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NON-THERMAL PLASMAS: SIMPLE REMOVAL
EQUATIONS AND FIGURES-OF-MERIT

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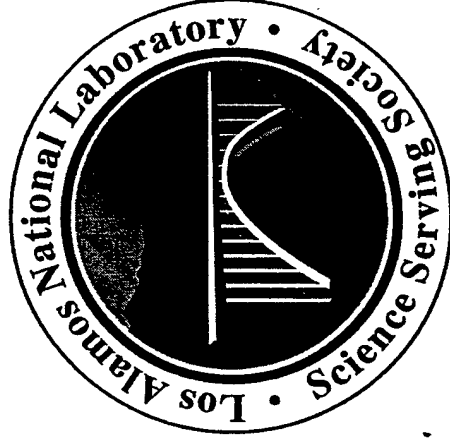
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Gas-Phase Pollutant Decomposition with Non-Thermal Plasmas: Simple Removal Equations and Figures-of-Merit

5th International Conference on Advanced Oxidation Technologies for Water & Air Remediation (AOTs-5)

Louis A. Rosocha

Los Alamos National Laboratory

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GAS-PHASE POLLUTANT DECOMPOSITION WITH NON-THERMAL PLASMAS (NTPS): SIMPLE REMOVAL EQUATIONS AND FIGURES-OF-MERIT

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Abstract

Non-thermal plasmas (NTPs) are a type of advanced oxidation and reduction technology for treating gas-phase chemical pollutants. Such plasmas are good sources of highly reactive oxidative and reductive species (free radicals and others), e.g., $O(^3P)$, OH, N, H, NH, CH, O_3, O_2 ($^1\Delta$), and plasma electrons. Because radical-attack reaction rate constants are very large for many chemical species, entrained pollutants are readily decomposed by NTPs. Via these reactive species, one can direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas. NTPs are commonly created by an electrical discharge in a gas or the injection of an energetic electron beam into a gas. Both methods create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature). In NTPs, the electrons are highly energetic (*hot*) and the ions and background gas species are at near-ambient temperature (*cold*). For this reason, these plasmas are sometimes called *cold plasmas*.

Applications of the technology include flue-gas treatment (SO_x and NO_x), environmental remediation of volatile organic compounds (VOCs) in soil or groundwater, or the abatement of other regulated industrial air emissions.

In this talk, we will describe a simple free-radical-based, reaction-kinetics model that predicts the form of the pollutant-removal plots (degree of removal *vs.* specific plasma energy) for various air pollutants and/or hazardous chemicals (e.g., the flue gases SO_x and NO_x and chlorinated and non-chlorinated VOCs), using removal equations derived from the model. Here, we consider the NTP reactor to be a 'black box' which reduces the concentration of entrained pollutants in a gas-phase stream from an initial value $[X]_0$ to a value $[X]$ under the influence of a reactor specific energy (active-plasma energy per unit volume) $\bar{E}$.

In general, a pollutant-removal equation is exponential in character, depending only on the applied specific energy $\bar{E}$ and a parameter β. The β-value characterizes the particular pollutant of interest and, for general cases, depends on the active decomposing-species formation efficiency G (number of active molecules produced per 100 eV of plasma-deposited electrical energy), the initial pollutant concentration, and the chemical kinetics of radical-pollutant attack and radical scavenging.

We will examine three special cases: 1) radical scavenging dominates radical attack, 2) radical attack dominates radical scavenging, and 3) radical-radical scavenging is dominant. In the first case, the removal plot is relatively insensitive to $[X]_0$; in the second case, it significantly depends on $[X]_0$; and in the third case, the plot is insensitive to $[X]_0$ but has an explicit dependence on the gas residence time τ_r in the NTP reactor – in contrast to the other two cases.

From the removal equations, one can derive figures-of-merit for both the instantaneous (γ_i) and average (γ) removal energy costs (energy efficiency) for pollutant removal. We will present example figure-of-merit calculations for representative pollutants and carrier gases to illustrate the dependence on initial concentration $[X]_0$, the degree of pollutant removal $[X]/[X]_0$, and the G-value.

Acknowledgment

This work has been partially supported by
the US Strategic Environmental Research & Development Program
(SERDP)

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Outline of talk

- Simple "black-box" model of an NTP reactor
- Active-species production functional relationships
- Decomposition chemistry overview
- Simple kinetics model and generalized pollutant-removal equations.
- Figures-of-merit & costs for decomposition of example pollutants
- Summary

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Non-thermal Plasmas Decompose Pollutants Via Active Species Generated in the Process Gas

Electrical Energy

Influent Stream (w/pollutants)

Effluent Stream (w/decomposed pollutants, simpler compounds)

