EFFECT OF MULTIPLE PULSES ON THE HETEROGENEOUS AND HOMOGENEOUS CHEMISTRY DURING THE PLASMA REMEDIATION OF NO_X AND OXIDATION OF SOOT USING DIELECTRIC BARRIER DISCHARGES *

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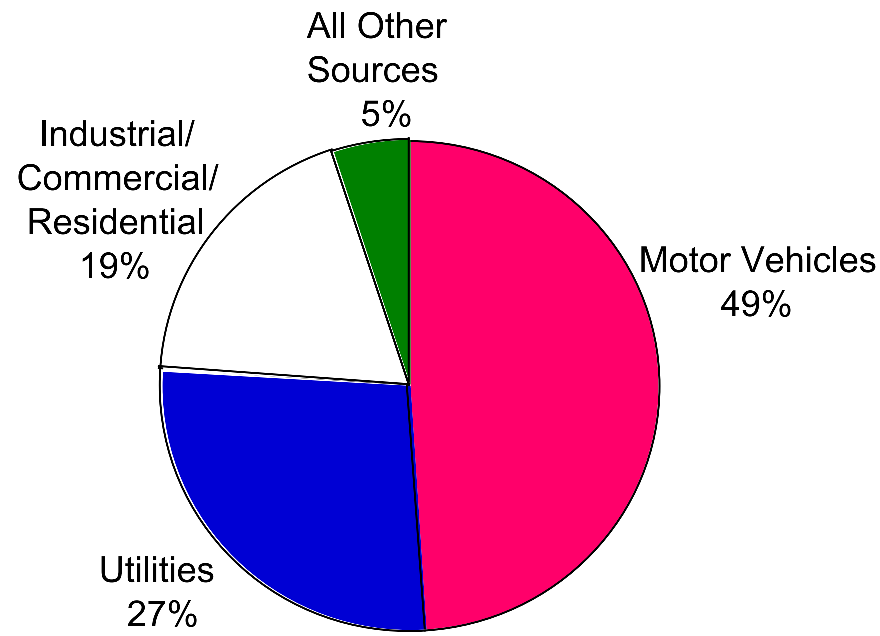
INTRODUCTION

- **Nitrogen oxides (NO, NO_2) - NO_X, are one of the six major pollutants identified by the EPA, others being CO, Pb, SO_X, volatile matter and particulates. All emissions have decreased except for NO_x (EPA, 1998).**

- **Harmful effects of NO_X**
  - **Acid deposition**
  - **Formation of ozone**
  - **Eutrophication of water bodies**
  - **Inhalable fine particles**
  - **Visibility degradation**

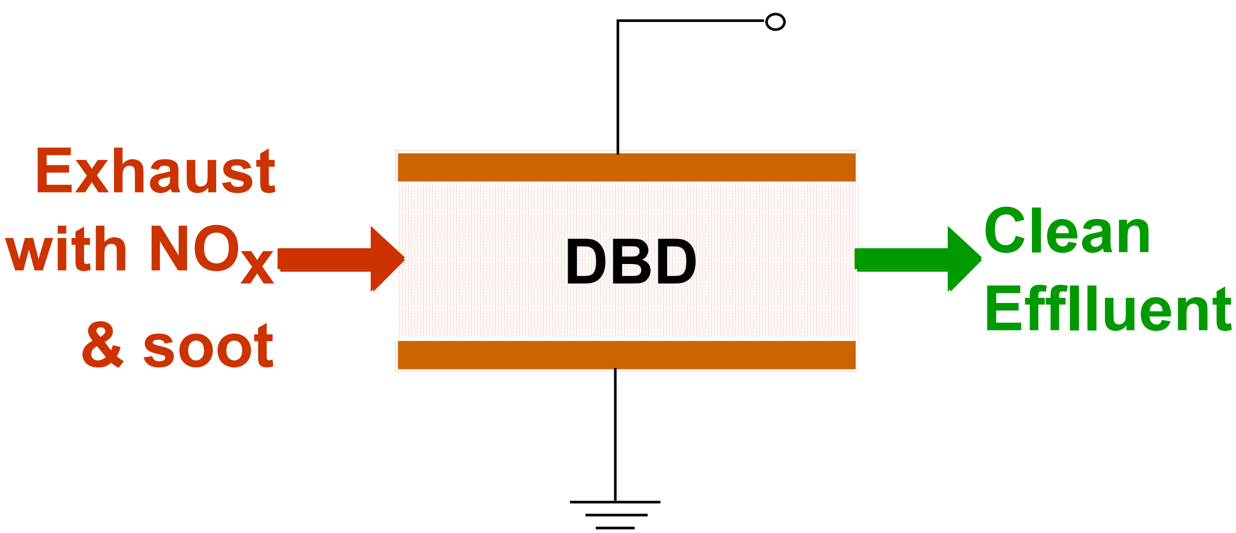


Major sources of NO_x (EPA, 1998)

