CONSEQUENCES OF SOOT PARTICLES ON THE PLASMA REMEDIATION OF NO_X IN THE PRESENCE OF HYDROCARBONS*

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AGENDA

- NO_x - A BRIEF INTRODUCTION
- ROLE OF PLASMA IN NO_X REMEDIATION
- IMPORTANCE OF UNBURNED HYDROCARBONS (UHC) IN NO_X REMEDIATION
- SURFACE REACTIONS OF NO_X ON SOOT PARTICLES AND THEIR IMPLICATIONS ON THE OVERALL PLASMA CHEMISTRY
- CHARGING OF SOOT PARTICLES
- CONCLUSIONS

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NO_X - THE NEED FOR ITS REMOVAL

- The Environmental Protection Agency (EPA) has tracked the emissions of six major pollutants [CO, lead, nitrogen oxides (NO_x), particulate matter, SO_x and volatile organic compounds] since 1970. All emissions have significantly decreased except for NO_x which has increased by 10%. (EPA, 1998)

- Harmful effects of NO_x.
  - Formation of Ozone
  - Eutrophication of water bodies
  - Visibility degradation
  - Acid deposition
  - Inhalable fine particles

- Major sources of NO_x
  - Automotives
  - Gas Turbines
  - Electric utilities
  - Cement Manufacturing industries

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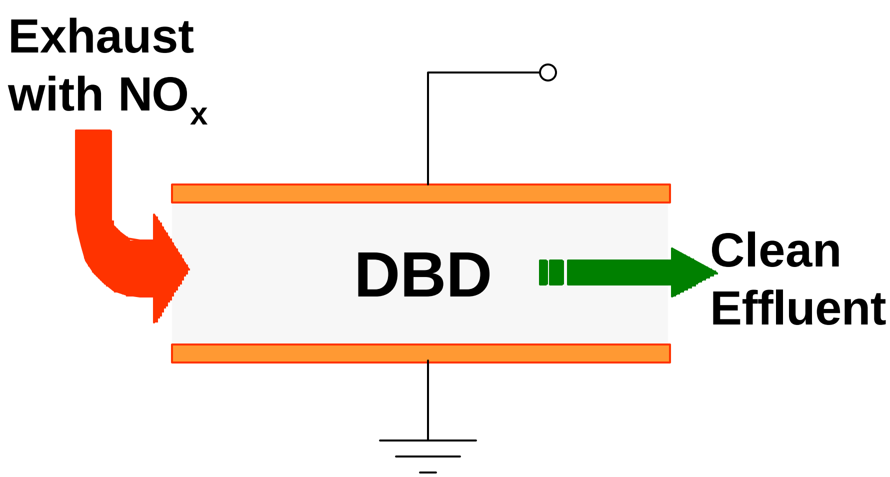
PLASMA REMEDIATION OF NO_X USING DBDs

- Dielectric barrier discharges (DBDs) are well suited for the generation of gas-phase radicals at atmospheric pressures.
- Electron impact processes in DBDs produce atoms and reactive radicals which initiate the plasma chemistry.



$$e + N_2 \rightarrow N + N + e$$
$$e + O_2 \rightarrow O + O + e$$
$$e + H_2O \rightarrow OH + H + e$$