Plasma & active species (e.g., free radicals)
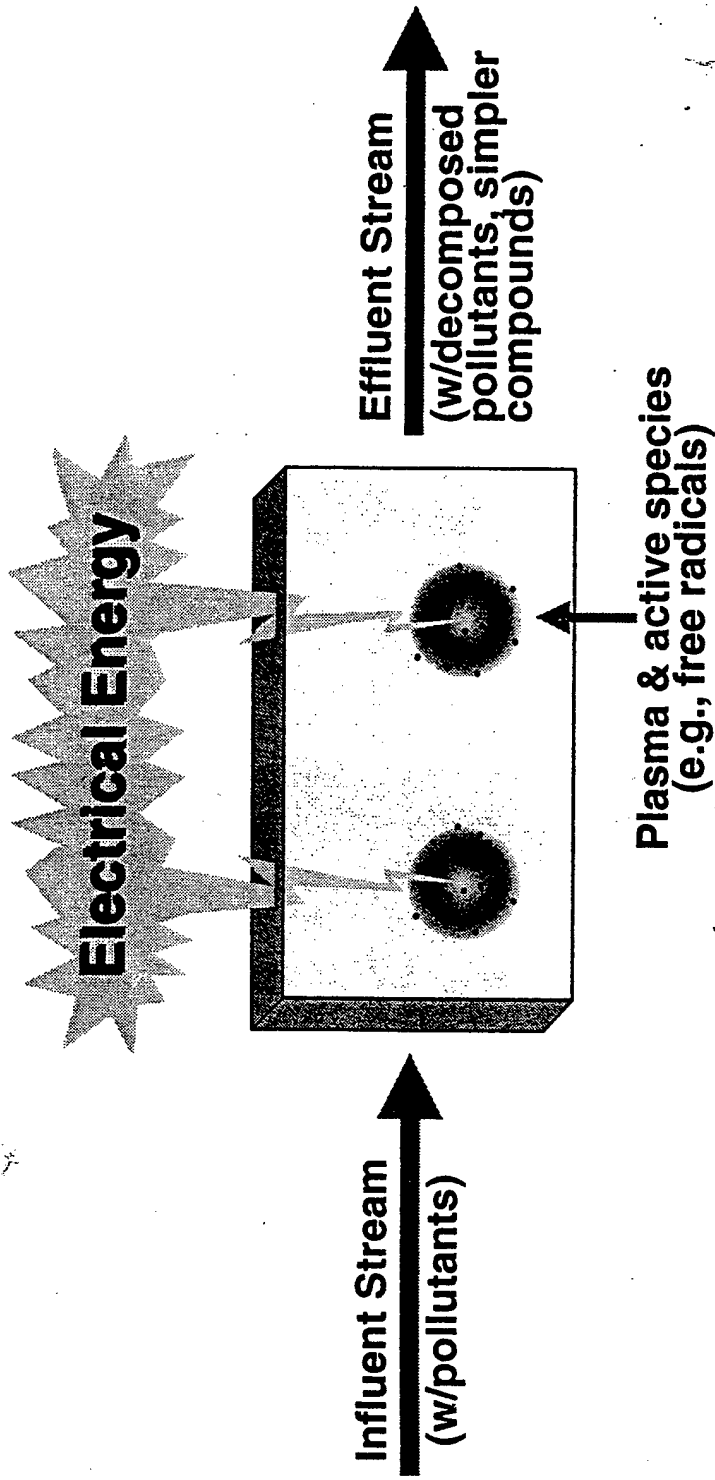
The radical production efficiency (G-value) depends on the gaseous electronics. Radical generation is mainly initiated by energetic-electron collisions.

$$G = f\left(\frac{k_{rad}}{\mathbf{v}_d} \frac{E}{N}\right)$$

- E/N is the reduced field,
- $\mathbf{v}_d$ is the electron drift velocity, which depends on E/N,
- k_{rad} is the rate constant for radical formation (e.g., a dissociation rate constant, which depends on E/N), and/or other rate constants.

Gas-phase plasma chemical decomposition is driven by electron impact and radical attack.

(1) e + X → products

(2) O, OH, N, etc. + X → products

- The first reaction is dominant at large pollutant mole fractions.

- The second dominates at smaller mole fractions.

(More energy is directly absorbed by pollutant at high mole fraction, hence electron channel dominates.)