PLASMA REMEDIATION OF NO_X USING DBDs

- 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

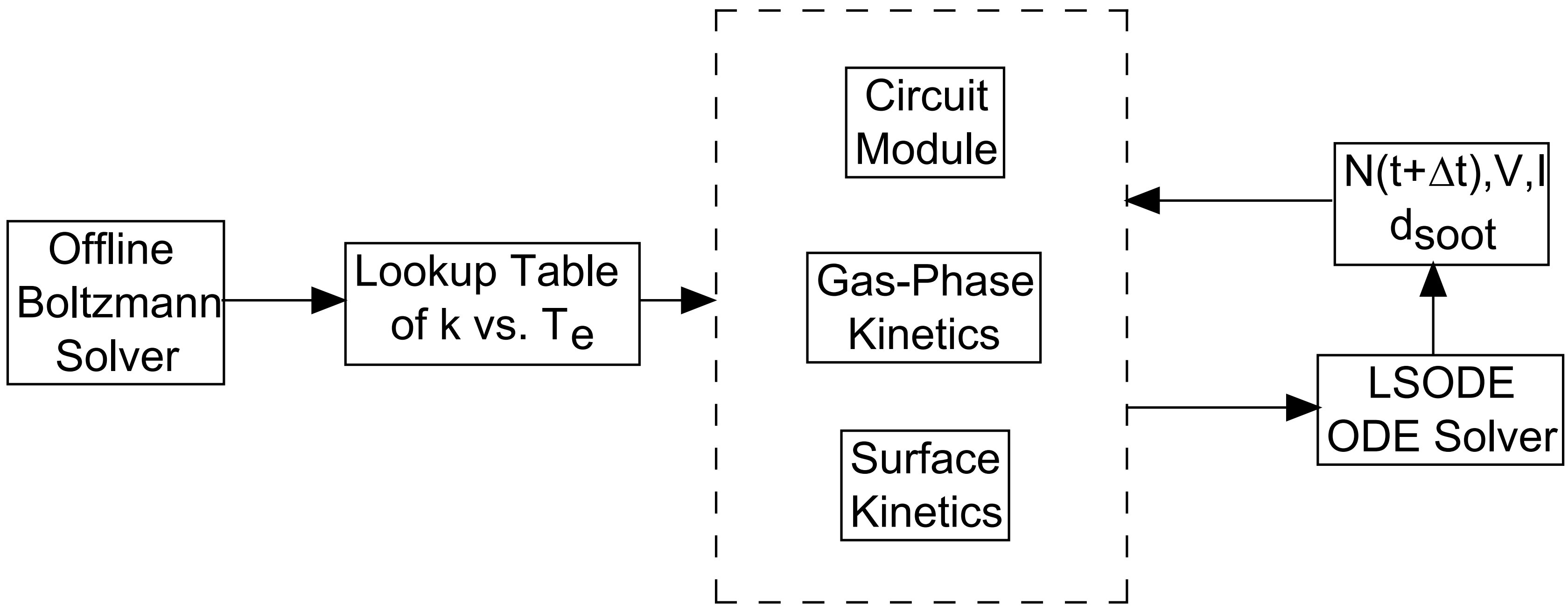
$NO + O \rightarrow NO_2$

$NO_2 + OH \rightarrow HNO_3$

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 e-impact reaction rate coefficients.**



OPERATING CONDITIONS

- Typical diesel exhausts contain N_2, O_2 (excess air); H_2O, CO_2 (products) and trace amounts of NO, CO, H_2 and unburned hydrocarbons (UHCs).

- To simulate actual exhausts, we have used propane (C_3H_8) and propene (C_3H_6) as representative of the UHCs.

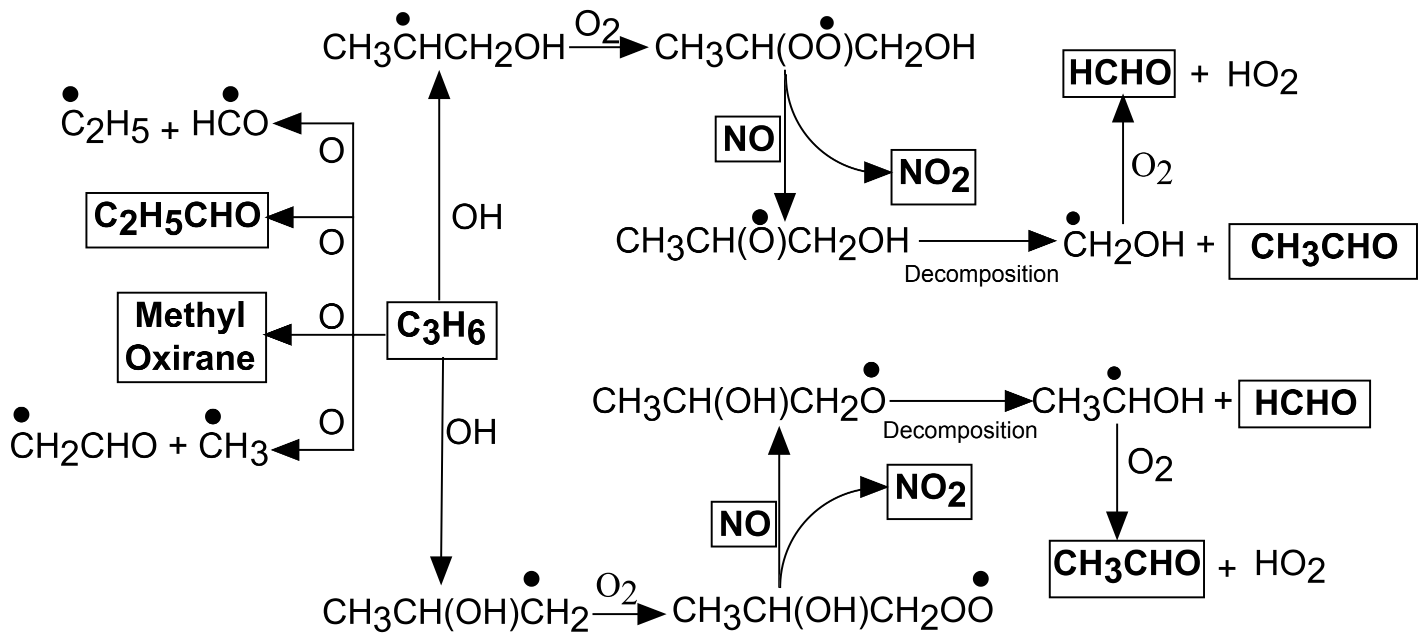
- Inlet gas composition

  $N_2/O_2/H_2O/CO_2$=78/8/6/7 NO=260 ppm, CO=400 ppm, H_2=133 ppm
  C_3H_6=500 ppm , C_3H_8=175 ppm

- T=180 ^{o}C, P=1atm
  τ = residence time of exhaust in DBD = 0.2 s

REACTION MECHANISM: NO-C_3H_6

- **C_3H_6 reactions are initiated by O and OH.**
- **Peroxy radicals formed from OH-initiated reactions with propene, oxidize NO to NO_2.**
- **NO_x is also converted to other organic nitrates and nitrites, but most of the initial NO_x (NO) is primarily oxidized to NO_2.**



