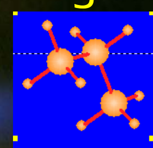
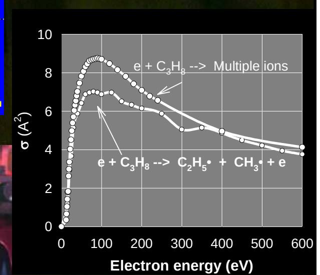
Atmospheric-Pressure, Non-Thermal Plasma Processing

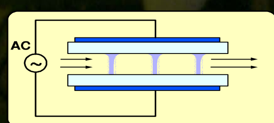
P-24 Summer School Short Course

Louis Rosocha,

Applied Plasma Technologies Team Leader



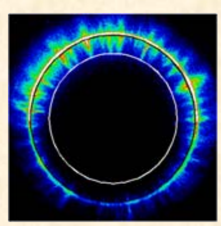




June 24 & 30, 2004

A non-thermal plasma efficiently couples electrical energy into favorable chemistry

- **Thermal plasma**
  - ➢ Equilibrium among electrons, ions, neutrals
  - ➢ Waste heat
- **Non-thermal plasma**
  - ➢ Cool ions & neutrals, but
  - ➢ Energetic electrons (1 ~ 10 eV)



Electron energy of NTP → Favorable chemistry !

Our primary applications of non-thermal plasma processing

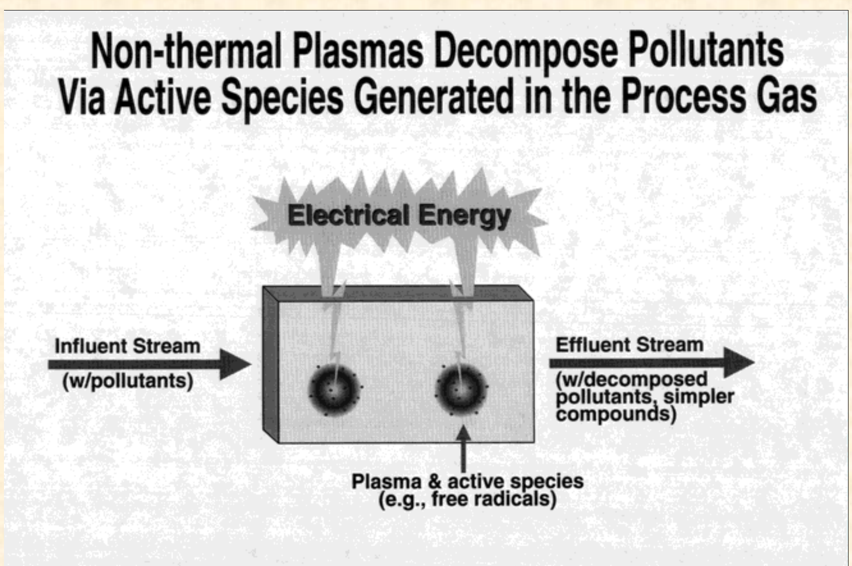
Pollutant/Hazardous Chemical Destruction	Surface Modification or Decontamination
Air pollutants •VOCs •NO_x, SO_x •Odors (H_2S, food processing) **Environmental remediation** •VOCs/haz chemicals in soil or groundwater	**Modification** •Adhesion •Stain resistance •Dye uptake **Decontamination** •Chem/bio warfare agents •Actinides
Combustion enhancement •IC engines (automotive) •Gas turbines •Burners	**Combined systems** •Thermal packed-bed reactor + NTP reactor for haz chem destruction

Atmospheric-pressure non-thermal plasma technology has a history of ~ 150 years

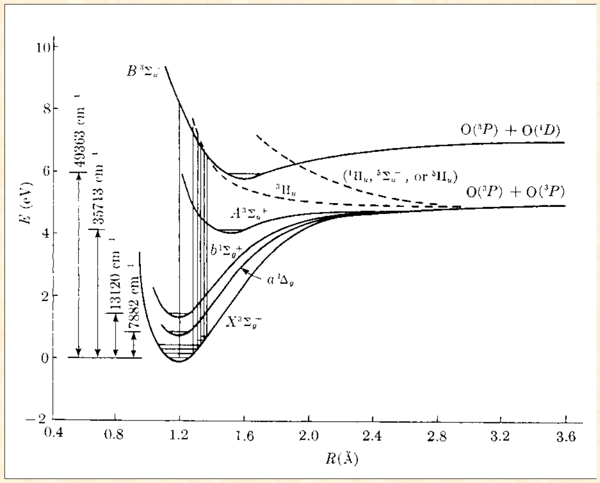
- **1857:** von Siemens invents ozonizer (barrier discharge)
- **1890s:** Lodge invents electrostatic precipitator (corona)
- **1904:** Warburg names "silent discharge"
- **1939:** Glockler & Lind publish "The Electrochemistry of Gases and Other Dielectrics" (plasma synthesis)
- **1943:** Manley develops power measurement technique
- **1970:** Electron beams applied to SOx/NOx removal
- **1970s** Electrical discharges applied to chemical agent destruction for military
- **1980s:** Electron beams applied to VOC removal
  Electrical discharges applied to VOC removal
- **1990s:** Atmospheric pressure plasma jet applied to materials processing & CBW decontamination
- **2000s**: Atmospheric pressure plasma jet applied to actinide decontamination

Advanced oxidation & reduction processes use free radicals to decompose pollutants.