Plasma chemical decomposition of VOCs produces a variety of terminal products.

e, O, OH, N, etc. + X → products

- **Manageable products:** CO_2, CO, Cl_2, HCl, $COCl_2$

- **Undesirable products:** Other halocarbons, hazardous byproducts (e.g., DCAC - $CHCl_2COCl$); polymers

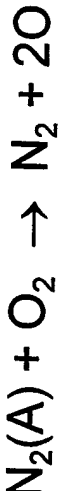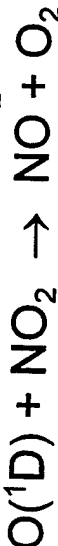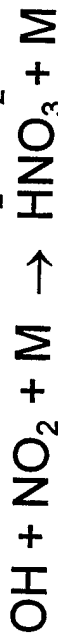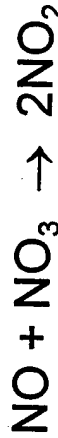- **Secondary treatment:**
$CO_2 + NaOH \rightarrow NaHCO_3$
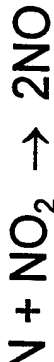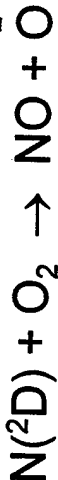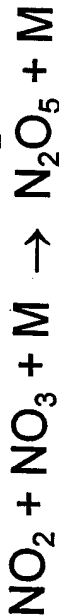$CO + catalyst \rightarrow CO_2$
$Cl_2 + NaHCO_3 \rightarrow NaCl + HCl + \ldots$
$HCl + NaOH \rightarrow NaCl + H_2O$
$COCl_2 + H_2O \rightarrow 2HCl + CO_2$

Major de-NO$_x$ Reactions in Moist Gas Mixtures w/o HCs

$O + NO + M \rightarrow NO_2 + M$

$O + NO_2 \rightarrow NO + O_2$

$O + N_2 \rightarrow NO + N$

$O + O_2 + M \rightarrow O_3 + M$

$O_3 + NO \rightarrow NO_2 + O_2$

$O_3 + NO_2 \rightarrow NO_3 + O_2$

$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$

$N(^2D) + O_2 \rightarrow NO + O$

$N + NO \rightarrow N_2 + O$

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

$N + NO_2 \rightarrow N_2O + O$

$N + NO_2 \rightarrow 2NO$

$N(^2D) + H_2O \rightarrow NH + OH$

$NH + NO \rightarrow N_2 + OH$

$NH + O_2 \rightarrow NO + OH$

$NO + NO_3 \rightarrow 2NO_2$

$NO + OH + M \rightarrow HNO_2 + M$

$OH + HNO_2 \rightarrow NO_2 + H_2O$

$OH + NO_2 + M \rightarrow HNO_3 + M$

$N + NO_2 \rightarrow N_2 + O_2$

$N + N_2O \rightarrow NO + N_2$

$O(^1D) + NO_2 \rightarrow NO + O_2$

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

$N_2(A) + O_2 \rightarrow N_2 + 2O$

$N_2(A) + N_2O \rightarrow N_2 + N + NO$
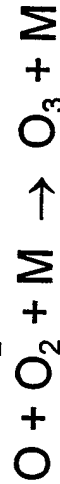
Primary Acid-Formation Pathways:

$NO + OH + M \rightarrow HNO_2 + M$

$OH + NO_2 + M \rightarrow HNO_3 + M$

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The presence of SO_2 recycles OH radicals & reduces effective de-NO_x energy cost

$OH + SO_2 + M \rightarrow HSO_3 + M$

$HSO_3 + O_2 \rightarrow HO_2 + SO_3$

$HO_2 + NO \rightarrow NO_2 + OH$
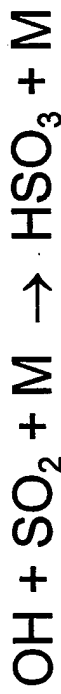
The OH radical then goes on to be used again in de-NO_x

$OH + NO + M \rightarrow HNO_2 + M$

$OH + HNO_2 \rightarrow NO_2 + H_2O$

$OH + NO_2 + M \rightarrow HNO_3 + M$
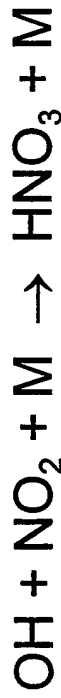
Acid is also formed by the reaction

$HSO_3 + H_2O \rightarrow H_2SO_4$

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With ammonia (NH_3) addition, useful particulates (fertilizer) can be formed from NO_x

$$e + NH_3 \;\rightarrow\; NH_2 + H + e$$
$$e + NH_2 \;\rightarrow\; NH + H + e$$
$$NH + H \;\rightarrow\; N + H_2$$
$$NH_2 + NO \;\rightarrow\; N_2 + H_2O$$
$$NH + NO \;\rightarrow\; N_2 + OH$$
$$N + NO \;\rightarrow\; N_2 + O$$
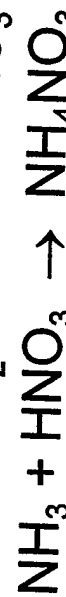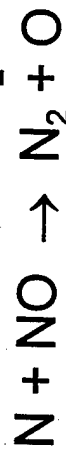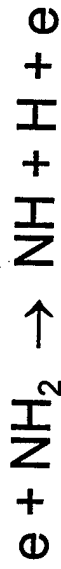
$$OH + NH_3 \;\rightarrow\; NH_2 + H_2O$$
$$OH + NO + M \;\rightarrow\; HNO_2 + M$$
$$OH + HNO_2 \;\rightarrow\; NO_2 + H_2O$$
$$OH + NO_2 + M \;\rightarrow\; HNO_3 + M$$
$$NH_3 + HNO_3 \;\rightarrow\; NH_4NO_3$$
(Ammonium Nitrate fertilizer)

Simple, first-order kinetics model gives exponential pollutant-removal function.