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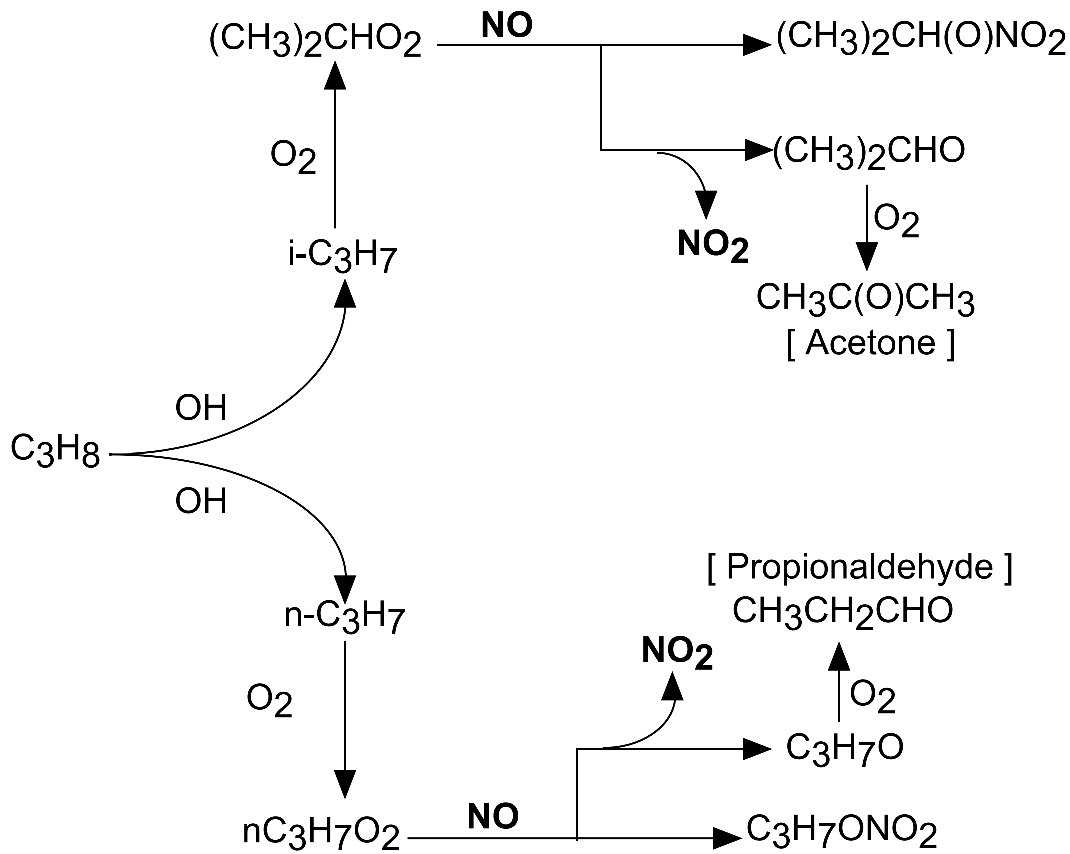
REACTION MECHANISM: NO-C_3H_8

- **The initiating reaction with propane is an abstraction by OH and the resulting radicals then consume O_2 to form the peroxy radicals.**

- **These peroxy radicals then react with NO to convert it to NO_2.**

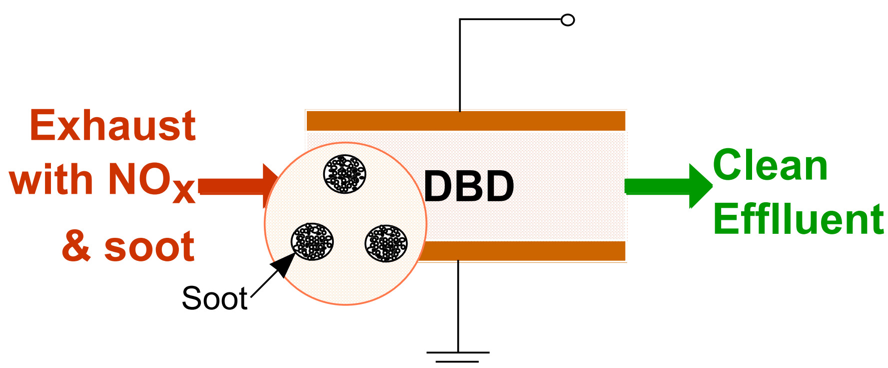


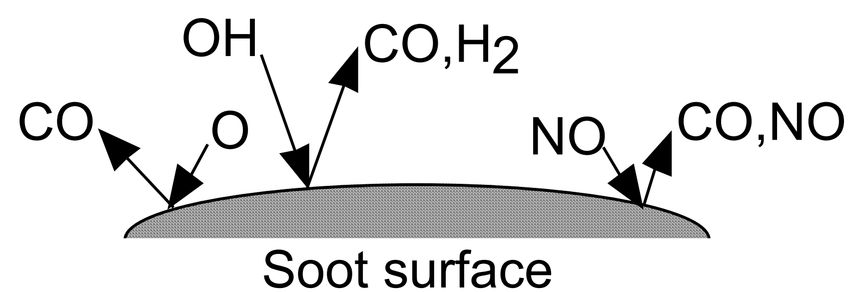
SOOT PARTICLES – EFFECT ON NO_X REMEDIATION

