EFFECT OF RADIAL TRANSPORT ON THE PLASMA REMEDIATION OF NITROGEN-OXIDES USING DIELECTRIC BARRIER DISCHARGES*

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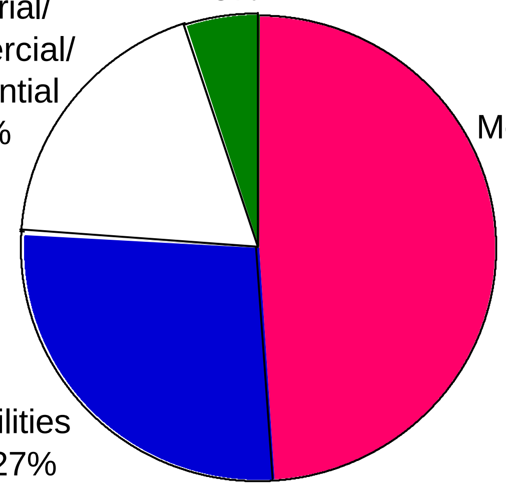
AGENDA

- Introduction
- Description of the model – DBDONED
- Reaction mechanisms - Unburned hydrocarbons (UHCs)
- Results
  - NO_x remediation
  - Effect of UHCs
  - Diffusion
- Concluding remarks

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)

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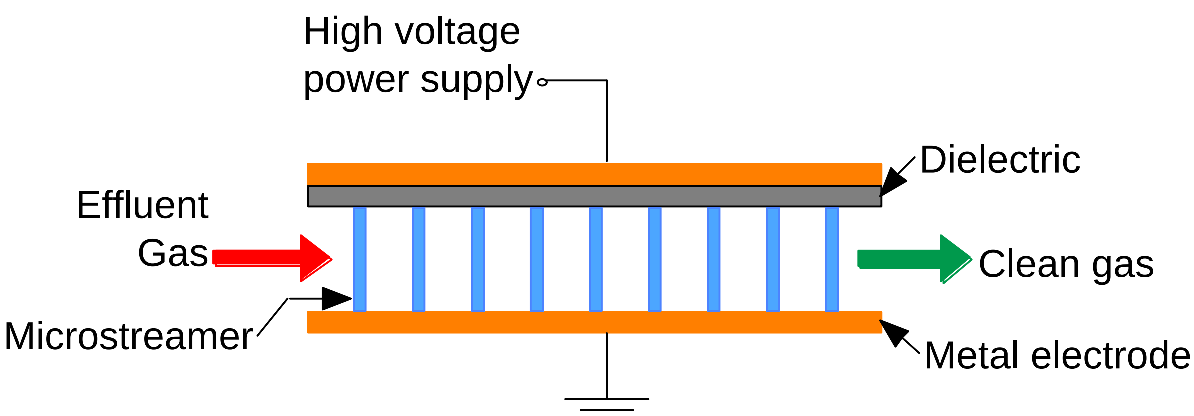
PLASMA REMEDIATION OF NO_X USING DBDs

- **Dielectric barrier discharges (DBDs) are well suited for generation of gas-phase radicals at atmospheric pressure.**