Chemical Reactions

Rate Equations

$e + A \rightarrow R^{\bullet} + A'$ (1) $\dfrac{d[R^{\bullet}]}{dt} = \dfrac{d[R^{\bullet}]}{d\bar{E}} \cdot \dfrac{d\bar{E}}{dt} = G\bar{P}$

$R^{\bullet} + X \rightarrow$ Products   (2) $\dfrac{d[X]}{dt} = -k[R^{\bullet}][X]$

$R^{\bullet} + S_i \rightarrow$ Products   (3) $\dfrac{d[R^{\bullet}]}{dt} = -k_{S_i}[R^{\bullet}][S_i]$

Assume steady state: $\dfrac{d[R^{\bullet}]}{dt}(net) = G\bar{P} - k[R^{\bullet}][X] - \sum_{i} k_{S_i}[R^{\bullet}][S_i] = 0$.

Solve for $[R]_{ss}$ and insert into (2) to obtain generalized removal equation.

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A generalized removal equation depends on plasma chemistry (radical yields), reaction chemistry, and applied plasma specific energy.

Generalized differential equation:

$$\frac{k[X] + \sum_i k_{S_i}[S_i]}{k[X]}\, d[X] = -G\, d\bar{E}$$

Integration with limits $[X]_0 \rightarrow [X]$ and $0 \rightarrow \bar{E}$ gives:

$$\frac{[X]}{[X]_0} + \frac{\sum_i k_{S_i}[S_i]}{k\,[X]_0}\, \ln\frac{[X]}{[X]_0} - 1 = -\frac{G\bar{E}}{[X]_0}$$

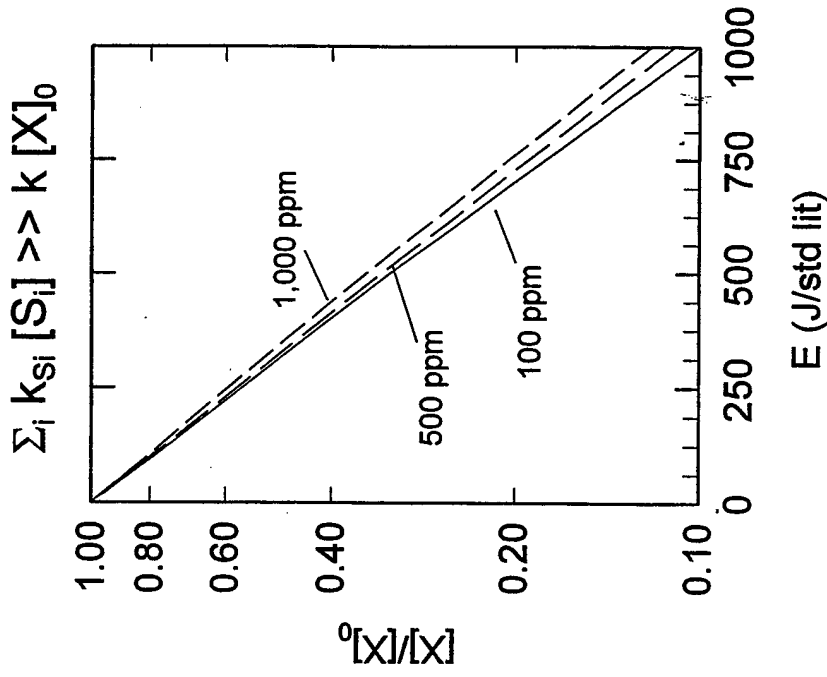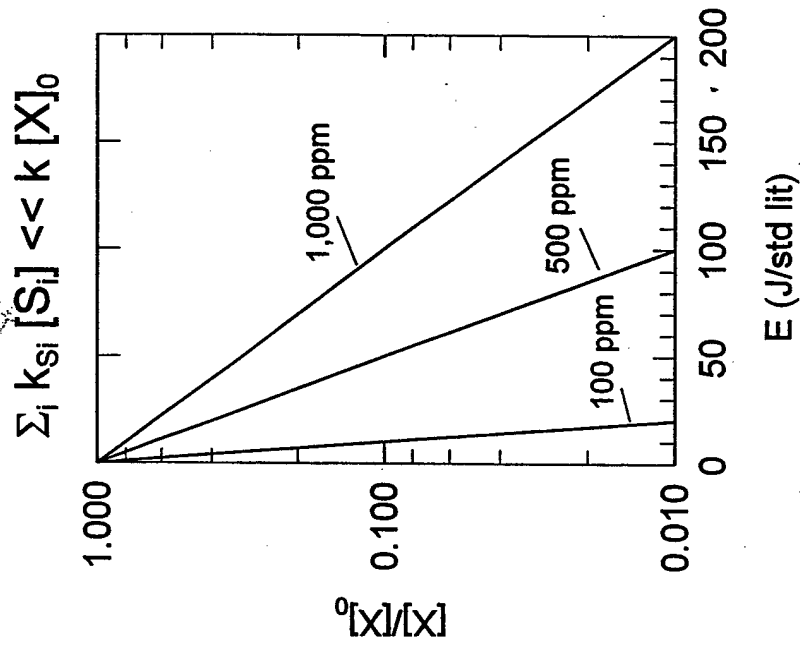**For low degree of removal (i.e., $[X]/[X]_0 \sim 1 + \ln\{[X]/[X]_0\}$), an analytical solution is obtained:**
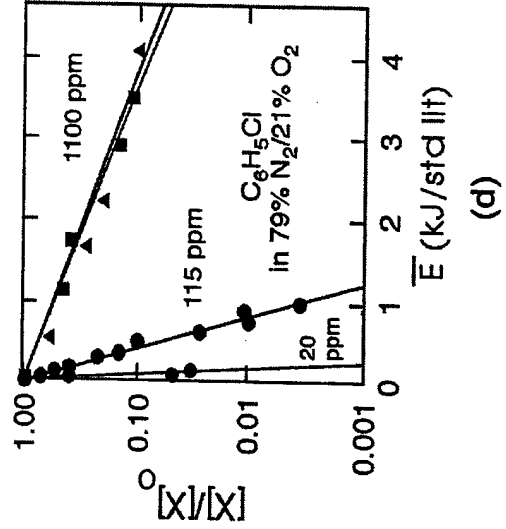
$$[X]/[X]_0 = \exp(-\bar{E}/\beta)$$

