SIMULTANEOUS REMEDIATION OF NO\textsubscript{X} AND OXIDATION OF SOOT USING DIELECTRIC BARRIER DISCHARGES*

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AGENDA

• Introduction

• Description of the model – GLOBAL_KIN

• Reaction mechanisms

• Effect of soot particles on NO$_x$ remediation

• Results
  • NO$_x$ remediation
  • Soot oxidation
  • Effect of multiple pulses on NO$_x$ chemistry

• Concluding remarks
• Nitrogen oxides (NO, NO₂) - NOₓ, are one of the six major pollutants identified by the EPA, others being CO, Pb, SOₓ, volatile matter and particulates. All emissions have decreased except for NOₓ (EPA, 1998).

• Harmful effects of NOₓ
  • Acid deposition
  • Formation of ozone
  • Eutrophication of water bodies
  • Inhalable fine particles
  • Visibility degradation

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Major sources of NOₓ (EPA, 1998)

- Motor Vehicles: 49%
- Utilities: 27%
- Industrial/Commercial/Residential: 19%
- All Other Sources: 5%
Dielectric barrier discharges (DBDs) are well suited for generation of gas-phase radicals at atmospheric pressures.

Electron impact processes in DBDs produce radicals and ions which initiate the plasma chemistry.

\[
e + N_2 \rightarrow N + N + e
\]
\[
e + O_2 \rightarrow O + O + e
\]
\[
e + H_2O \rightarrow OH + H + e
\]

Reduction
\[
NO + N \rightarrow N_2 + O
\]

Oxidation
\[
NO + O \rightarrow NO_2
\]
\[
NO_2 + OH \rightarrow HNO_3
\]
GLOBAL-KIN is a spatially homogeneous plasma chemistry simulation coupled with circuit and surface reaction modules.

The model uses a lookup table generated by an offline Boltzmann solver to obtain the e-impact reaction rate coefficients.
OPERATING CONDITIONS

• Typical diesel exhausts contain N\textsubscript{2}, O\textsubscript{2} (excess air); H\textsubscript{2}O, CO\textsubscript{2} (products) and trace amounts of NO, CO, H\textsubscript{2} and unburned hydrocarbons (UHCs).

• To simulate actual exhausts, we have used propane (C\textsubscript{3}H\textsubscript{8}) and propene (C\textsubscript{3}H\textsubscript{6}) as representative of the UHCs.

• Inlet gas composition

\[
\begin{align*}
\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2 = & 78/8/6/7 \\
\text{NO} = & 260 \text{ ppm}, \text{CO} = 400 \text{ ppm}, \text{H}_2 = 133 \text{ ppm} \\
\text{C}_3\text{H}_6 = & 500 \text{ ppm}, \text{C}_3\text{H}_8 = 175 \text{ ppm}
\end{align*}
\]

• T=180 °C, P=1atm

\( \tau = \) residence time of exhaust in DBD = 0.2 s
In the presence of UHCs, the primary reaction is oxidation of NO by the peroxy radicals.

Propene reactions are initiated both by O and OH whereas propane reactions are mainly OH initiated.

\[
\begin{align*}
\text{Methyl} & \xrightarrow{\text{O}} \underset{\text{O}}{\text{C}_3\text{H}_6} \xrightarrow{\text{OH}} \text{C}_3\text{H}_6\text{OH} \xrightarrow{\text{O}_2} \text{C}_3\text{H}_6(\text{OO})\text{OH} \xrightarrow{\text{NO}} \cdots \xrightarrow{\text{NO}_2} \text{CH}_3\text{CHO}, \text{HCHO} \\
\text{Oxirane} & \quad \text{C}_2\text{H}_5\text{CHO} \\
\text{C}_3\text{H}_8 & \xrightarrow{\text{OH}} \text{C}_3\text{H}_7 \xrightarrow{\text{O}_2} \text{C}_3\text{H}_7\text{O}_2 \xrightarrow{\text{NO}} \cdots \xrightarrow{\text{NO}_2} \text{CH}_3\text{C(0)}\text{CH}_3, \text{CH}_3\text{CH}_2\text{CHO}
\end{align*}
\]
Soot particles found in diesel exhausts are typically 100 nm and containing C/H/O=89/1/10.

