = H_2O + O$	1.9e-12	72	$HO + HO = H_2O_2$	5.2e-12
58	$HO + HO_2 = H_2O + O_2$	1.1e-10	73	$HO_2 + NO_3 = NO_2 + HO + O_2$	3.5e-12
59	$HO + H_2O_2 = HO_2 + H_2O$	1.7e-12	74	$HNO + NO_2 = HONO + NO$	5.0e-13
60	$HO + HNO = NO + H_2O$	1.5e-11	75	$O(^1D) + H_2O = 2HO$	2.2e-10
61	$HO + HONO = NO_2 + H_2O$	6.5e-12	76	$N_2(A) + H_2O = H + HO + N_2$	5.5e14
62	$HO + HONO_2 = NO_3 + H_2O$	1.5e-13			
63	$HO + NO = HONO$	9.6e-12			
64	$HO + NO_2 = HONO_2$	1.4e-11			

Table 4. Additional Reactions for Alkene (PE)[a]

No.	Reaction	k	No.	Reaction	k
78	$O + PE = R + A$	4e-12	84	$RO + O_2 = HO_2 + A$	1e-14
79	$HO + PE = R$	3e-11	85	$O + A = HO + R$	4e-13
80	$N_2(A) + PE = 2R$	1e-10	86	$HO + A = H_2O + R$	2e-11
81	$N_2(B) + PE = 2R$	1e-10	87	$N_2(A) + A = 2R$	1e-10
82	$R + O_2 = RO_2$	1e-11	88	$N_2(B) + A = 2R$	1e-10
83	$RO_2 + NO = RO + NO_2$	1e-11	89		

a. PE = generic alkene based on propene, A = generic aldehyde such as CH3CHO, R = any radical.