where

$$\beta = \frac{1}{G}\left([X]_0 + \frac{\sum_i k_{S_i}[S_i]}{k}\right)$$

When $k[X] << \sum_i k_{S_i}[S_i]$, the β-value and, hence the degree of removal $[X]/[X]_0$ shows no dependence on the initial concentration $[X]_0$.

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The simple model predicts the form of the removal function (plot of degree of removal *vs* plasma specific energy).

$\sum_i k_{Si} [S_i] << k [X]_0$

$[X]/[X]_0$

1.000
0.100
0.010

1,000 ppm
500 ppm
100 ppm

E (J/std lit)

0   50   100   150   200

$\sum_i k_{Si} [S_i] >> k [X]_0$

$[X]/[X]_0$

1.00
0.80
0.60
0.40
0.20
0.10

1,000 ppm
500 ppm
100 ppm

E (J/std lit)

0   250   500   750   1000

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Example removal data for various compounds

Negative Corona

Dielectric Barrier

(a) — Negative Corona plot: vertical axis $[X]/[X]_O$ from 1.00 down to 0.08; horizontal axis $\overline{E}$ (kJ/std lit) from 0 to 80. Labels: H₂S in 8.5% H₂/91.5% He, 2.0% H₂S, 1.05% H₂S.

(b) — vertical axis $[X]/[X]_O$ from 1.00 to 0.04; horizontal axis $\overline{E}$ (kJ/std lit) from 0 to 60. Labels: 17,000 ppm, 7,400 ppm, 3600 ppm, CFC-12 CCl₂F₂ in dry air.

(c) — vertical axis $[X]/[X]_O$ from 1.00 to 0.01; horizontal axis $\overline{E}$ (J/std lit) from 0 to 750. Labels: 190 ppm TCE in air/1.5% H₂O, 400 ppm NO in 72% N₂/18% O₂/10% H₂O.

(d) — vertical axis $[X]/[X]_O$ from 1.00 to 0.001; horizontal axis $\overline{E}$ (kJ/std lit) from 0 to 4. Labels: 1100 ppm, 115 ppm, 20 ppm, C₆H₅Cl in 79% N₂/21% O₂.

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Example removal data for various compounds (cont'd.)