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



e + N_2 ® N + N + e

e + O_2 ® O + O + e

e + H_2O ® OH + H + e

<u>Reduction</u>

NO + N ® N_2 + O

<u>Oxidation</u>

NO + O ® NO_2

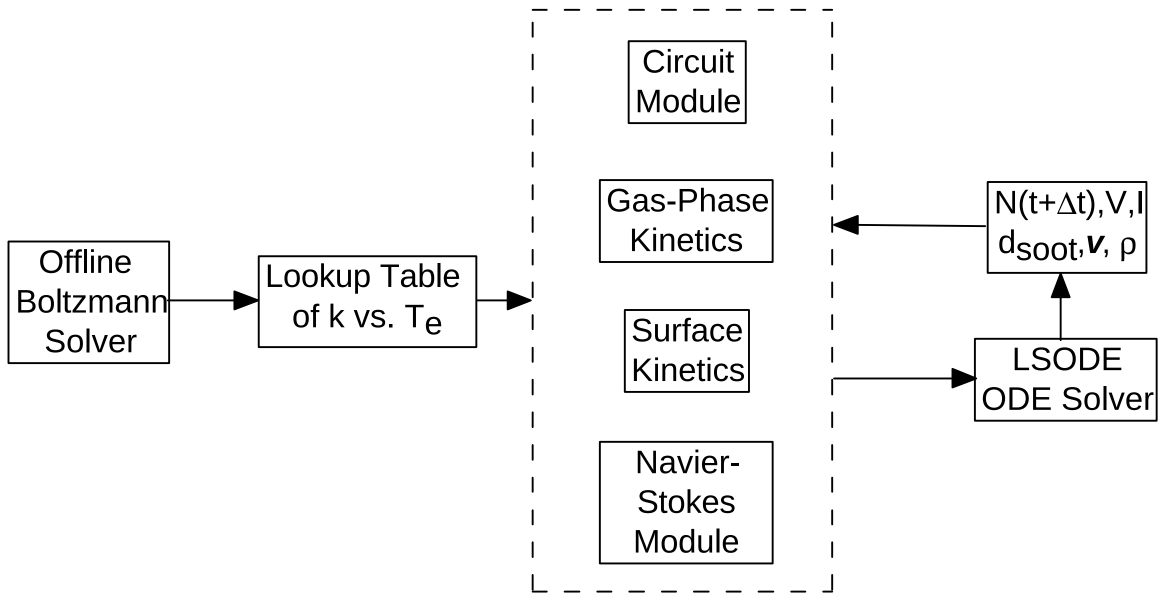
NO_2 + OH ® HNO_3

DESCRIPTION OF THE MODEL - DBDONED

- **In actual microdischarges, inhomogeneities exist and hence, for more realistic investigations, effects of species transport should be included.**

- **DBDONED is a one dimensional (radial) plasma chemistry simulation coupled with hydrodynamics and circuit modules.**

- **To obtain e-impact reaction rate coefficients, the model uses a lookup table generated by an offline Boltzmann solver.**



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 propene (C_3H_6) as representative of the UHCs.

- Previous studies have shown that saturated hydrocarbons (propane) do not contribute significantly to the overall NO_x remediation and hence, they were not included in this investigation.

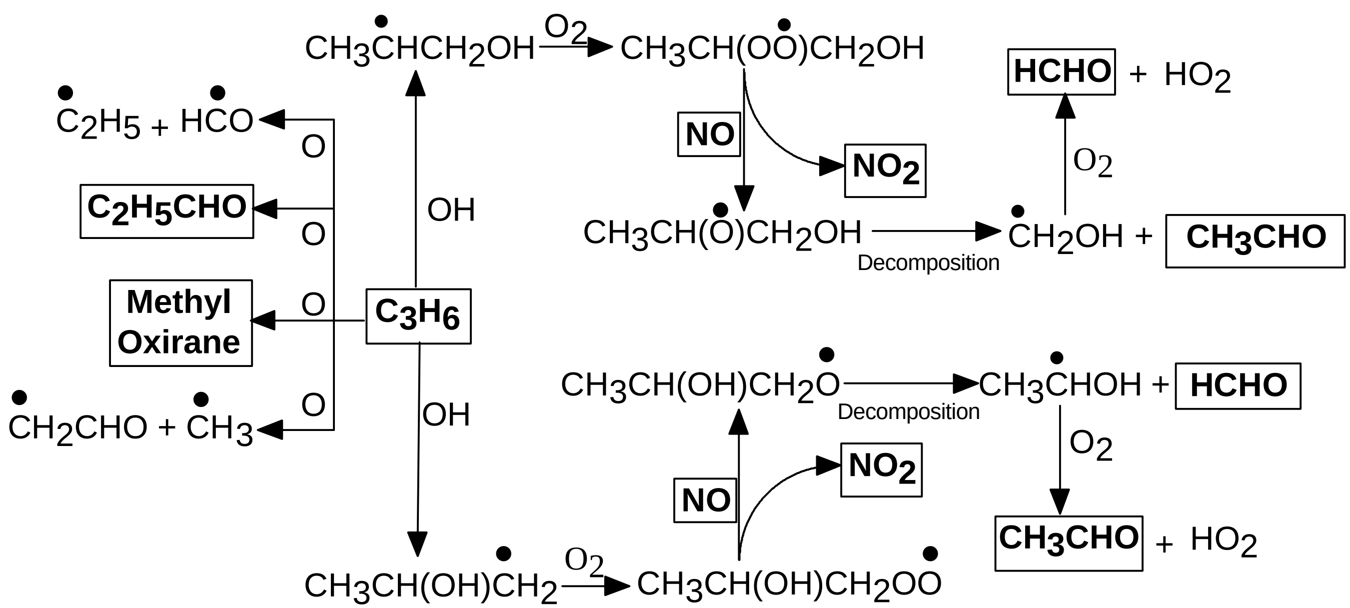
- Inlet gas composition

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

- T=180 ^{o}C, P=1atm
  t = 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.

