Title: NON-THERMAL PLASMAS AS GAS-PHASE ADVANCED OXIDATION PROCESSES (Paper for Proceedings)

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Non-thermal plasmas are useful for generating reactive species (free radicals) in a gas stream. Because radical-attack reaction rate constants are very large for many chemical species, entrained pollutants are readily decomposed by radicals. Such plasmas can generate both oxidative and reductive radicals; therefore, they show promise for treating a wide variety of pollutants.

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NON- THERMAL PLASMAS AS GAS-PHASE ADVANCED OXIDATION PROCESSES

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ABSTRACT
Non-thermal plasmas are useful for generating reactive species (free radicals) in a gas stream. Because radical-attack reaction rate constants are very large for many chemical species, entrained pollutants are readily decomposed by radicals. Such plasmas can generate both oxidative and reductive radicals; therefore, they show promise for treating a wide variety of pollutants.

1. INTRODUCTION
To prevent toxic substances from entering and spreading through the environment and to meet increasingly stringent regulations, more effective methods of destroying chemical pollutants are being examined. Advanced oxidation processes [1], historically used for the treatment of recalcitrant water pollutants via oxidative hydroxyl radicals (OH), are now being applied to the decomposition of gas-phase pollutants using non-thermal plasmas (NTPs). AOPs show particular promise for the treatment of hazardous and toxic pollutants (e.g., volatile hydrocarbons and halocarbons and oxides of sulfur and nitrogen) because the reaction rates of free radicals with organic compounds can be orders of magnitude larger than a strong oxidizer like O$_3$.

A non-thermal plasma (or non-equilibrium plasma) is characterized by electrons which are not in thermal equilibrium with the other gas species, i.e., hot electrons (few to tens of eV temperature) and cold neutral gas species and ions (near-ambient temperature). Such plasmas are good sources of highly reactive oxidative and reductive species, e.g., O($^3$P), OH, N, H, NH, CH, O$_3$, O$_2$(^1$\Delta$), and plasma electrons. Via these reactive species, one can direct electrical energy into favorable gas chemistry through energetic electrons. NTPs are commonly created by an electrical discharge in a gas or the injection of an energetic electron beam into a gas [2]. Both methods create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature).

This paper is intended to serve as an introduction to the subject of nonthermal-plasma-driven pollutant decomposition. In this paper, we will discuss NTPs in the context of an AOP - namely a tool for free-radical-initiated decomposition reactions. The main points covered are the generation of free radical species, simple analytical models for decomposition-scaling relationships, and specific energy requirements for the decomposition of example pollutants.

2. TECHNICAL OVERVIEW
2.1 Non-Thermal Plasma Reactors
Figure 1 shows example NTP reactors for gas-phase pollutant processing [2, 3, 4, 5, 6, 7, 8]. In an electrical discharge, a high voltage is applied across electrodes in the gas or along a surface adjacent to the gas. An electron-beam reactor requires an electron accelerator to produce the energetic electron beam (~ 100 keV - 1 MeV) that is injected into the process gas. The energetic plasma electrons are responsible for pollutant decomposition, either through direct electron collisions or indirectly through the creation of free radicals that attack the pollutants.
and prevent thermal arc formation. Silent discharges use charge buildup on a capacitive barrier to achieve a similar end result. An electrified packed bed is closely related to a barrier discharge. A related discharge reactor uses streamers across a dielectric surface. Streamers can be thought of as cylindrical current filaments with typical radius $\sim 100 \, \mu m$. They are transient discharges (e.g., lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when the electric field is reduced to the point where electron attachment becomes dominant. For streamers in pure oxygen and air, the average electron energy and electron density are $T_e \sim 3-5 \, eV$, $[e] \sim 10^{14}/cm^3$, while a typical breakdown reduced electric field strength in the gas is $E/N \sim 100 - 200 \, \text{Td}$. Multiple streamers typically give accumulated plasma energy loadings of $10^5 - 1,000\, J/liter\, atm$.

In an electron-beam reactor, the source of electrons (the cathode) can be separate from the accelerating-field section (as in thermonic-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. For typical electron-beam reactors, the mean electron energies can be much larger than those for discharge reactors (e.g., $\sim 10 \, eV$ for electron-beam, as compared to $\sim$ few $eV$ for discharges). Similar energy loadings can usually be obtained in both types of reactors.

**2.2 Active Species Generation and Pollutant Decomposition**

In the decomposition process, plasma physics and plasma chemistry are intercon-
nected. The electrical discharge or electron beam creates the plasma which, in turn, generates active species in the pollutant-containing gas. The active species then react with and decompose the chemical pollutants. Below, for an air-like gas, we briefly discuss active species (i.e., radical) generation and the decomposition chemistry for two example pollutant classes: the flue gas nitric oxide (NO) and the chlorocarbons trichloroethylene (C<sub>2</sub>HCl<sub>3</sub>) and carbon tetrachloride (CCl<sub>4</sub>).