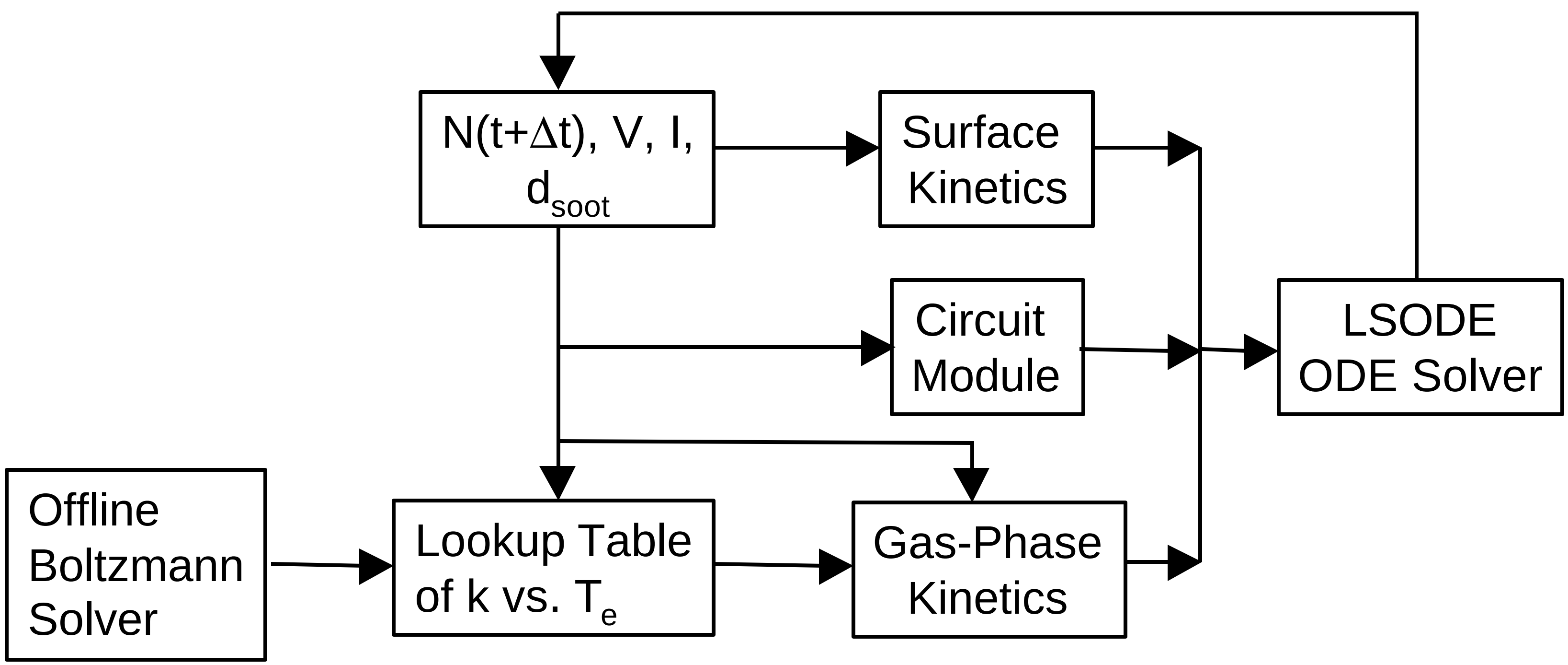
Reduction $NO + N \rightarrow N_2 + O$

Oxidation $NO + O \rightarrow NO_2$

$NO_2 + OH \rightarrow HNO_3$

DESCRIPTION OF GLOBAL-KIN

- 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 reaction rate coefficients for e-impact reactions.



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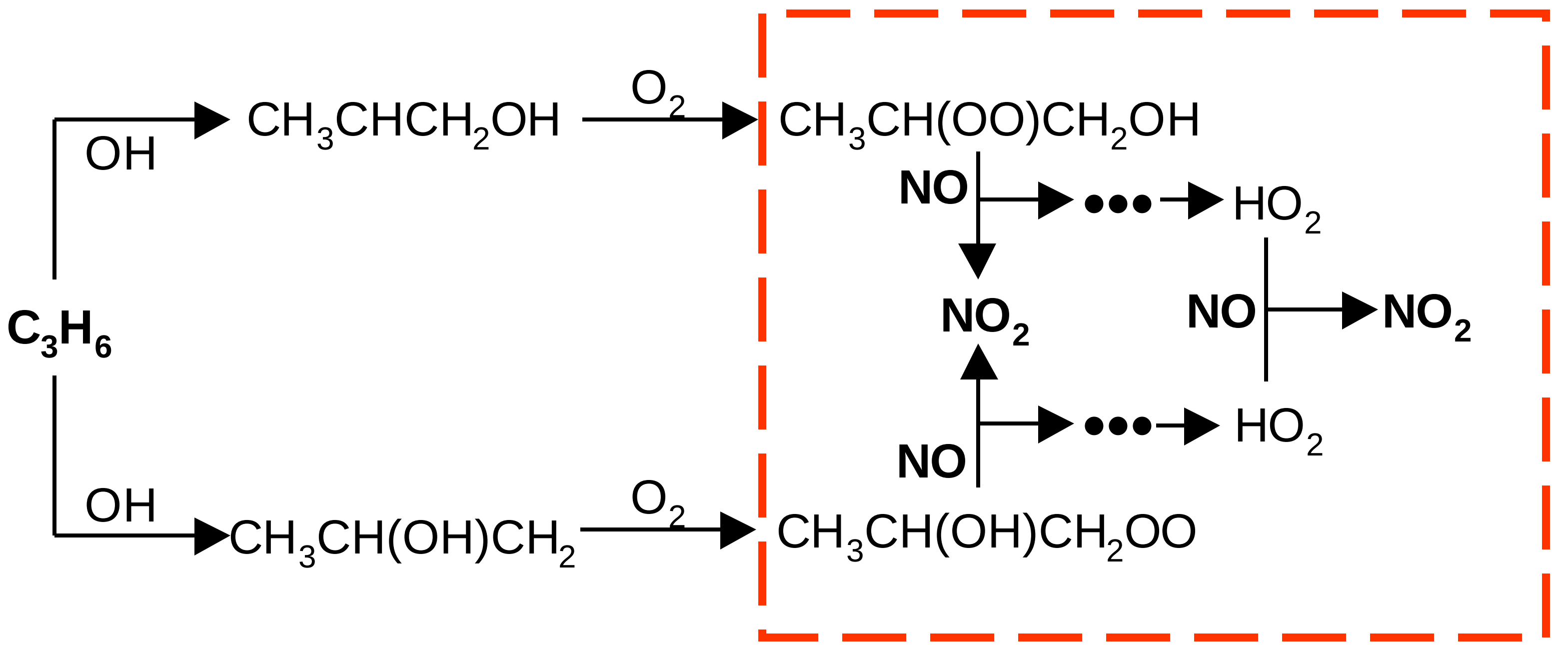
REACTION MECHANISMS : NO_X, C_3H_6 (PROPENE)