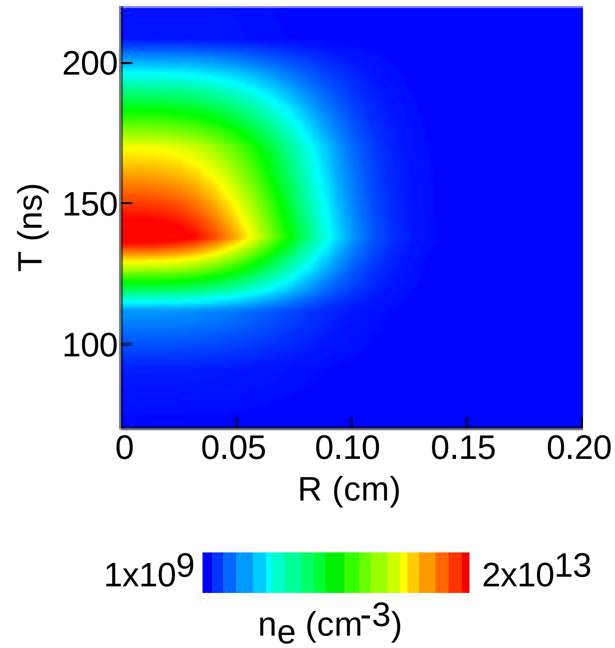


PLASMA PARAMETERS - n_e, T_e

- For these results, only diffusion is taken into account (low energy deposition - 7 J/L).
- The current pulse usually lasts ~ 150 ns.
- Peak values T_e » 3 eV, n_e ~ 10^{13} cm^{-3}.
- Electrons are produced by the ionization of N_2, O_2, CO_2 and H_2O.
- After the current pulse, electrons are mainly lost by reactions with O_2 and H_2O (dissociative attachment).

e + O_2 ® O^- + O

e + H_2O ® H^- + OH



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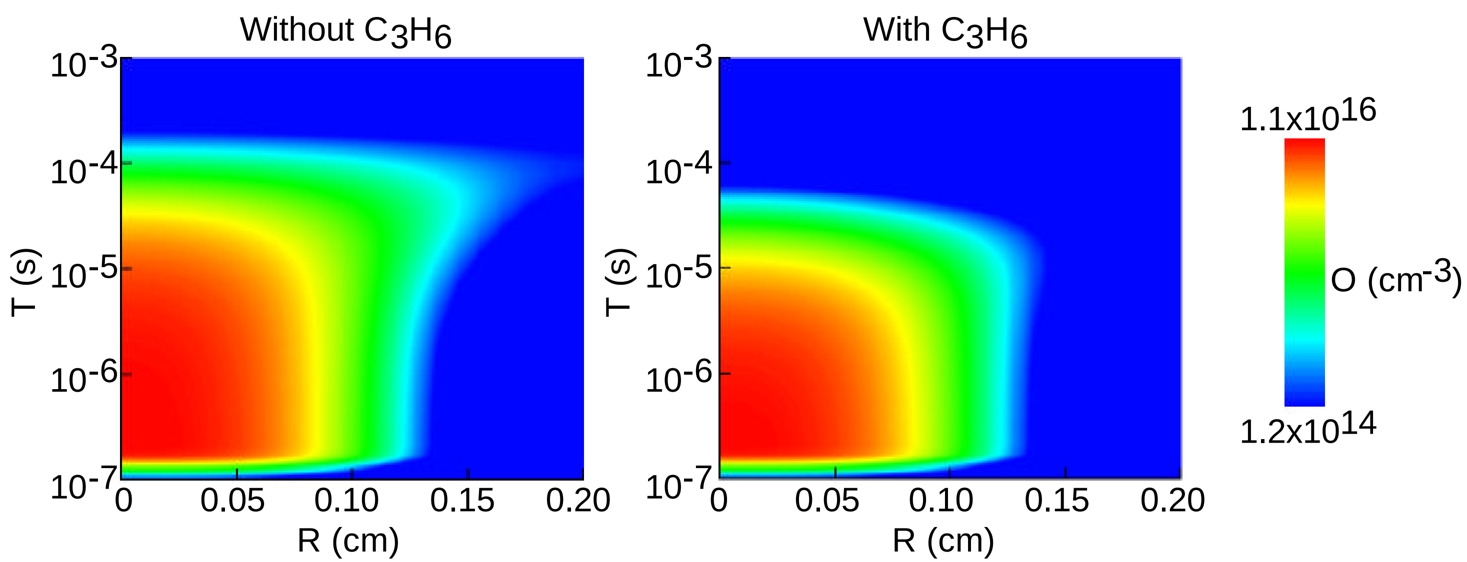
INITIATOR RADICALS - O ATOMS