2.2-1 Radical Production

Active species can be formed in a variety of ways in non-thermal plasmas. Table 1 shows the main processes for an air-like carrier gas. Ammonia (NH<sub>3</sub>) is also included in the example because it is sometimes employed as an additive in flue-gas processing.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Example Radical Formation Mechanisms</th>
</tr>
</thead>
</table>
| **Electron impact** | e + O<sub>2</sub> → O + O* + e  
 | e + N<sub>2</sub> → N + N + e  
 | e + O<sub>2</sub> → O + O + e  
 | e + H<sub>2</sub>O → OH + H + e  
 | e + N<sub>2</sub> → N<sub>2</sub>* + e  
 | e + NH<sub>3</sub> → NH + H<sub>2</sub> + e |

| **Quenching** | O* + H<sub>2</sub>O → 2OH  
 | N<sub>2</sub>* + O<sub>2</sub> → N<sub>2</sub> + O + O |

| **Ionization/Clusters** | e + O<sub>2</sub> → O<sub>2</sub>* + e  
 | O<sub>2</sub>* + H<sub>2</sub>O → O<sub>2</sub>* (H<sub>2</sub>O)  
 | O<sub>2</sub>* (H<sub>2</sub>O) + H<sub>2</sub>O → HO<sub>3</sub>* + O<sub>2</sub> + OH  
 | O<sub>2</sub>* (H<sub>2</sub>O) + H<sub>2</sub>O → HO<sub>3</sub>* (OH) + O<sub>2</sub>  
 | HO<sub>3</sub>* (OH) + H<sub>2</sub>O → HO<sub>3</sub>* + H<sub>2</sub>O + OH |

| **Others** | H + O<sub>3</sub> → OH + O<sub>2</sub>  
 | HO<sub>2</sub> + NO → OH + NO<sub>2</sub>  
 | H + O<sub>2</sub> + M → HO<sub>2</sub> + M |

In chlorine-compound-containing mixtures, Cl and ClO radicals are also produced from reactions of radicals and other gas species with the entrained pollutants. These can further participate in decomposition chain reactions.

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. Consider humid, atmospheric pressure air; here the yields of O<sup>(3P)</sup>, OH, and N radicals in typical electric-discharge reactors are of order 10, 1, and 1 per 100 eV of deposited energy, respectively [3]. For electron-beam reactors, the O<sup>(3P)</sup> yield is about one-third less, the yield of OH is roughly twice as large, and the yield of N is nearly 10 times larger than in discharge reactors [2, 9]. Another way of stating this difference 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. Usually, pollutants in the concentration range of interest (100s to 1000s ppm) do not affect the electron distribution function or the associated electron temperatures and radical yields.

2.2-2 Basic Decomposition Chemistry

The plasma-generated active species (radicals and secondary electrons) are the initiators of pollutant decomposition reactions. Two major decomposition channels for a gas-phase chemical pollutant X are direct electron impact or chemical (radical-promoted) attack:

\[ e + X \rightarrow \text{products} \]

\[ O, OH + X \rightarrow \text{products}. \]
The first path is expected to dominate at large contaminant concentrations (when a higher energy fraction is absorbed by the pollutant), while the second should dominate at smaller concentrations.

The decomposition chemistry for NO is tractable and largely described as follows [2]:

\[ O + NO + M \rightarrow NO_2 + M \]
\[ OH + NO_2 + M \rightarrow HNO_3 + M \]
\[ O + NO_2 \rightarrow NO + O_2 \]
\[ N + NO \rightarrow N_2 + O \]
\[ N + NO_2 \rightarrow N_2 O + O \]

Oxidative-mode reactions involving O-atoms can trap total NO\(_x\) as NO and NO\(_2\). Oxidative-mode reactions involving OH-radicals produce nitric acid HNO\(_3\), which can be easily removed by a caustic scrubber. Reductive-mode reactions involving N-atoms instead drive more NO\(_x\) to N\(_2\) and O\(_2\) but require higher energy electrons. SO\(_x\) removal is similarly driven by O-atom and OH-radical oxidative reactions, producing easily-neutralized sulfuric acid as a terminal product. Ammonia addition is sometimes used to produce other useful products such as ammonium nitrate or ammonium sulfate (agricultural fertilizers).

Other molecules, like many VOCs, will often undergo a series of more complicated reactions before the final products result. The decomposition of a chlorocarbon like trichloroethylene is dominated by free-radical reactions at the relatively high E/N of electric discharges [10, 11]

\[ O(^3P) \text{ or OH} + C_2HCl_3 \]
\[ \rightarrow CO_2 + HCl + Cl_2 + COCl_2 + \ldots \]

Strong electron attachers (e.g., CCl\(_4\)) are preferentially decomposed by dissociative electron attachment at low E/N [9, 12]

\[ e + CCl_4 \rightarrow CCl_3 + Cl^- \]
\[ CCl_3 + O_2 \rightarrow COCl_2 + Cl + ClO \]

Decomposition is not necessarily complete treatment - the goal is to produce less toxic or more easily managed final products. Byproducts must also be considered (e.g., COCl\(_2\) is toxic but is easily removed by reactions with water). In laboratory studies, the degree of decomposition and treatment byproducts are measured with an instrument like a gas chromatograph - mass spectrometer.