- In the presence of UHCs, the primary reaction is oxidation of NO by the peroxy radicals.
- The subsequent formation of HO_2 from this reaction scheme results in further oxidation of NO to NO_2



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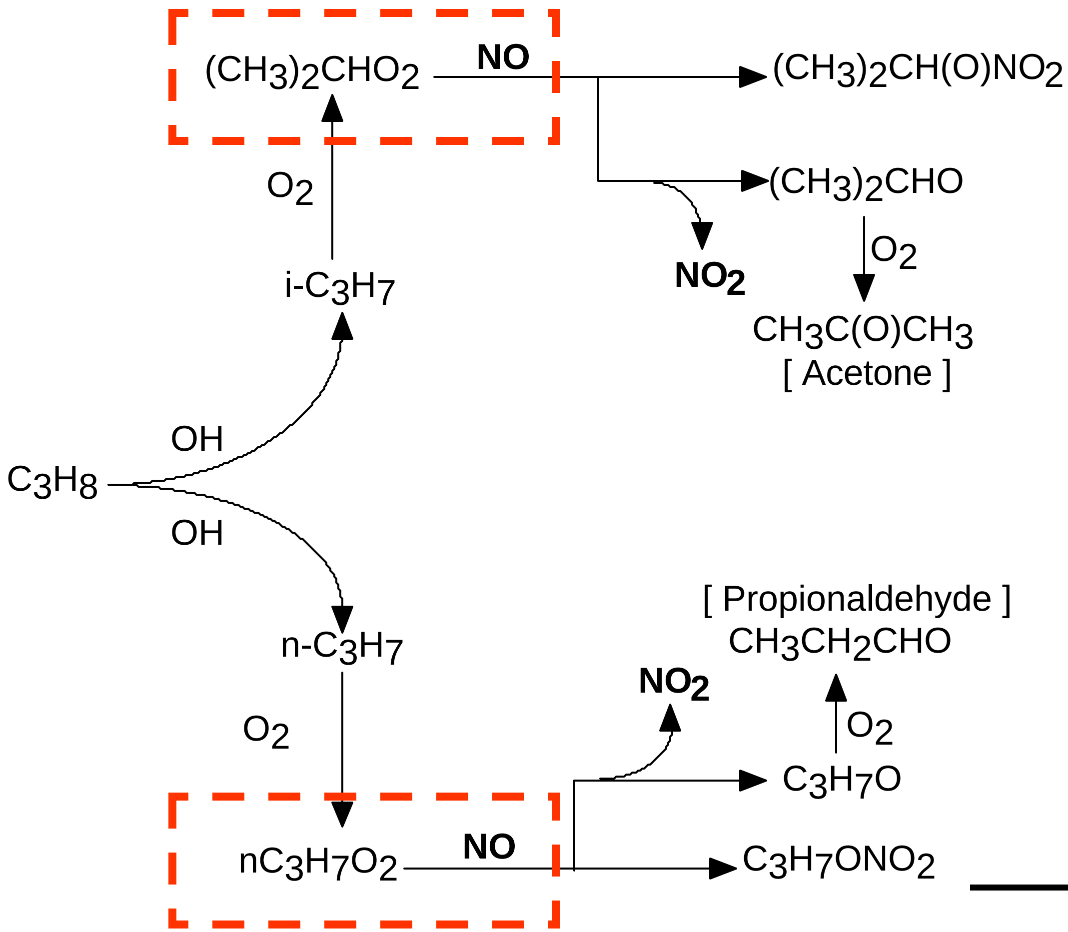
REACTION MECHANISMS : NO_X, C_3H_8 (PROPANE)

- The initiating reaction with propane is an abstraction by OH. The resulting radicals then react with O_2 to form the peroxy radicals.
- These peroxy radicals then react with NO to convert it to NO_2.



