Application of Non-Thermal Plasma to Diesel Particulate Control.

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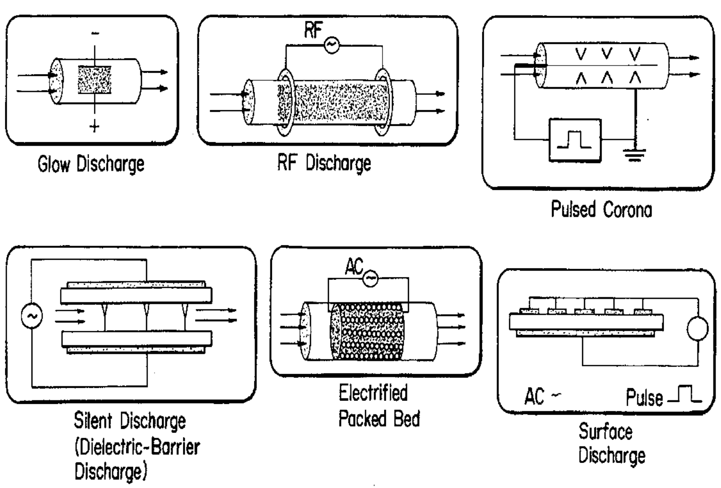
Background

- non-thermal plasma (NTP) has long been considered as a control strategy for noxious emissions,
- current focus is mainly on its application to NO_x abatement,
- does show some promise for PM control

What is a NTP?

- electrons have a much higher kinetic energy (temperature) than the other components of the gas.
  - electron impaction → dissociation
- contrast to a thermal plasma where all components are in thermal equilibrium and have high energy.
  - thermal dissociation

Generating a NTP.



Source: J. Hoard, US Patent 5,746,984, (1998).

Energy density

- Energy Density =
  Electrical Power / flow rate
- Joules/Standard liter (J/L)

Electron impact reactions in a NTP:

$$\boldsymbol{e + O_2 \rightarrow O + O + e,}$$
$$\boldsymbol{e + H_2O \rightarrow OH + H + e.}$$
$$e + N_2 \rightarrow N + N + e,$$

Electron impact reactions in a NTP:

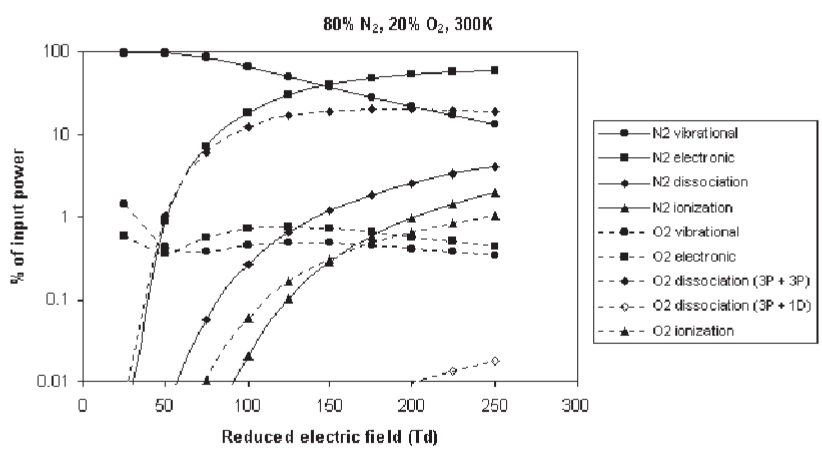
5.12 eV

$$\boldsymbol{e + O_2 \rightarrow O + O + e,}$$
$$\boldsymbol{e + H_2O \rightarrow OH + H + e.}$$
$$e + N_2 \rightarrow N + N + e,$$

3-6 eV

9.67 eV

Power distribution, electrical discharge NTP

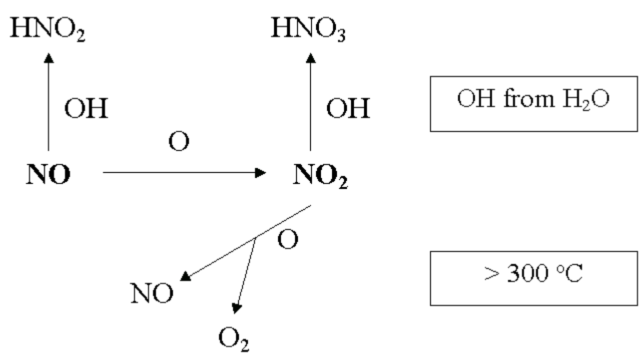


Source: McAdams, J. Phys. D: Appl. Phys. **34**, 2810–2821, (2001)..