CH$_3$OH, [X]$_0$ = 400 ppm
T = 120 C, Dry Air

After Hsiao et al

190 ppm

200 ppm

100 ppm

TCE in dry air

After Falkenstein; Korzekwa & Rosocha

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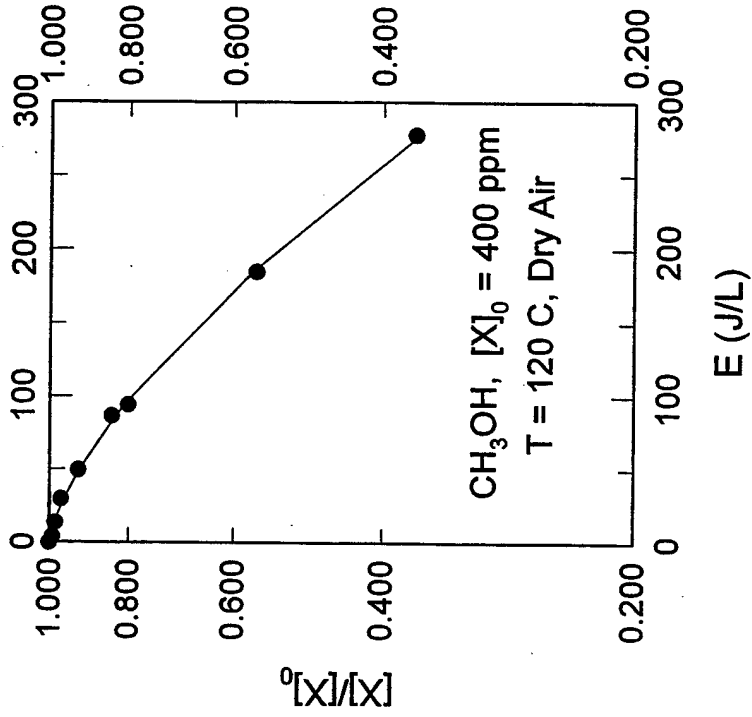
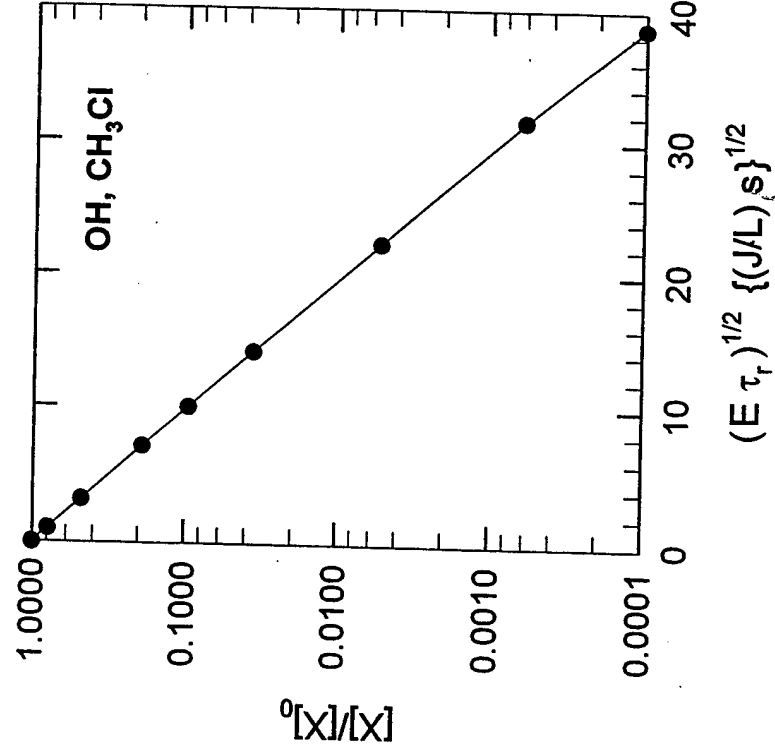# Example recombination-dominated removal plot (calculated).

Additional example case (explicit residence-time dependence):

$\Sigma_i k_{Si} [S_i] >> k [X]_0$ and dominant scavenging pathway is recombination of the radicals, e.g., $[R^\bullet] = [S]$, where S represents the primary scavenger

$$[R^\bullet] = (G\bar{P}/k_s)^{1/2}$$

$$\frac{d[X]}{[X]} = -k \left(\frac{G\bar{P}}{k_s}\right)^{1/2} dt$$

$$[X]/[X]_0 = \exp\{- k (G\bar{E}/k_s)^{1/2} \tau_r^{1/2}\}$$

OH, CH_3Cl

x-axis: $(E\tau_r)^{1/2} \{(J/L)_\ell s\}^{1/2}$

y-axis: $[X]/[X]_0$

Ballpark β-value calculation for TCE (C_2HCl_3) in a dry, air-like gas mixture:

Simple Chemical Model

1) $e + O_2 \rightarrow O + O + e$

2) $O + TCE \rightarrow$ Products

3) $O + O_2 + M \rightarrow O_3 + M$

$G(O) \sim 10$ molec/100 eV

$k_2 = 5.3 \times 10^{-13}$ cm^3/s

$k_3 = 6.1 \times 10^{-34}$ cm^6/s (for M = O_2)

$k'_3 = 5.9 \times 10^{-34}$ cm^6/s (for M = N_2)