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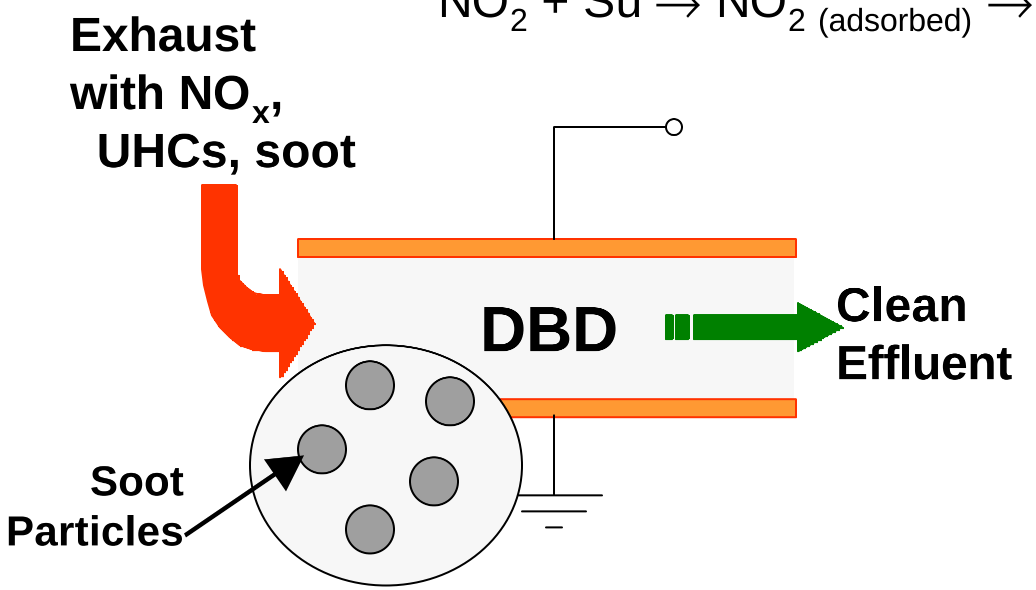
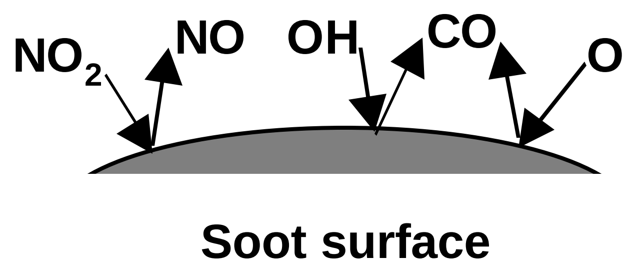
EFFECT OF SOOT PARTICLES ON NO_X REMEDIATION

- Soot particles in diesel exhausts are typically 100 nm in diameter with 87-95% carbon, 1% hydrogen and 6-11% oxygen.

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

$$O + Su \rightarrow O_{adsorbed} \rightarrow CO$$
$$OH + Su \rightarrow OH_{adsorbed} \rightarrow CO + H_2$$
$$NO_2 + Su \rightarrow NO_{2\ (adsorbed)} \rightarrow NO + CO$$





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SOOT OXIDATION

- The soot modifies the bulk gas chemistry by consuming the radicals produced in the plasma.

- Parameterizations were performed on the initial soot diameter, density of particles, reaction probabilities on soot surfaces and energy deposition.

- Base case conditions

    - T=180^{o}C , P=1 atm, $N_2/O_2/H_2O/CO_2$=79/8/6/7
    - CO=400 ppm, NO=260 ppm, H_2=133 ppm,
    - C_3H_6=500 ppm, C_3H_8=175 ppm
    - d_{soot}=100 nm
    - d_o=diameter of the spherules inside the soot=20 nm
    - $\rho_{soot}=10^8$ cm^{-3}
    - Fractal dimension of the soot=2.8

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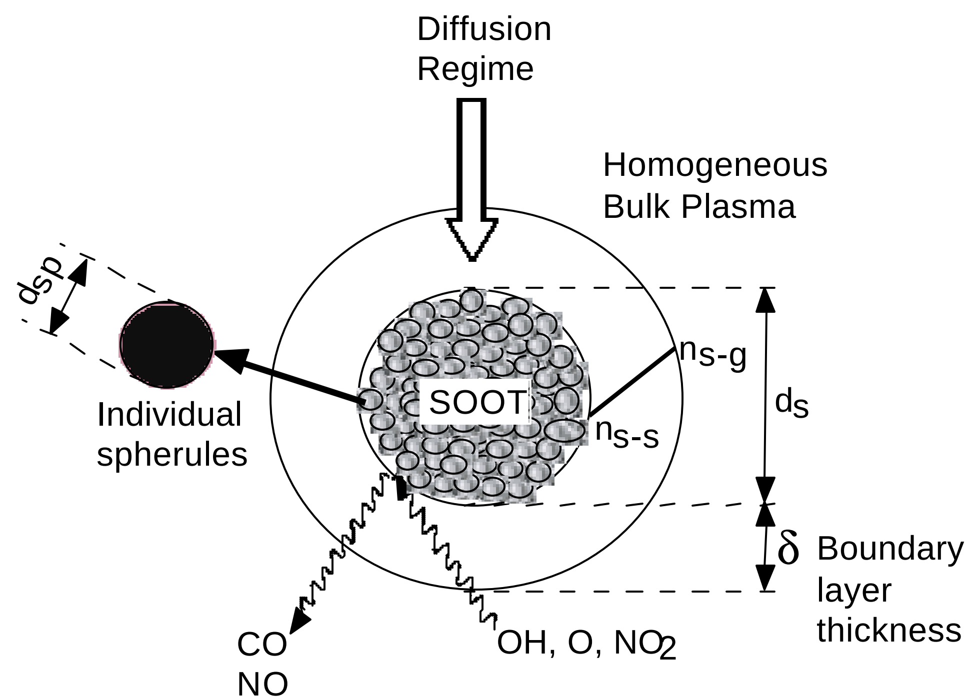
SOOT OXIDATION MODEL