- **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.**

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





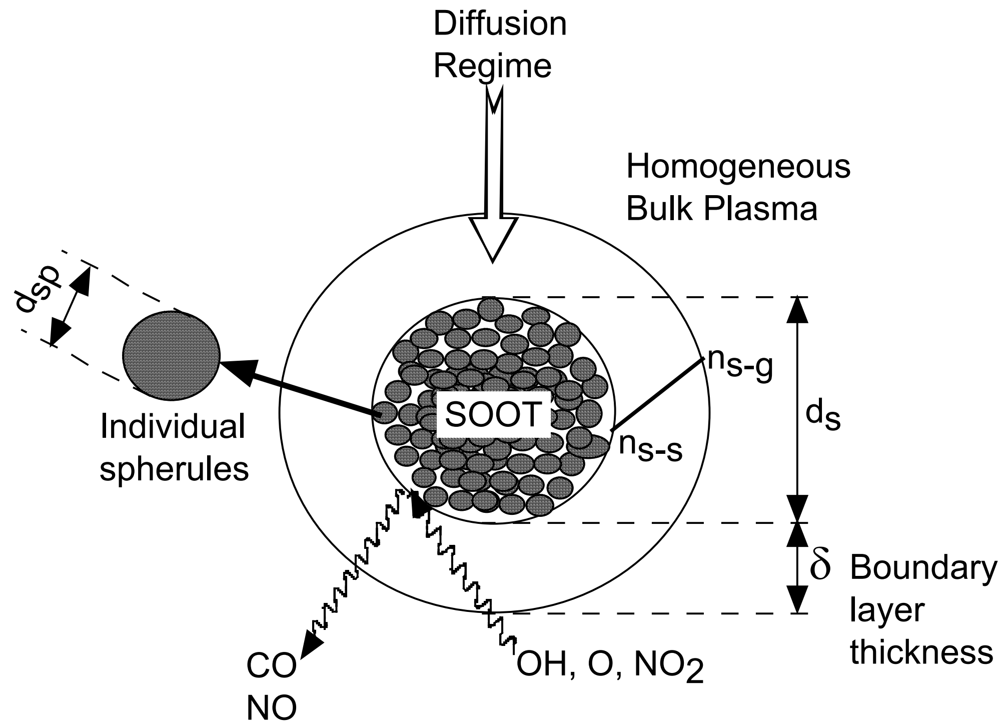
SOOT OXIDATION MODEL

- **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.**

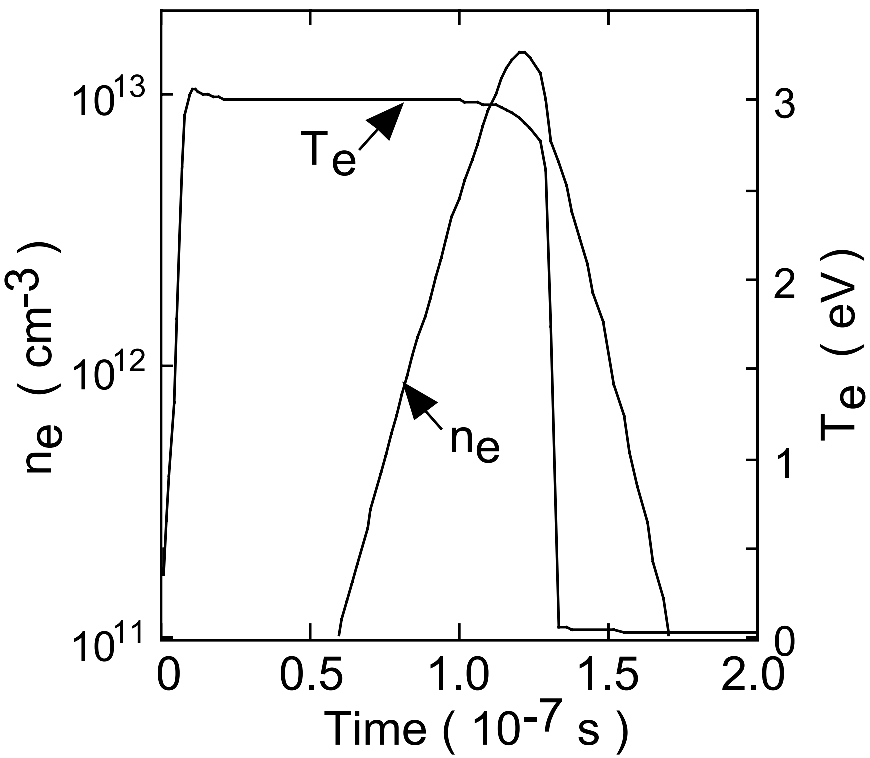
- **Boundary layer thickness, δ, is obtained from the Reynolds number. For low *Re*, $\delta \approx d_s/2$.**

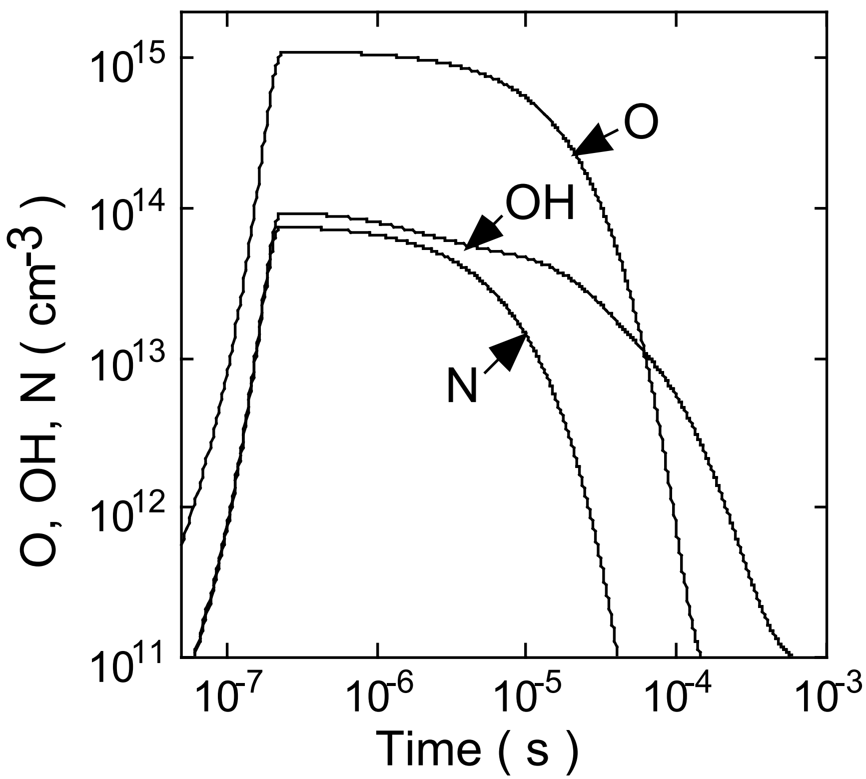
- **The diffusing species have a linear profile in the diffusion regime.**



PLASMA CONDITIONS : n_e, T_e, [N], [OH], [O]

- Peak $n_e \approx 10^{13}$ cm^{-3} and $T_e \approx 3$ eV with $E_{dep} \approx 38$ J/L.
- Electron impact dissociation of N_2, O_2 and H_2O produce N, O and OH respectively.