- **Electron impact dissociation of O_2 and CO_2 produces O.**

e + O_2 ® O + O + e
e + CO_2 ® CO + O + e

- **In the presence of UHCs (propene in this case), O is consumed by reactions with propene and hence diffusion of O is not as prominent as without UHCs.**



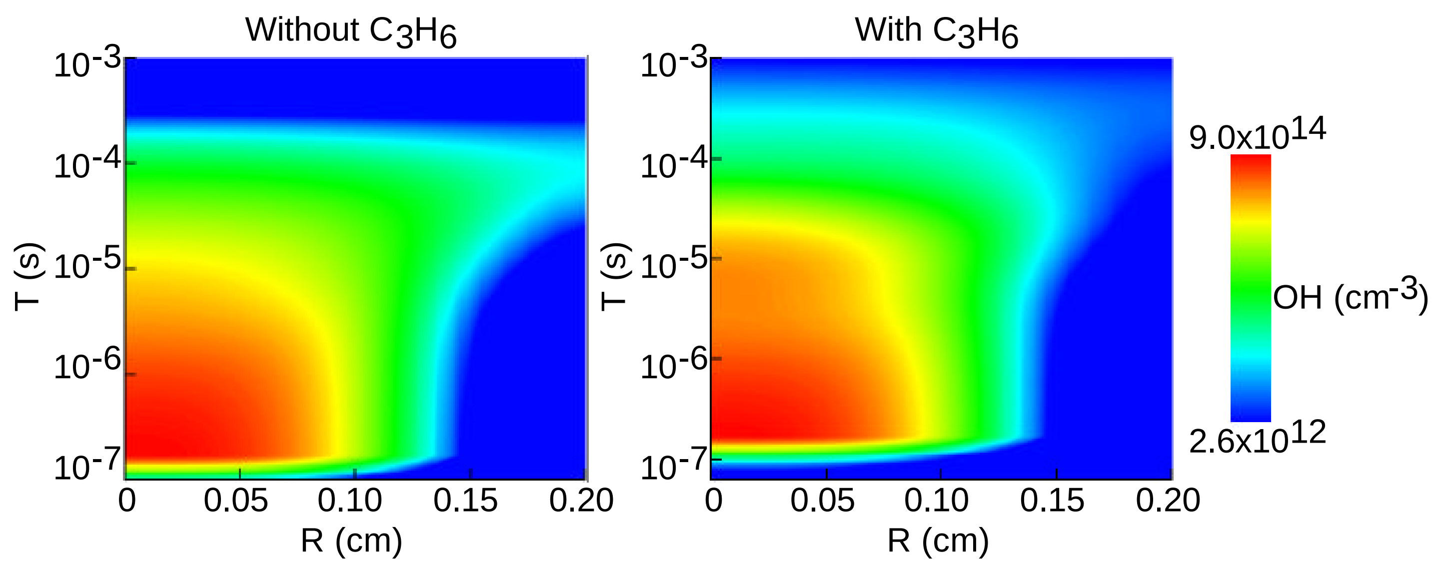
INITIATOR RADICALS - OH

- **Initially (t < 1 ms), OH is produced by the electron impact dissociation of H_2O and at later times, is produced by the reaction of NO with HO_2.**

e + H_2O ® H + OH + e   e + H_2O ® H^- + OH

NO + HO_2 ® NO_2 + OH

- **Since UHC initiated reactions result in the production of HO_2, OH densities are sustained for longer times (t > 0.1 ms).**