- The region surrounding the soot is divided into two zones :
  - Diffusion regime
  - Homogeneous Bulk Plasma
- Species that react on the soot surface diffuse through the boundary layer.
- The boundary layer thickness, δ, 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.



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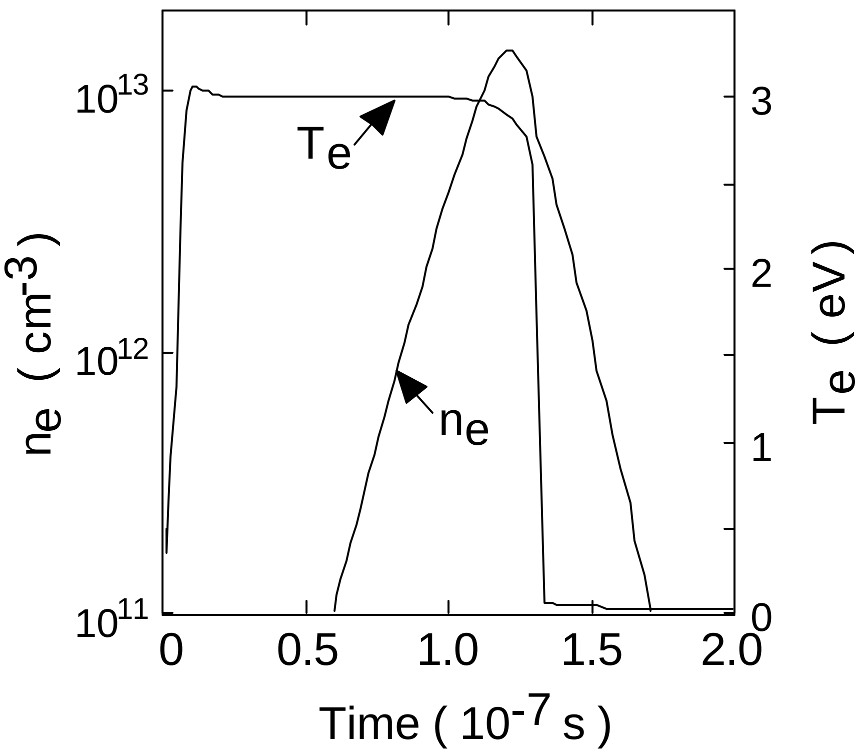
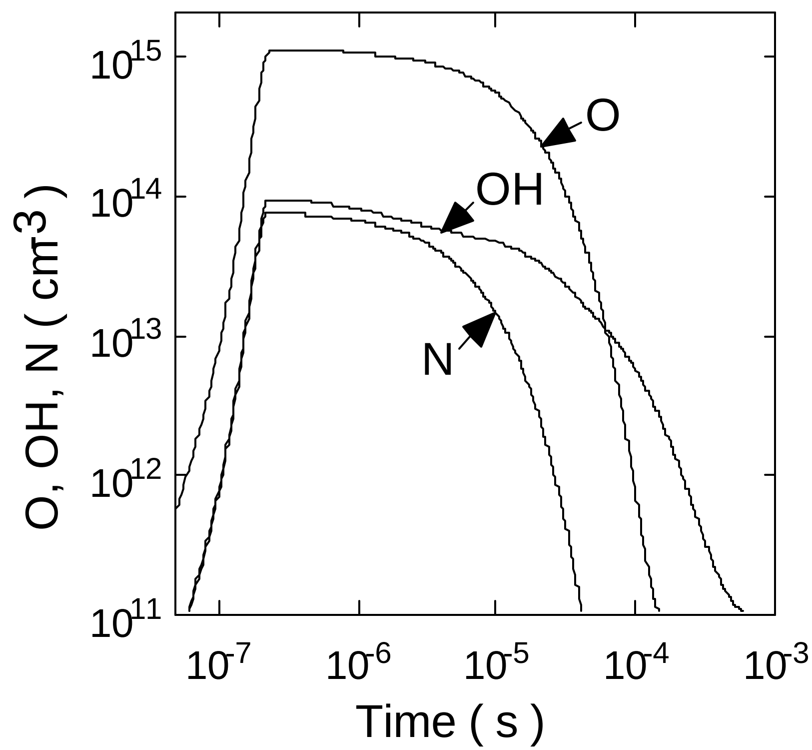
PLASMA CHEMISTRY - INITIATOR RADICALS : N, OH, O