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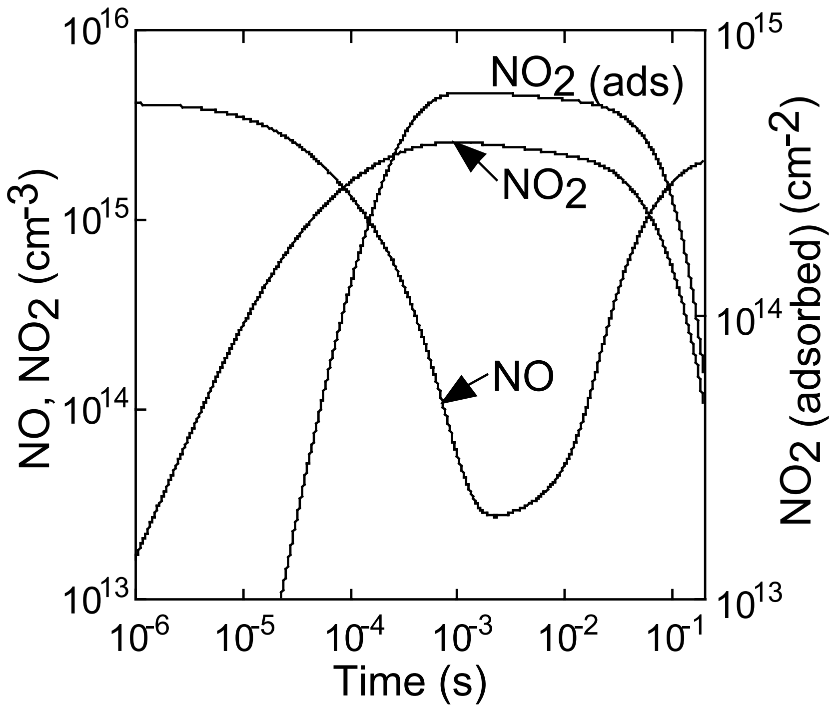
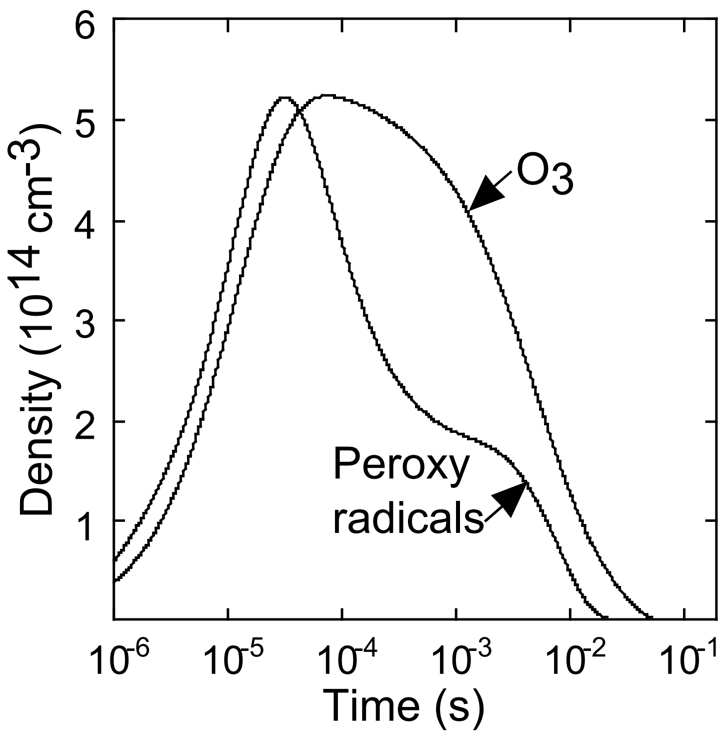
NO_X REMEDIATION : SINGLE PULSE

- **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 $NO_{2(ads)}$.**

$NO + O_3$ (or peroxies) $\rightarrow NO_2 \rightarrow NO_{2(ads)} \rightarrow NO$