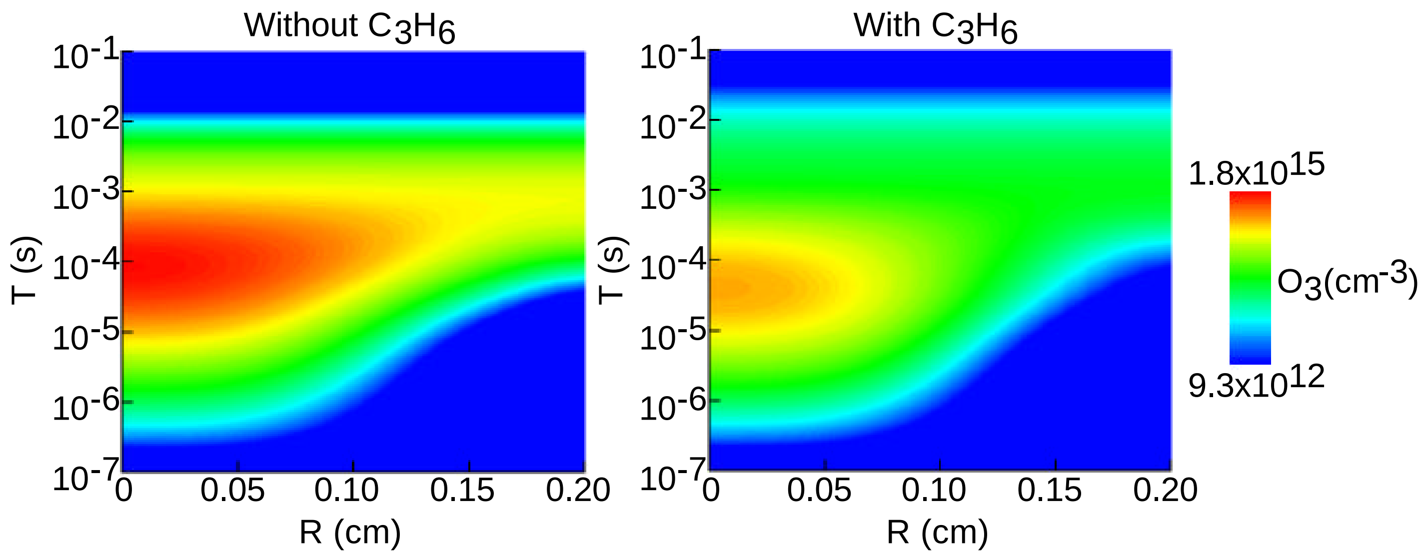
OZONE (O_3)

- **Ozone is produced mainly through the reaction of O with O_2.**

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

- **In the presence of UHCs, lesser O_3 is formed due to the competition from UHCs for the O atoms. O_3 oxidizes NO to NO_2.**

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



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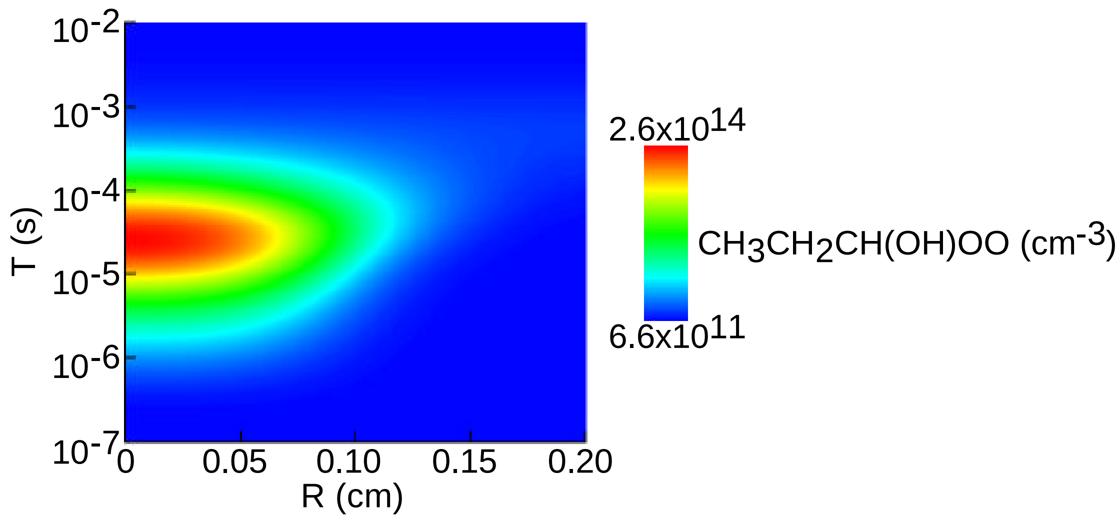
NO OXIDATION BY PEROXY RADICALS

- Peroxy radicals (R-OO) are produced by hydroxy initiated reactions with propene. These radicals oxidize NO to NO_2.

$$R\text{-}OO^{\cdot} + NO \text{ ® } NO_2 + R\text{-}O^{\cdot}$$

- The products of the decomposition of alkoxy radicals ($R\text{-}O^{\cdot}$) then react with O_2 to produced HO_2. This results in the further oxidation of NO.