- Peak $n_e \approx 10^{13}$ cm^{-3} and $T_e \approx 3$ eV are observed with $E_{dep} \approx 38$ J/L.
- The processes that trigger the plasma chemistry are electron impact dissociation of N_2, O_2 and H_2O producing N, O and OH.





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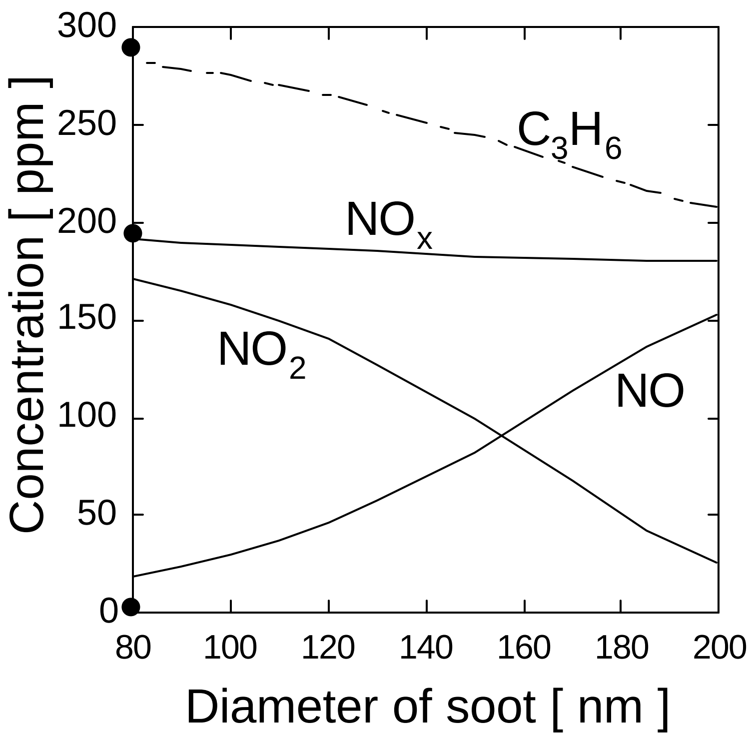
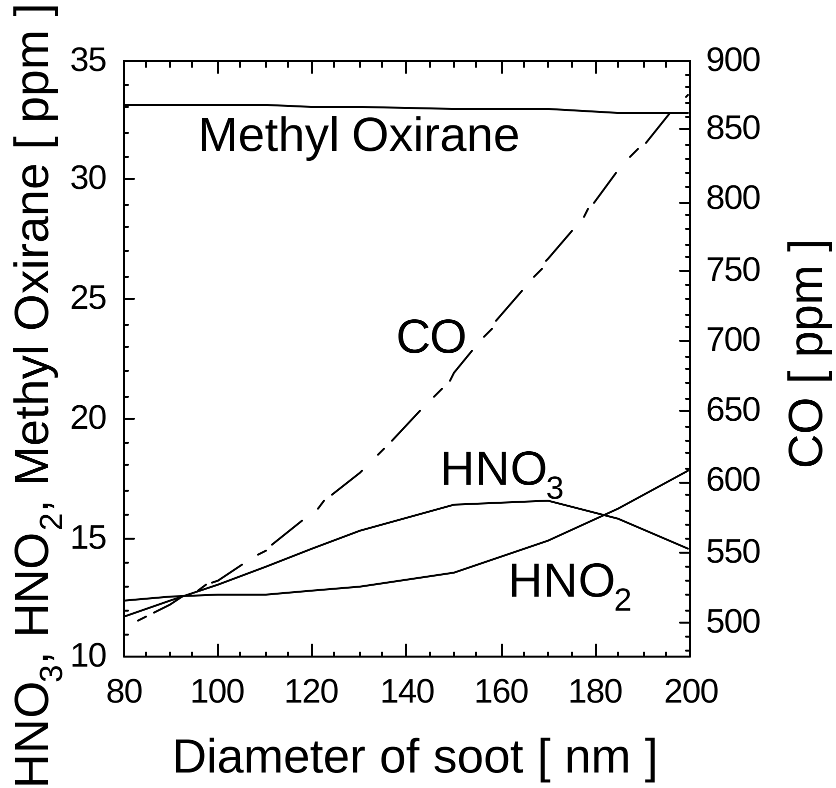
EFFECT OF INITIAL SOOT DIAMETER