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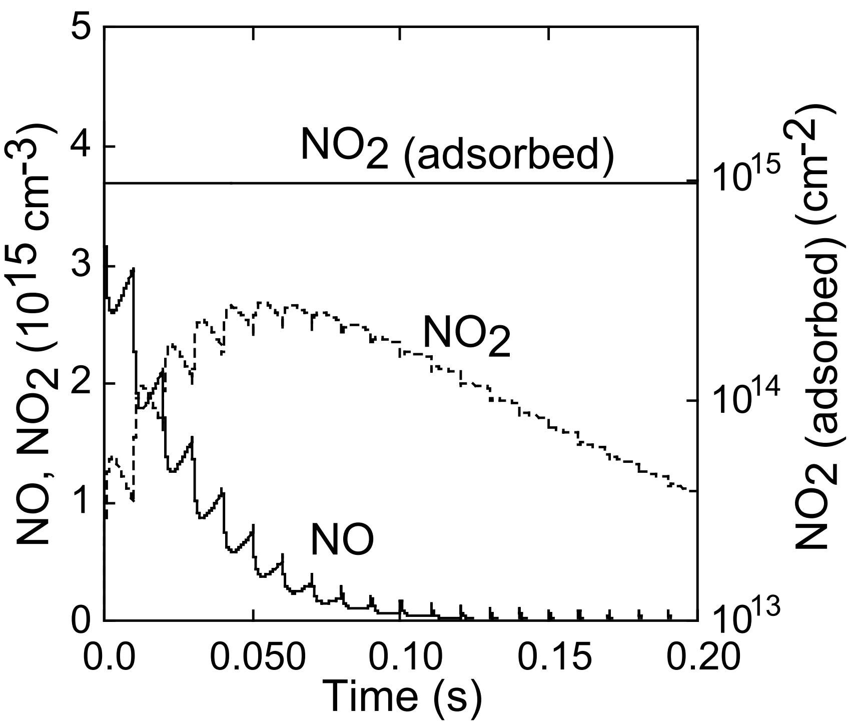
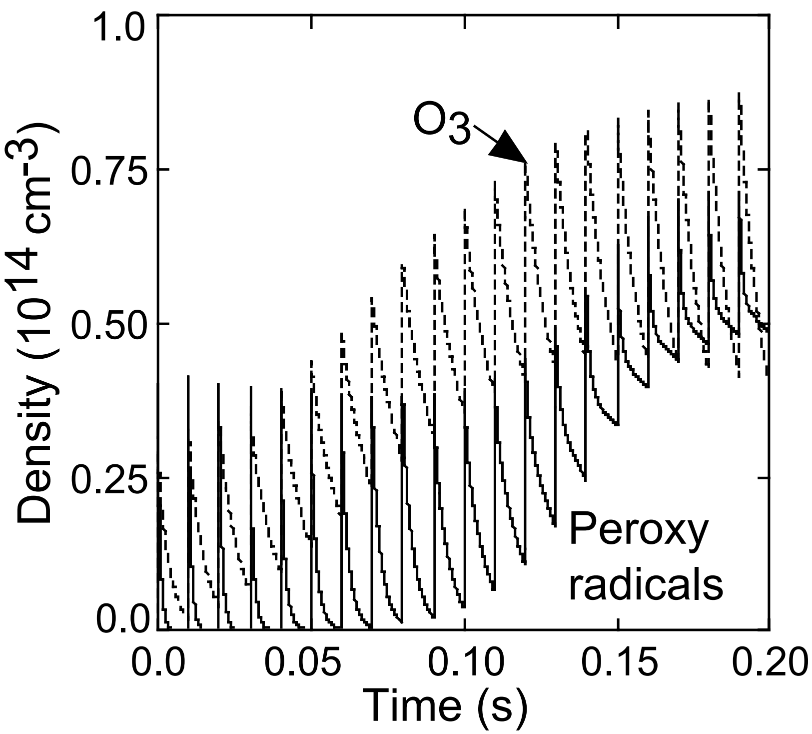
NO_X REMEDIATION : MULTIPLE PULSE

- **With multiple pulses, NO is converted to NO_2 by O_3 and peroxy radicals produced during each pulse.**

$$NO + O_3 \rightarrow NO_2 + O_2$$

- **The rate of adsorption of NO_2 being higher than the rate of desorption, the NO_x remains adsorbed on the surface of soot.**





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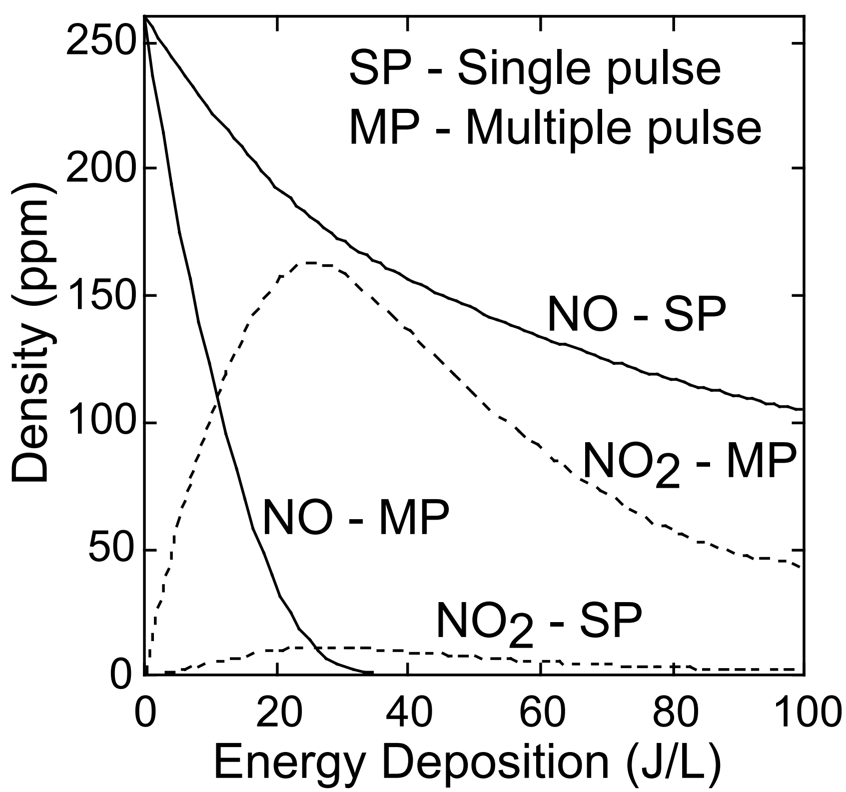
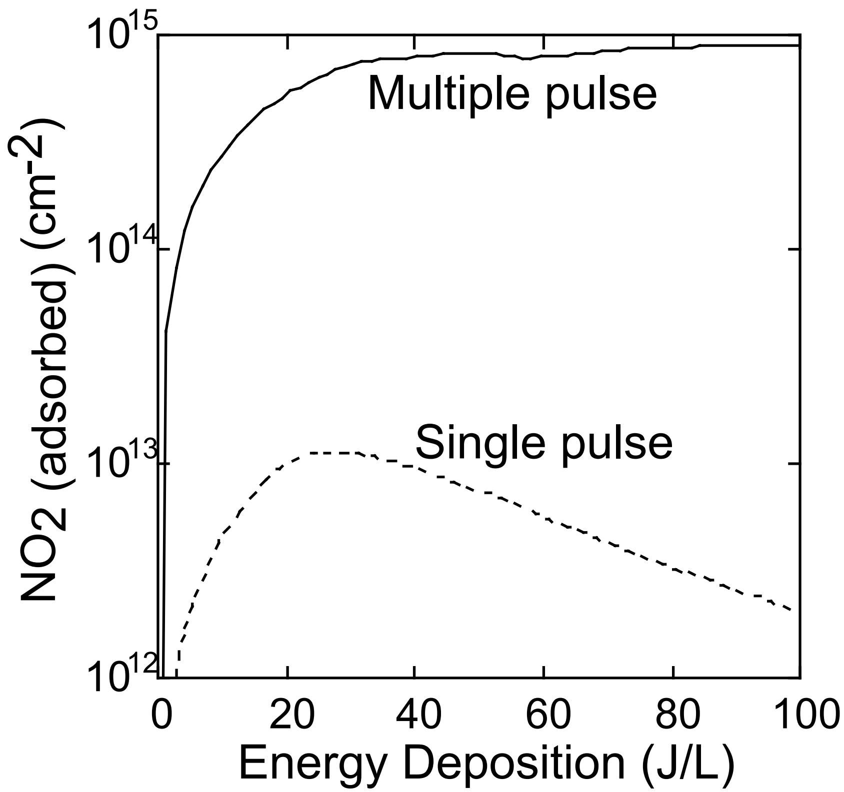
EFFECT OF ENERGY DEPOSITION