Chemical Mechanism

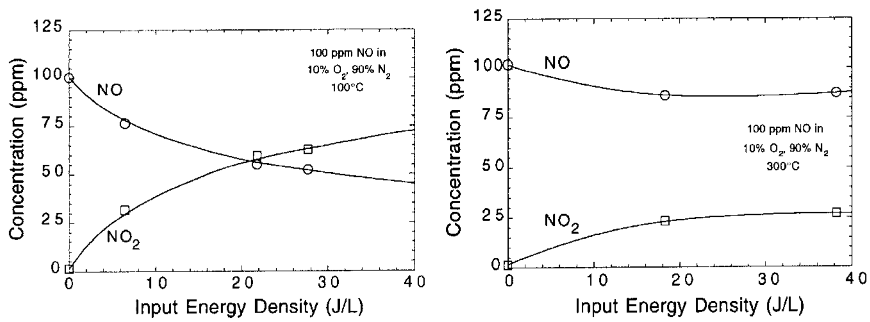
- the understanding of the chemistry in a NTP enhanced exhaust gas is a result of efforts to understand the effect on NO_x.
  1) NO in N_2, O_2 & H_2O
  2) hydrocarbon (propene)
  3) soot

NTP effect of NO in air



Basic conversion of NO to NO_2

Back-conversion of NO to NO_2



$O + NO_2 \rightarrow NO + O_2$

Source: Penetrante *et al.*, US Patent 6,038,854 Mar 21, 2000.

Hydrocarbon effect

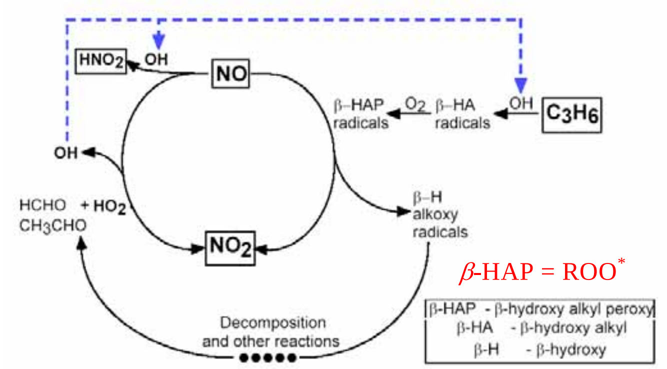
- adding a hydrocarbon (such as propene) has been shown to have a significant effect.

  1) lowers the energy requirement of NO to NO_2 oxidation,

  2) minimizes the formation of acids,

  3) prevents the oxidation of SO_2 to SO_3.

HC enhanced mechanism



$$HO_2 + NO \rightarrow NO_2 + OH$$

$$ROO^* + NO \rightarrow RO^* + NO_2$$

Source: Dorai *et al*. Journal of Applied Physics,. **88**, pp. 6060-6071, (2000).

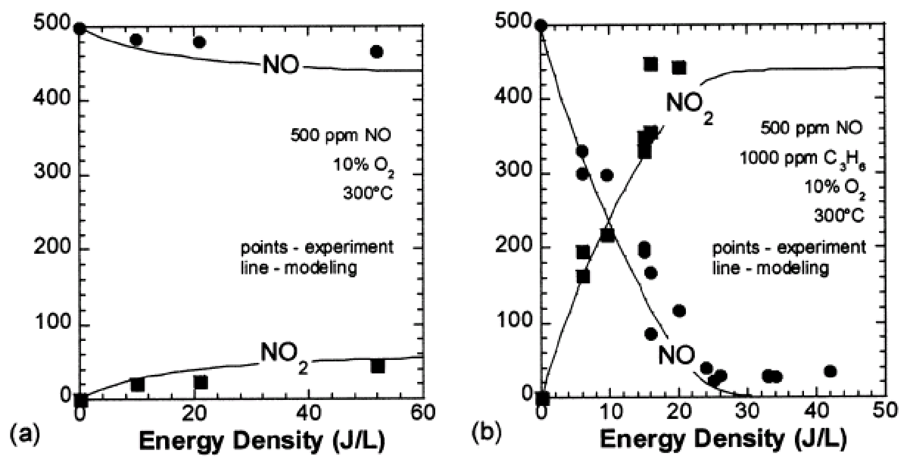


Fig. 1 Plasma processing of: (a) 500 p.p.m. NO in 10% O_2, balance N_2 at 300 °C, and (b) 500 p.p.m. NO, 1000 p.p.m. C_3H_6 in 10% O_2, balance N_2 at 300 °C.