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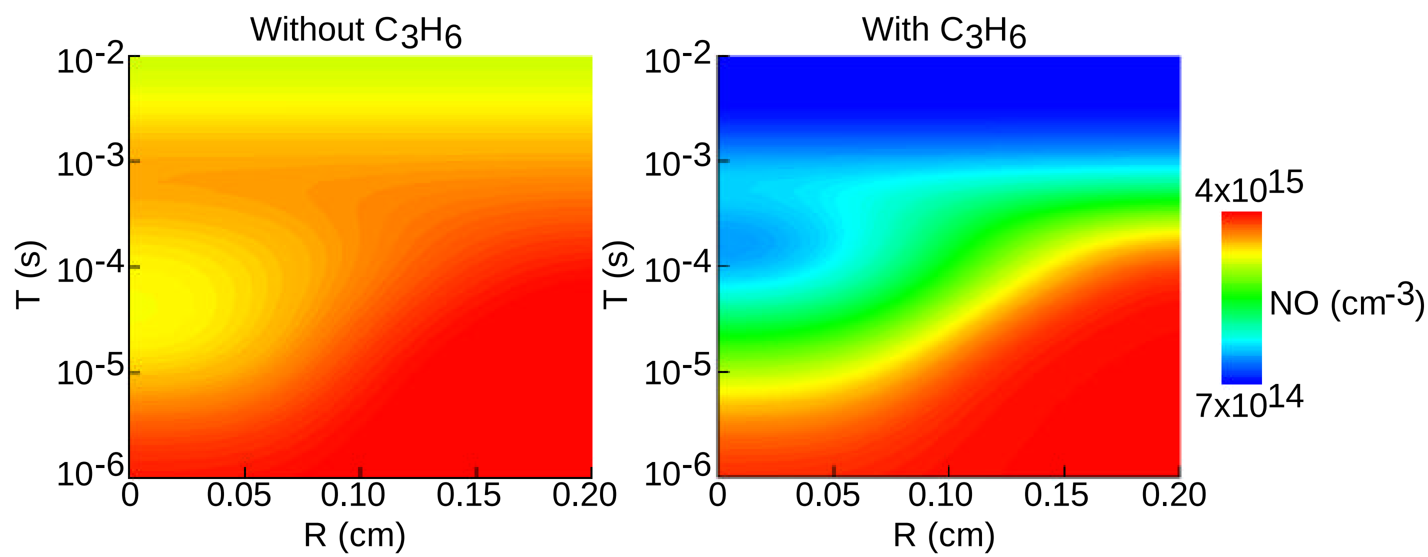
NO DENSITIES: WITH/WITHOUT C_3H_6

- **In the presence of UHCs, NO conversion significantly increases mainly due to oxidation by the peroxy radicals and HO_2. Some NO is also converted into nitrates and nitrites.**

$R\text{-}OO^{\cdot} + NO$ ® $NO_2 + R\text{-}O^{\cdot}$

- **As NO is depleted at small radii of the streamer, diffusion of NO from outer regions replenishes NO, thereby enabling further conversion by radicals.**