- **For a single pulse, exit NO densities are higher. Most of the adsorbed NO_2 desorbs back as NO. This does not happen in the case of multiple pulses because of the shorter interpulse time for NO_2 desorption.**

- **With a single pulse, the peroxy radicals which consume NO are lost by the time NO is regenerated from NO_2 and so, exit NO_x is mainly NO.**





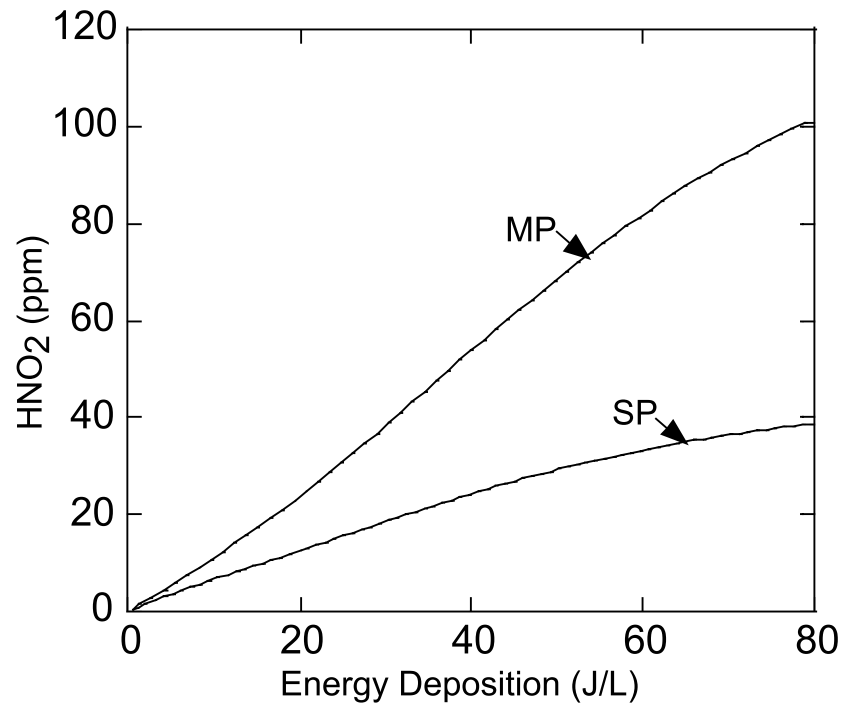
EFFECT OF ENERGY DEPOSITION: HNO_2 – SP vs. MP

- **HNO_2 is produced by the reaction of NO with OH and by HO_2 with NO_2.**

  $$NO + OH + M \rightarrow HNO_2 + M \qquad (1)$$
  $$NO_2 + HO_2 \rightarrow HNO_2 + O_2 \qquad (2)$$

- **With a single pulse, most of the HO_2 is consumed by the time NO_2 is formed and hence HNO_2 is mainly produced by reaction (1).**

- **NO_2 densities are higher with multiple pulses. HO_2 radicals are produced during each pulse. Hence, reaction (2) also contributes to HNO_2 production.**



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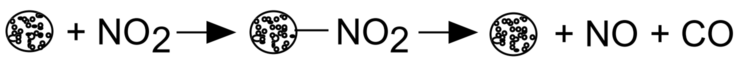
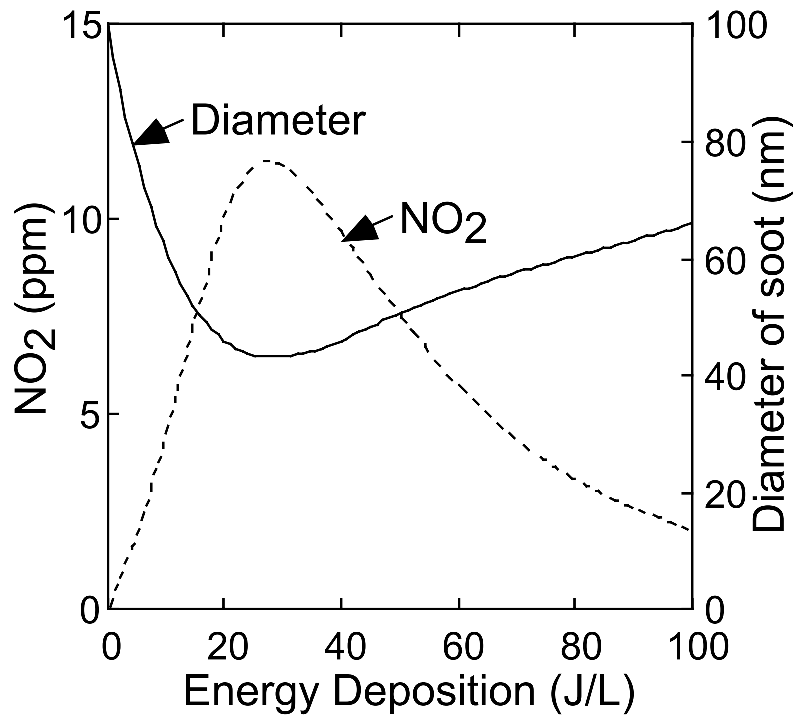
SOOT OXIDATION