The radicals produced in the plasma diffuse to the soot surface and react.

\[
\begin{align*}
O + Su & \rightarrow O_{\text{adsorbed}} \rightarrow CO \\
OH + Su & \rightarrow OH_{\text{adsorbed}} \rightarrow CO + H_2 \\
NO_2 + Su & \rightarrow NO_2 (\text{adsorbed}) \rightarrow NO + CO
\end{align*}
\]
• Region surrounding soot is divided into two zones.
  • Diffusion regime
  • Homogeneous Bulk Plasma

• Species that react on the soot surface diffuse through the boundary layer.

• Boundary layer thickness, $\delta$, is obtained from the Reynolds number. For low $Re$, $\delta \approx d_s/2$.

• The diffusing species have a linear profile in the diffusion regime.
PLASMA CONDITIONS: \( n_e, T_e, [N], [OH], [O] \)

- Peak \( n_e \approx 10^{13} \text{ cm}^{-3} \) and \( T_e \approx 3 \text{ eV} \) with \( E_{\text{dep}} \approx 38 \text{ J/L} \).

- Electron impact dissociation of \( \text{N}_2, \text{O}_2 \) and \( \text{H}_2\text{O} \) produce \( \text{N}, \text{O} \) and \( \text{OH} \) respectively.
• With a single pulse, exit NO densities are high because of the depletion of $O_3$ and peroxy radicals by the time of desorption of $NO_2(ads)$.

\[
NO + O_3 \text{ (or peroxies)} \rightarrow NO_2 \rightarrow NO_2(ads) \rightarrow NO
\]
• With multiple pulses, NO is converted to NO$_2$ by O$_3$ and peroxy radicals produced during each pulse.

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$$

• The rate of adsorption of NO$_2$ being higher than the rate of desorption, the NO$_x$ remains adsorbed on the surface of soot.
• For a single pulse, exit NO densities are higher because of the larger time available for NO$_2$ desorption from the soot surface.

• The peroxy radicals available for NO consumption are lost by the time NO is regenerated from NO$_2$. 

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![Graph showing the effect of energy deposition on density and NO$_2$ adsorption. The graphs compare single pulse (SP) and multiple pulse (MP) conditions. The x-axis represents energy deposition (J/L), and the y-axis represents density (ppm) or NO$_2$ adsorption (cm$^{-2}$). The graphs display curves for NO and NO$_2$ in both SP and MP conditions.](image-url)
• With increasing energy deposition, the diameter of the soot decreases due to the oxidation by NO$_2$.

\[ \text{Soot} + \text{NO}_2 \rightarrow \text{Soot-NO}_2 \rightarrow \text{Soot} + \text{NO} + \text{CO} \]

• At higher energies, the final diameter of soot increases because the density of NO$_2$ decreases due to the gas-phase reconversion to NO.

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]

• Note that the oxidation of soot is partial and results in CO and not CO$_2$.
  • CO – poisonous
  • CO$_2$ – greenhouse gas
CONCLUDING REMARKS

- Plasma remediation of NO\textsubscript{x}, by itself is not sufficient to completely remove NO\textsubscript{x}.

- Soot chemistry significantly affects the NO\textsubscript{x} composition in plasma remediation of NO\textsubscript{x}.

- Soot can be oxidized by plasma and as high as 30\% soot removal can be achieved at 60 J/L.

- Multiple pulse input results in \textit{apparent} NO\textsubscript{x} removal because of the increased adsorption onto the soot surface.

- With single pulse energy deposition, the exit-NO\textsubscript{x} is primarily NO because of the reconversion of NO\textsubscript{2} to NO on soot surface.