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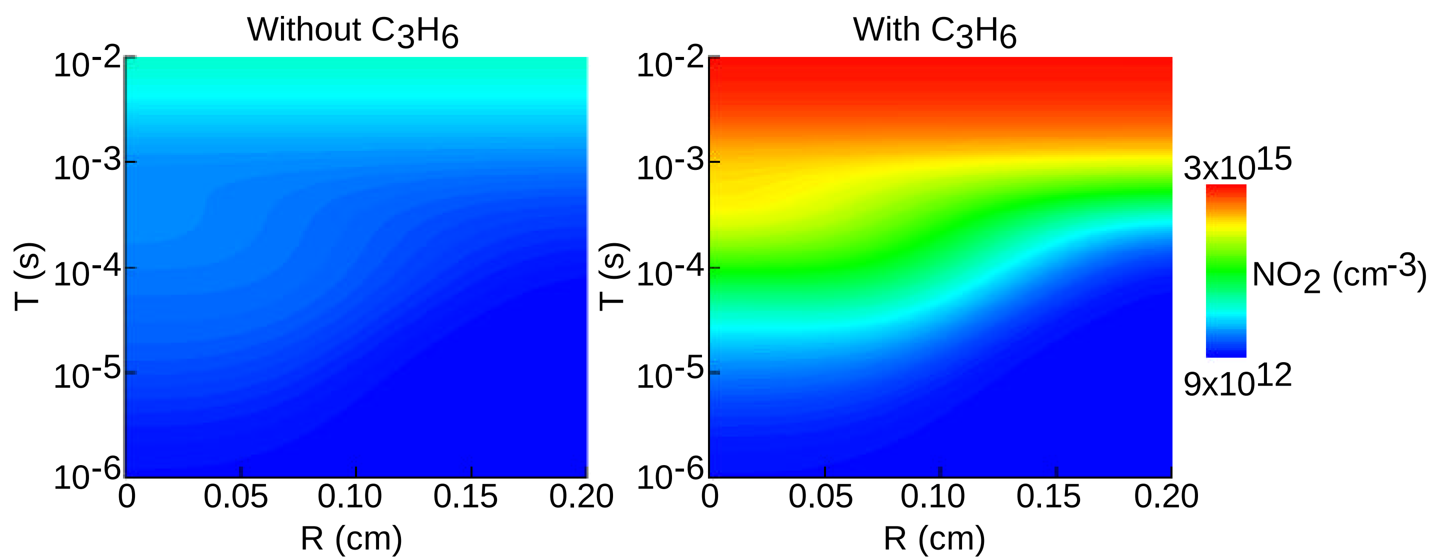
NO_2 DENSITIES: WITH/WITHOUT C_3H_6

- **Since UHCs provide extra reaction channels for the conversion of NO to NO_2, larger densities of NO_2 are achieved.**

- **NO_2 undergoes reactions with HO_2 to from HNO_2 and with OH to form HNO_3.**

$NO_2 + HO_2$ ® $HNO_2 + O_2$
$NO_2 + OH + M$ ® $HNO_3 + M$



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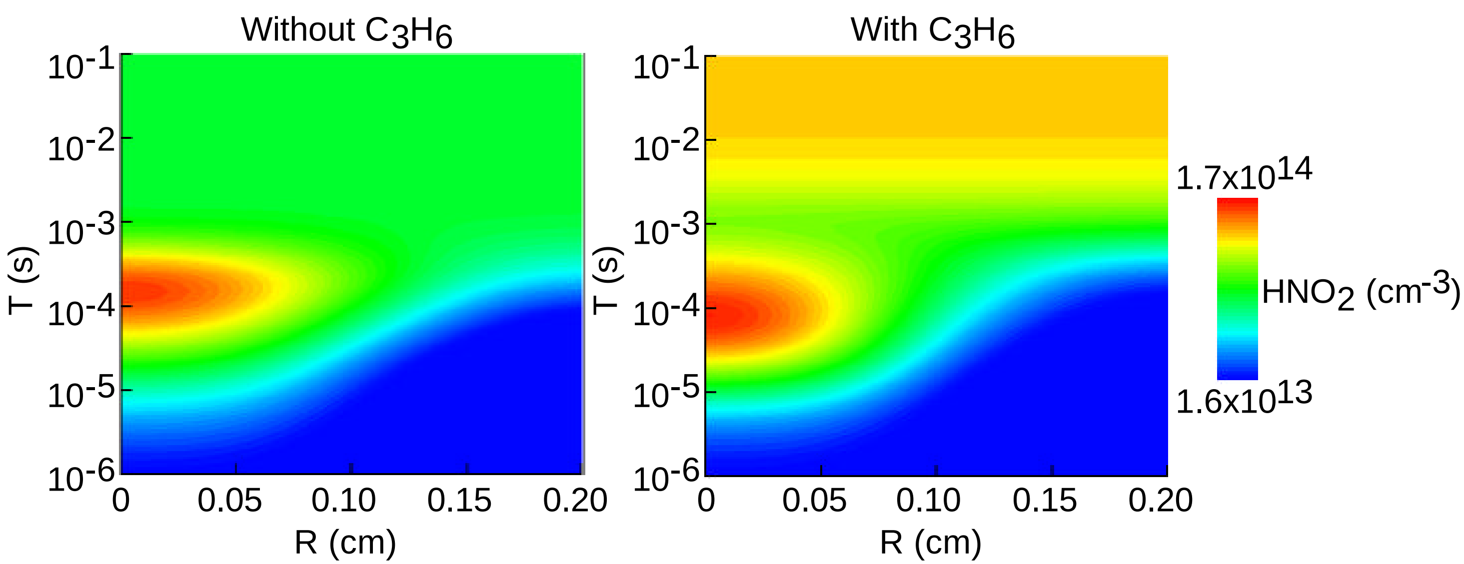
HNO_2