A key advantage of NTP processing is the ability to simultaneously remove multiple pollutants. The detailed plasma-initiated removal chemistry of a particular compound or mixture of compounds can be quite complicated and will not be addressed here. For more information, the reader is referred to the literature.

### 2.2.3 Decomposition-Scaling Relationships

In many non-thermal plasma devices (like gas lasers, ozonizers, etc..), a key process parameter is the specific energy (plasma energy density) deposited in the gas. This is also true for the decomposition of a pollutant in an NTP reactor. Experiments with various reactors have shown that the degree of removal of a particular contaminant depends on the applied plasma energy density E and a characteristic energy-density parameter which is related to the target compound, the carrier gas, and the reduced electric field E/N for the reactor [2, 3, 9].

Recent work on comparing different aqueous-phase AOPs has shown that simple overall kinetic models can be used to describe the rate of radical-initiated decomposition of a target species [13]. Using an analogous description for a gas-phase AOP based on an NTP process, one can write the following expression for the decomposition of pollutant X in the presence of radical scavengers S\(_i\)
where \([X]\) is the pollutant concentration, \(G\) is the radical production efficiency, \(\tilde{P}\) is the plasma power density, \(k\) is the radical-pollutant kinetic rate constant, \([S_i]\) is concentration of the \(i^{th}\) scavenger, and \(k_{Si}\) is the scavenging rate constant for the \(i^{th}\) species.

Assuming an idealized reactor (constant E/N and carrier gas temperature), given the scavenger concentrations, and making the substitution \(\tilde{P} = \frac{dE}{dt}\), one can integrate the above equation to get the pollutant concentration \([X]\) as a function of the starting concentration \([X]_0\) and the specific energy. When the rate of radical-pollutant attack \(k[X]\) is small compared to the rate of radical scavenging \(\Sigma_i k_{Si} [S_i]\), the pollutant decomposition can be ideally expressed as

\[
[X] = [X]_0 \exp \left(-\frac{E}{\beta}\right),
\]

where \([X]_0\) is the initial pollutant concentration, \([X]\) is the resulting concentration, \(\tilde{E}\) is the applied specific energy (or plasma power divided by gas flow rate, \(P/Q\)), and \(\beta\) is the e-fold energy density

\[
\beta = \frac{\sum_i k_{Si} [S_i]}{kG}.
\]

Supplying one \(\beta\) to the reactor reduces the concentration by \(1/e\), \(2\beta\) by \(1/e^2\), and so on. In this ideal case, when \(-\ln ([X]/[X]_0)\) is plotted versus \(\tilde{E}\), a straight line of slope \(1/\beta\) results. For real cases, the plot is not necessarily a straight line, so such a slope-determined \(\beta\)-value is only an approximation. In some cases, the removal function can additionally depend on the initial pollutant concentration. Figure 2 presents example decomposition data for two representative compounds, the flue gas nitric oxide (NO) and the chlorinated hydrocarbon trichloroethylene (TCE), C\(_2\)HCl\(_3\).

The \(\beta\)-value links the generation of radicals through gaseous electronics/plasma chemistry (G-values) with their utilization through the decomposition chemistry. The G-value is a function of an effective rate constant for radical generation \(k_{rad}\) (e.g., the dissociation rate constant for dissociating O\(_2\) molecules into O-atoms), the electron drift velocity \(v_d\), and the reduced electric field strength \(E/N\)

\[
G = f \left( \frac{k_{rad}}{E \left( \frac{v_d}{N} \right)} \right).
\]

The rate constant \(k_{rad}\) and the drift velocity \(v_d\) also depend on the reduced field \(E/N\) (electron temperature), so the \(\beta\)-value essentially depends on \(E/N\) and the chemical kinetics.

3. CONCLUSIONS

Many hazardous organic chemicals and the flue gases NO\(_x\) and SO\(_x\) are readily attacked by the free radicals generated in non-thermal plasmas. In general, the degree of removal of a par-
ticular chemical species scales exponentially with the plasma energy density. The characteristic e-fold energy density depends on the specific pollutant and the carrier gas composition. The plasma-initiated decomposition chemistry of a particular compound or mixture can be quite complicated and has been the subject of both laboratory and field investigations. NTP treatment is expected to be particularly advantageous for the simultaneous removal of multiple pollutants. This application is only about a decade old. Therefore, more work is needed to optimize and mature the process.

4. REFERENCES