- With surface reactions, the NO_x composition in the gas-phase is significantly modified. NO/NO_2 increases with increasing soot diameter due to the reaction $NO_2 + Su \rightarrow NO_{2\ (adsorbed)} \rightarrow NO + CO$



• = no soot



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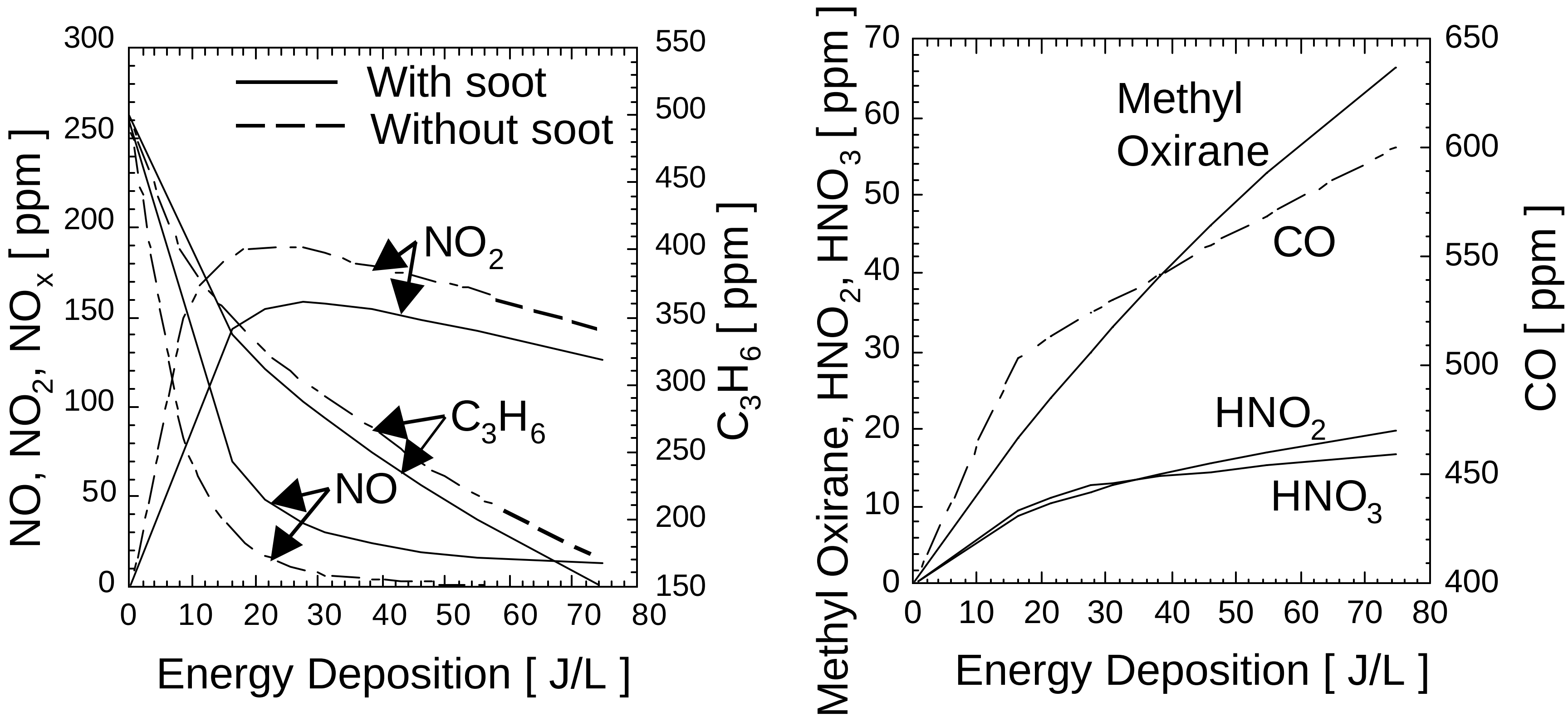
EFFECT OF ENERGY DEPOSITION

- With increasing energy deposition, NO_x remediation improves in the presence of soot.
- NO is not completely removed due to the conversion of NO_2 to NO on soot.