- **With increasing energy deposition, the diameter of the soot decreases due to the oxidation by NO_2.**





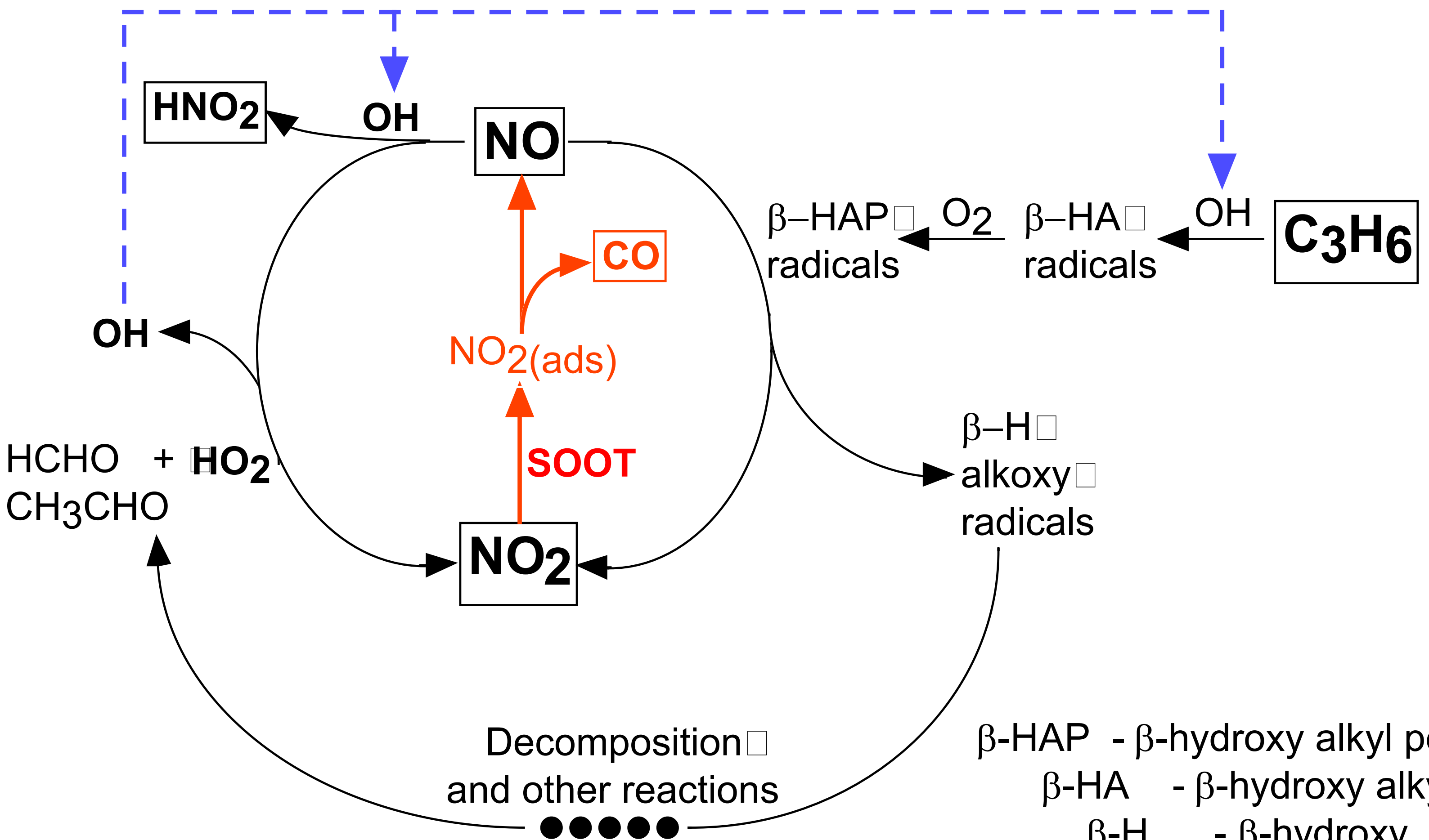
- **At higher energies, the final diameter of soot increases because the density of NO_2 decreases due to the increased conversion to products such as HNO_2, CH_3ONO_2.**

$$NO_2 + HO_2 \rightarrow HNO_2 + O_2$$
$$NO_2 + CH_3O + M \rightarrow CH_3ONO_2 + M$$

- **Note that the oxidation of soot is partial and results in CO and not CO_2.**
  - **CO – poisonous**
  - **CO_2 – greenhouse gas**

MODIFICATION OF PLASMA CHEMISTRY BY SOOT

- **Soot affects the overall plasma chemistry by affecting the densities of OH, HO_2, NO and NO_2.**



β-HAP - β-hydroxy alkyl peroxy
β-HA - β-hydroxy alkyl
β-H - β-hydroxy

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CONCLUDING REMARKS

- **Plasma remediation of NO_x, by itself is not sufficient to completely remove NO_x.**

- **Soot chemistry significantly affects the NO_x composition in plasma remediation of NO_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 *apparent* NO_x removal because of the increased adsorption onto the soot surface.**

- **With single pulse energy deposition, the exit-NO_x is primarily NO because of the reconversion of NO_2 to NO on soot surface.**