Source: Penetrante *et al.,* Pure Appl. Chem., **71**, pp. 1829-1835, (1999).

Sulfur

- Insensitive to sulfur when hydrocarbon is present
  - the hydrocarbon preferentially consumes O and OH so that oxidation of SO_2 to SO_3 is minimum.

Effect of solid PM (soot)

- process not fully understood
- main effects are:
  - back-conversion of NO_2 to NO and
  - oxidation of soot to CO

Soot reactions

NO_2 is adsorbed on the soot via one of the two following steps:

$(C_xH_y) + NO_2 \rightarrow (C_{x-1}H_y)\text{-C-}NO_2$

$(C_xH_y) + NO_2 \rightarrow (C_{x-1}H_y)\text{-C-ONO}$

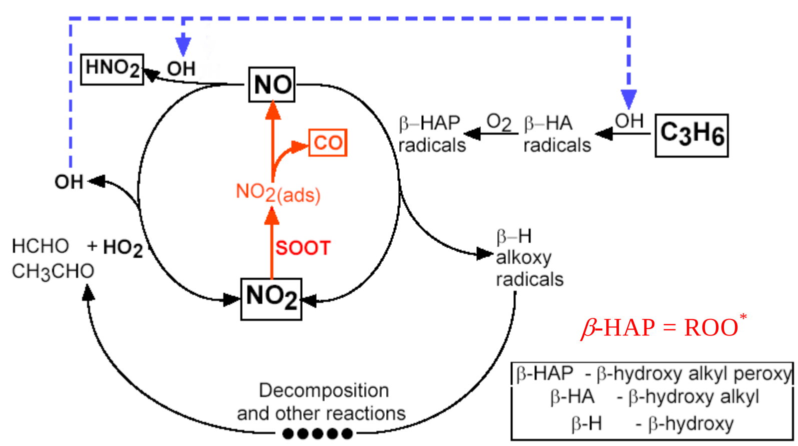
The adsorbates are then reduced to NO and CO.

$(C_{x-1}H_y)\text{-C-}NO_2 \rightarrow (C_{x-1}H_y) + NO + CO$

$(C_{x-1}H_y)\text{-C-ONO} \rightarrow (C_{x-1}H_y) + NO + CO$

Source: Dorai *et al*. Journal of Applied Physics, **88**, pp. 6060-607, (2000).

Summary of overall mechanism



Source: Dorai *et al*. Journal of Applied Physics, **88**, pp. 6060-607, (2000).

Mechanism Summary

- without hydrocarbons, NTP does not provide good conversion of NO to NO_2 at temperatures > 300 ^oC because of back-conversion

Mechanism Summary

- Hydrocarbon serves three purposes in NTP enhanced NO oxidation:
  1) reduces energy requirement - oxidizing peroxy radicals are produced by the reaction
  2) reduces the production of acid - HC preferentially consumes O and OH
  3) reduces the formation of SO_3 - HC preferentially consumes O and OH

Mechanism Summary

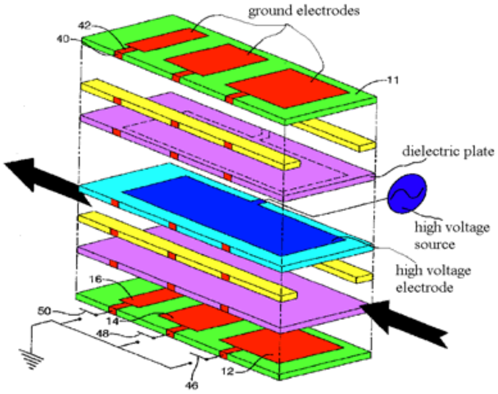
- main effect of soot is the adsorption of NO_2 and
  - its subsequent back-conversion to NO,
  - oxidation of soot to CO.
- may deactivate ROO*?