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SOOT OXIDATION

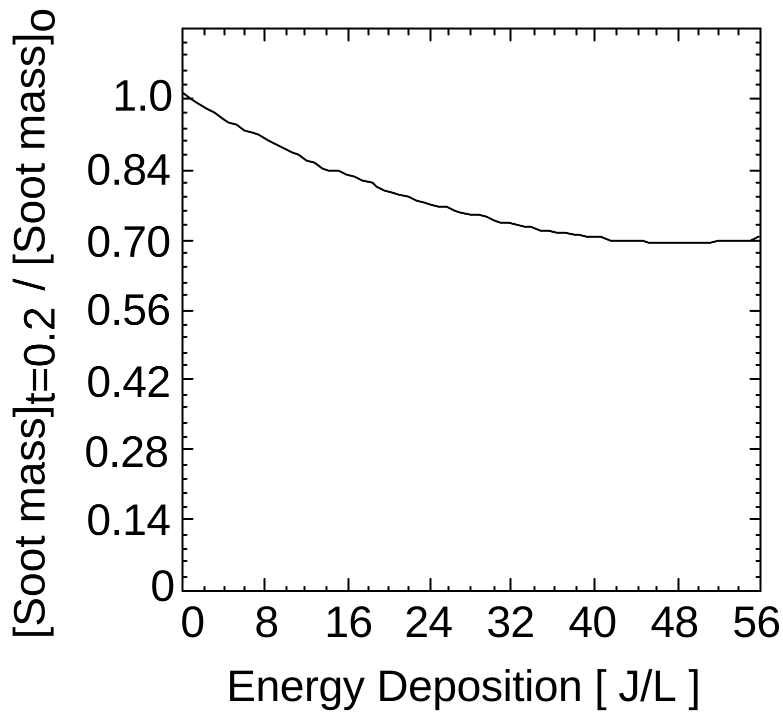
- 30% soot oxidation is achieved at high energy deposition due to

$$Su_{(\text{adsorbed O})} \rightarrow Su + \underline{CO}$$

$$Su_{(\text{adsorbed OH})} \rightarrow Su + H_2 + \underline{CO}$$

$$Su_{(\text{adsorbed NO2})} \rightarrow Su + NO + \underline{CO}$$

- This oxidation is only partial since the product is CO and not CO_2.
    - CO - poisonous
    - CO_2 - greenhouse gas



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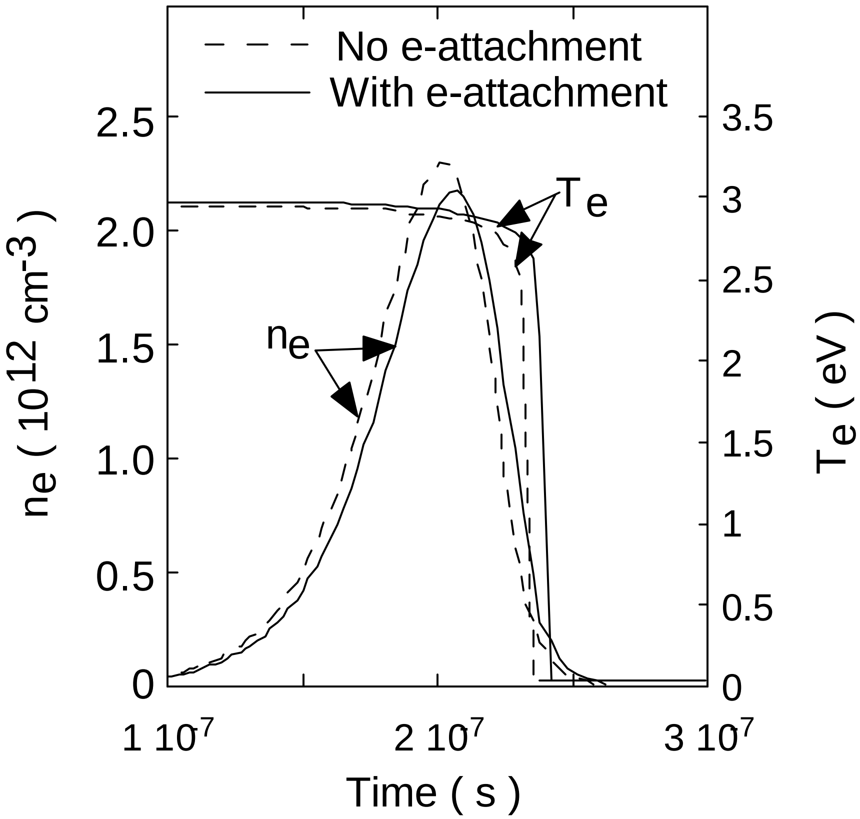
ELECTRON ATTACHMENT TO SOOT

- Electron attachment to soot was significant only for $d_s \geq 150$ nm and $n_p \geq 10^9$ cm^{-3}.

- Peak electron densities decreased by 5% and electron temperatures were slightly higher to increase ionization to compensate for loss to soot.

- Under normal operating conditions, (100 nm and 10^8 cm^{-3} particle densities) electron attachment is not significant and can be neglected.



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CONCLUSIONS / KEY POINTS

- Soot chemistry significantly affects the NO_x composition in plasma remediation of NO_x.
- Soot particles are oxidized by plasmas with primary products CO, H_2 and NO.
- Electron attachment to soot is not significant at the normal operating conditions (10^8 cm^{-3} and 100 nm).
- Water adsorption on the soot surface can significantly affect the soot properties. Future studies will investigate these effects.

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