β-Value Estimates

Without Chain Reactions

$\beta = 1/G \{ [X]_0 + 1/k_2 (k_3 [O_2]^2 + k'_3 [O_2] [N_2]) \}$

$\beta \sim 260$ J/liter

With Cl Chain Reactions

Chain length 2: $\beta \sim 130$ J/liter

Chain length 5: $\beta \sim 52$ J/liter

Chain length 10: $\beta \sim 26$ J/liter

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Example scaling laws for pollutant removal (no $[X]_0$ dependence)

(1) $[X] = [X]_0 \exp(-\bar{E}/\beta)$,

where $[X]_0$ is the initial pollutant concentration, $[X]$ is the resulting concentration, $\bar{E}$ is the applied specific energy (or plasma power divided by gas flow rate, P/Q), and β is the e-fold energy density. Supplying one β to the reactor reduces the concentration by $1/e$, 2β by $1/e^2$, and so on.

A useful figure of merit for the decomposition of pollutants is defined by the energy delivered to the plasma per hazardous molecule removed from the gas stream. At any instant, this can be expressed as the following quantity obtained by solving Equation 1 for $\bar{E}$ and taking the derivative:

(2) $\gamma_i = -\dfrac{d\bar{E}}{d[X]} = -\dfrac{d[-\beta \ln(\frac{[X]}{[X]_0})]}{d[X]} = \dfrac{\beta}{[X]}$.

This is the instantaneous energy cost per molecule removed.

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Scaling laws for pollutant removal (cont'd)

A more practically-useful parameter is the integral, or average, energy cost γ

$$(3) \quad \gamma = \frac{\bar{E}}{[X]_0 - [X]} = \frac{-\beta \ln(\frac{[X]}{[X]_0})}{[X]_0 (1 - \frac{[X]}{[X]_0})} \qquad (= \beta/[X]_0 \text{ (at optimum; i.e., } [X]/[X]_0 \sim 1).$$

Here, the energy cost per molecule is expressed in terms of the β-value, the degree of removal, and the initial concentration.

When radical-pollutant attack dominates $\beta \approx [X]_0/G$ and the removal cost is then independent of the initial concentration

$$(4) \quad \gamma = \frac{\bar{E}}{[X]_0 - [X]} = \frac{-\ln(\frac{[X]}{[X]_0})}{G (1 - \frac{[X]}{[X]_0})} \qquad (= 1/G \text{ at optimum; i.e., } [X]/[X]_0 \sim 1).$$

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Figures-of-merit for pollutant removal
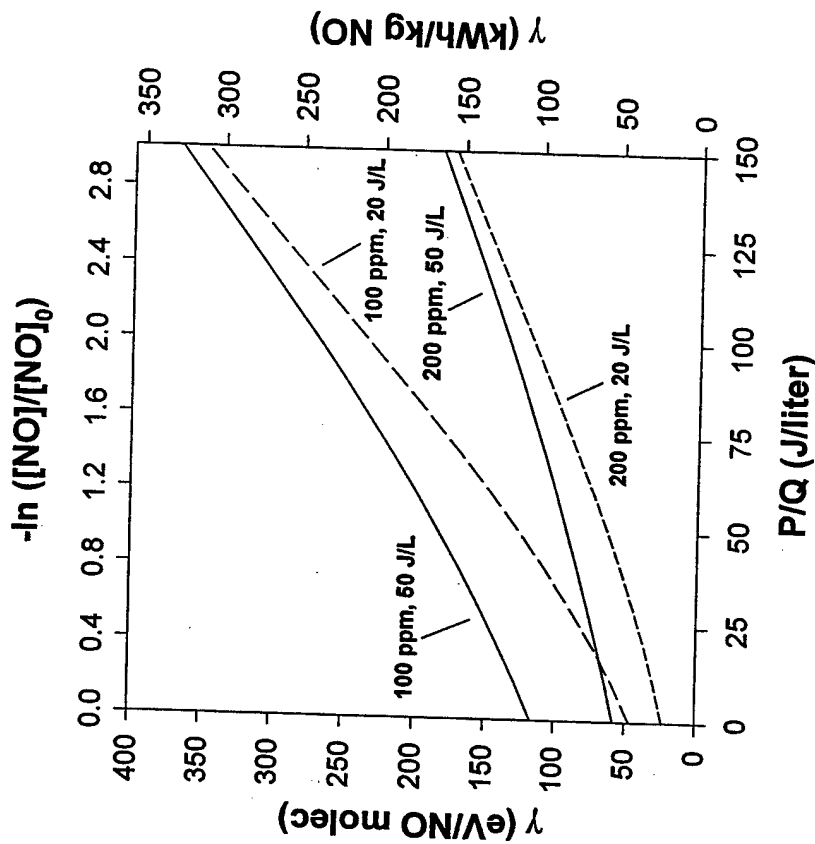
Energy costs and degree of removal for NO removal in an NO-air mixture with one e-fold plasma specific energies of 50 J/liter and 20 J/liter. NO is a compound whose β-value is not very sensitive to the initial concentration; therefore, the removal energy costs decrease as the concentration increases (note 200 ppm case vs 100 ppm case).