Practical Applications

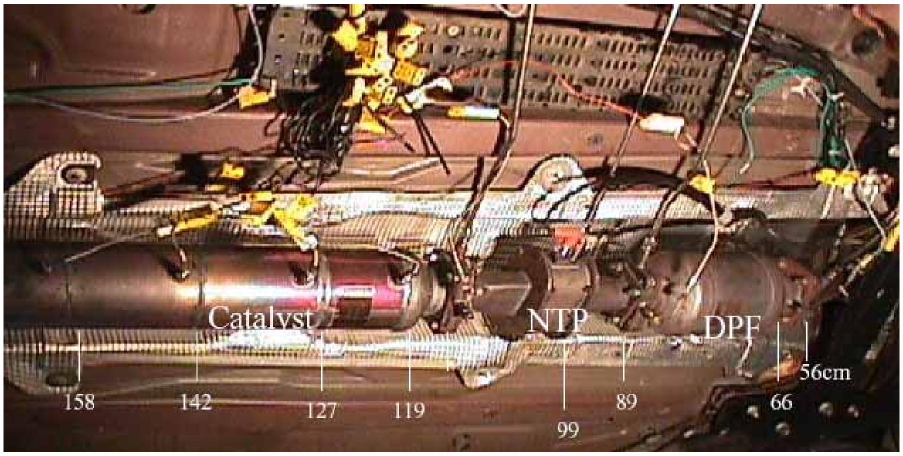
- Several approaches:
  1) electrically charge the particles so they could be collected, e.g. with an oil mist
  2) regeneration of a diesel particulate filter (DPF) by placing it in the exhaust flow upstream of the filter ($NO \rightarrow NO_2$)
  3) place a packed bed reactor in the plasma field (combination of 1 & 2)
  4) generate ionized air for DPF regeneration

DPF regeneration

NO oxidized to NO_2



Source: Hemingway *et al*. US Patent Application 2002/0134666, Sept 26, 2002.



Source: Bonadies *et al*., 8th DEER Conference, San Diego, California, August 25-29, 2002

Performance Summary

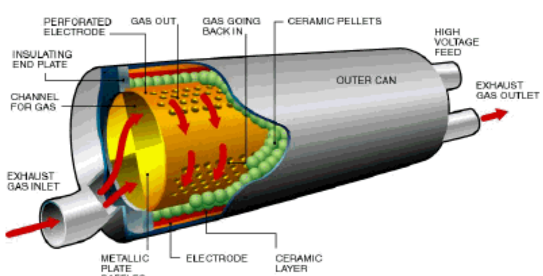
	DPF Regeneration
Power @ Engine Power	600 W @ 17.8 kW (3.4%)
Energy Density	16 J/L
Soot oxidized	6 μg/L *
Specific energy	2.6 MJ/g_{PM} *

* soot loading at 25 hrs

Packed bed reactor

•Ferro-electric beads collect PM

•NO oxidized to NO_2



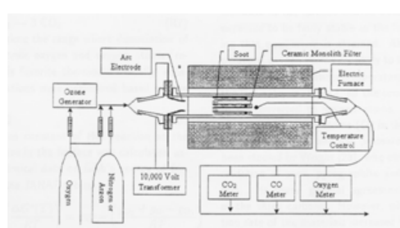
Source: S. Thomas, *et al*., SAE paper 2000-01-1926, (2000).

Performance Summary

	DPF Regeneration	Packed Bed
Power @ Engine Power	600 W @ 17.8 kW (3.4%)	800 W @ 40.6 kW (2.0%)
Energy Density	16 J/L	18 J/L
Soot oxidized	6 μg/L	14 μg/L
Specific energy	2.6 MJ/g_{PM}	1.2 MJ/g_{PM}

DPF regeneration with ionized air

- preliminary study with bench top reactor
- regeneration of uncatalyzed PDF @ 350 ^{o}C
- < 1.7 MJ/g_{PM}
- needs further study to determine its potential



Source: Levendis and Larsen, SAE paper 1999-01-0114, (1999).

Conclusions

- much of the current understanding of NTP relates to its ability to facilitate NO_x reduction,
- electrical discharge NTP formation process is about 10% efficient in an exhaust environment because of the presence of N_2,

Conclusions

- understanding of the chemistry as it relates to NO_x is starting to emerge,
- understanding of the chemistry as it relates to soot still needs attention,
- when HC is present, SO_2 does not oxidize well to SO_3,

Conclusions

- Approaches to practical applications:
  - electrically charge the particles so they could be collected, e.g. with an oil mist
  - regeneration of a diesel particulate filter (DPF) by placing it in the exhaust flow upstream of the filter
  - place a packed bed reactor in the plasma field
  - generate ionized air for DPF regeneration

Conclusions

- Issues that need attention:
  - low efficiency of electrical discharge NTP,
  - limited understanding of the effect of heterogeneous chemical reaction on soot with the gas-phase,
  - The current approach of using the plasma to oxidize NO to NO_2 and then the NO_2 to oxidize soot leads to back-conversion of NO_2 to NO and very little NO_x reduction. Other approaches, such as using ionized air to oxidize soot, need to be examined more closely.