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

NO + OH + M ® HNO_2 + M
NO_2 + HO_2 ® HNO_2 + O_2

- **In the presence of UHCs, more HO_2 is produced as a result of UHC initiated reactions and so more OH is produced. This increases HNO_2 production.**

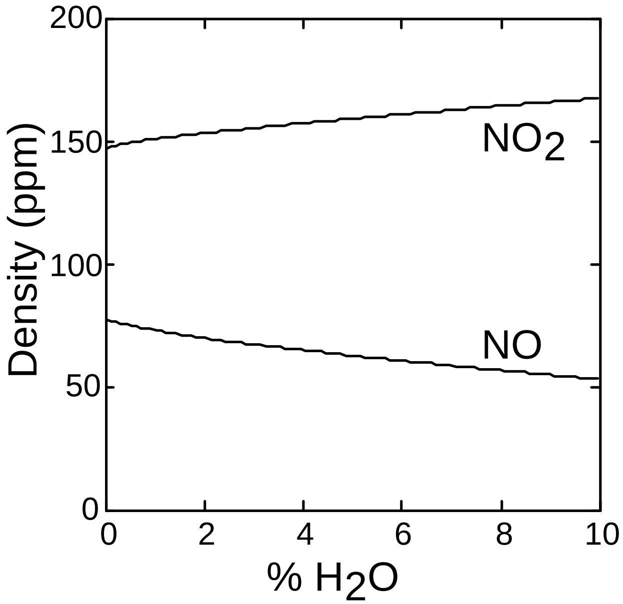


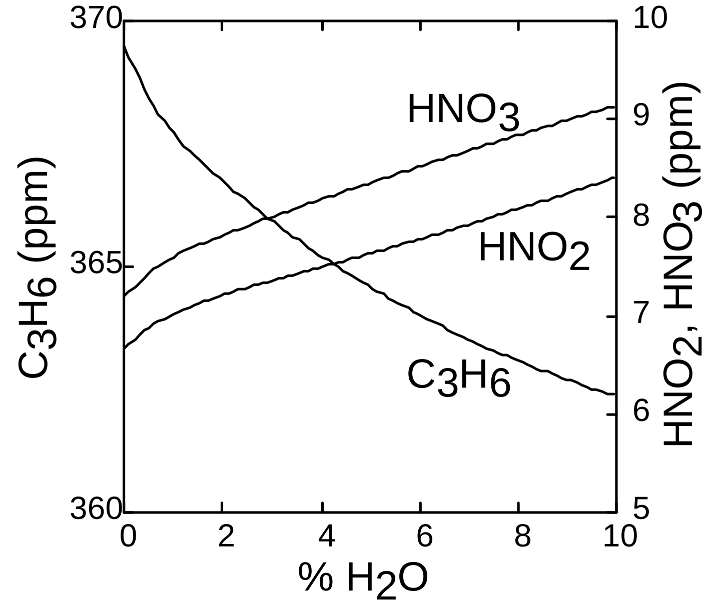
EFFECT OF H_2O ON NO_X REMEDIATION

- **H_2O affects NO_x remediation through the production of OH radicals.**

- **OH radicals not only react with NO directly but also initiate reactions with C_3H_6 which result in the oxidation of NO to NO_2.**

NO + OH + M ® HNO_2 + M
OH + C_3H_6 ® · · · ® peroxies + NO ® NO_2





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CONCLUDING REMARKS

- **A one-dimensional plasma chemistry simulation coupled with diffusion and circuit model has been developed.**

- **NO conversion is increased due to diffusion of NO from unprocessed volumes into the microstreamer and due to the diffusion of radicals from the streamer to outer regions.**

- **C_3H_6 mainly acts as an oxidizing agent for NO (to convert it to NO_2).**

- **The presence of C_3H_6 results in added consumption of O and OH in the microstreamer due to which transport of these radicals to outer regions is reduced.**

- **At higher energy depositions, advection is important and should be considered.**