Figures-of-merit for pollutant removal: generalized compound, scavenging dominant.

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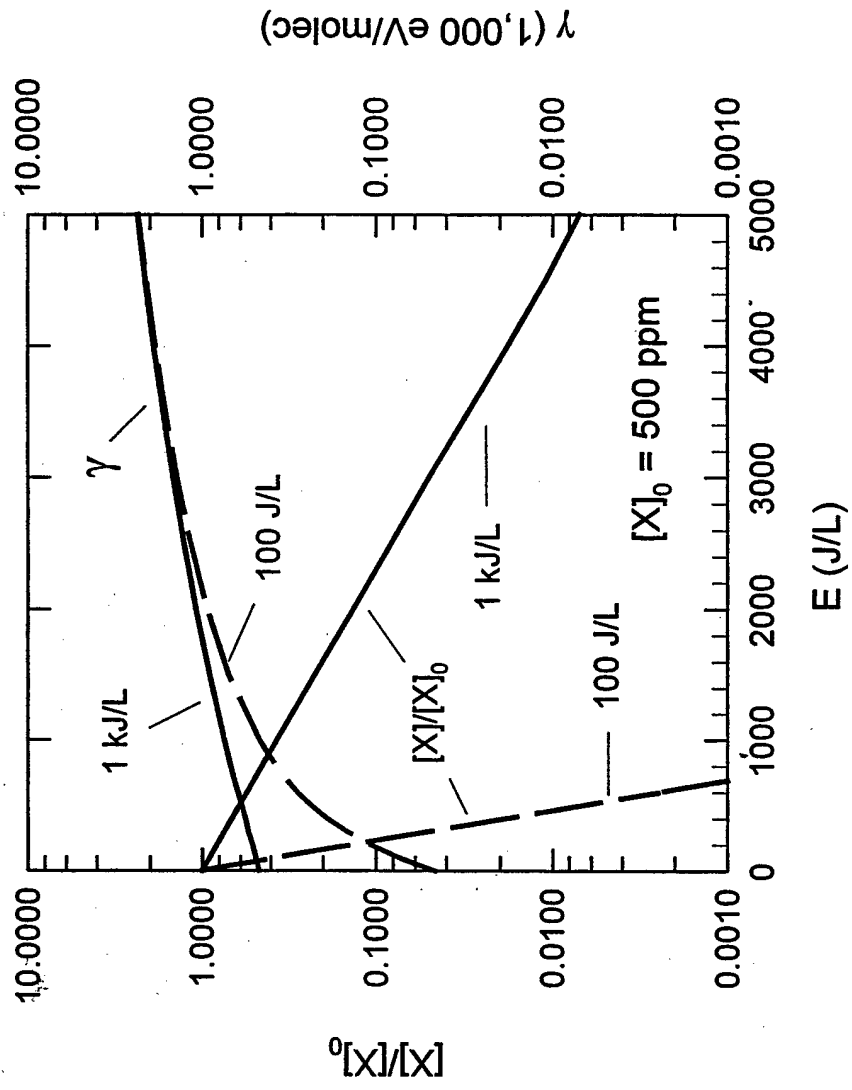
Summary

- Most technical literature on treating air emissions with NTPs mainly presents phenomenological descriptions of reactor performance and, in most cases, does not provide a consistent way to compare and/or predict the scaling and optimization properties of different NTP systems.

- A simple way of comparing different types of NTP reactors, is based on the concept of: the plasma specific energy (electrical energy per unit volume deposited in the reactor active volume) required to remove a particular pollutant to a prescribed level in a defined exhaust-gas mixture and the associated yield (electrical energy cost per mass of pollutant removed.

- We have described simple models for pollutant-removal and figures-of-merit for energy-removal costs in generalized NTP reactors.

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13. ABSTRACT (Maximum 200 Words)

Non-thermal plasmas (NTPs) are a type of advanced oxidation and reduction technology for treating gas-phase chemical pollutants. Such plasmas are good sources of highly reactive oxidative and reductive species (free radicals and others), e.g., $O(^3P)$, OH, N, H, NH, CH, O_3, O_2 ($^1\Delta$), and plasma electrons. Because radical-attack reaction rate constants are very large for many chemical species, entrained pollutants are readily decomposed by NTPs. Via these reactive species, one can direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas. NTPs are commonly created by an electrical discharge in a gas or the injection of an energetic electron beam into a gas. Both methods create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature). In NTPs, the electrons are highly energetic (hot) and the ions and background gas species are at near-ambient temperature (cold). For this reason, these plasmas are sometimes called cold plasmas.

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