Non-thermal plasmas are a type of AOP making use of "cold combustion" via free-radical reactions.	**Applications** • **Flue gases:** e.g., NO_x & SO_x • **VOCs:** e.g., hydrocarbons & halocarbons • **Odors:** H_2S, others
The key idea is to direct electrical energy into favorable chemistry for oxidizing and/or reducing pollutants to more manageable forms (simpler or mineralized terminal products).	**Potential Advantages** • In-situ generation of chemical reactants • No added fuel (greenhouse gases) • Simultaneous removal of multiple species • Electronic feedback for optimal process control



Molecular Oxygen Potential Energy Diagram



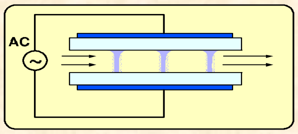
The radical production efficiency (G-value) depends on the gaseous electronics. Radical generation is mainly initiated by energetic-electron collisions.

$$G = f\left(\frac{k_{rad}}{v_d \frac{E}{N}}\right)$$

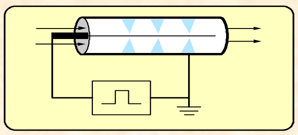
- E/N is the reduced field,
- V_d is the electron drift velocity, which depends on E/N,

k_{rad} is the rate constant for radical formation (e.g., a dissociation rate constant, which depends on E/N), and/or other rate constants.

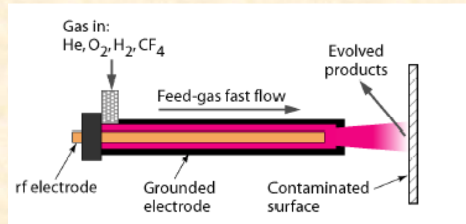
We mainly employ four types of NTP reactors



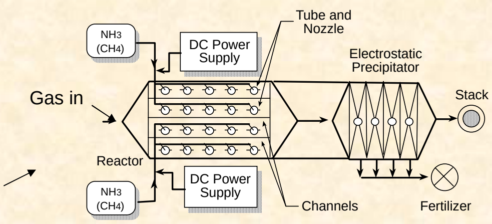
Silent discharge
(dielectric-barrier discharge)



Pulsed or DC corona



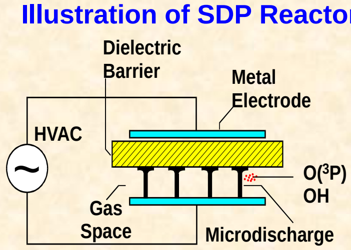
Atmospheric pressure plasma jet



Corona radical shower

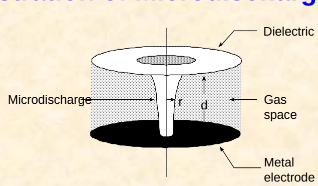
Silent Discharge Plasma (SDP) or Dielectric-Barrier Discharge Fundamentals

Illustration of SDP Reactor



- Dielectric-Barrier Discharge (DBD) inventen by W. von Siemens in 1857
- Referred to as Silent Electrical Discharge by Andrews & Tait, 1860
- Used for over 150 years to produce ozone
- Is a non-thermal plasma (electrons are 'hot', while ions & neutrals are 'cold")

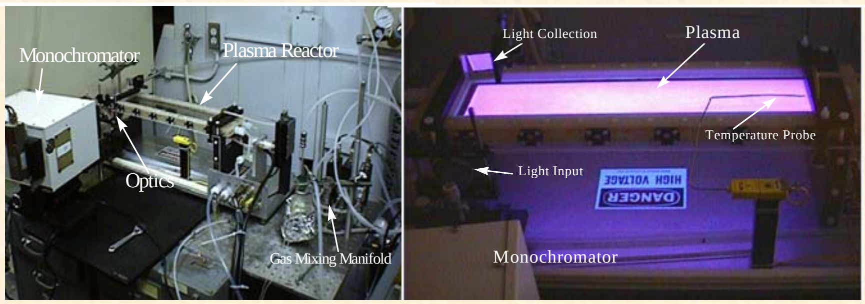
Illustration of Microdischarge



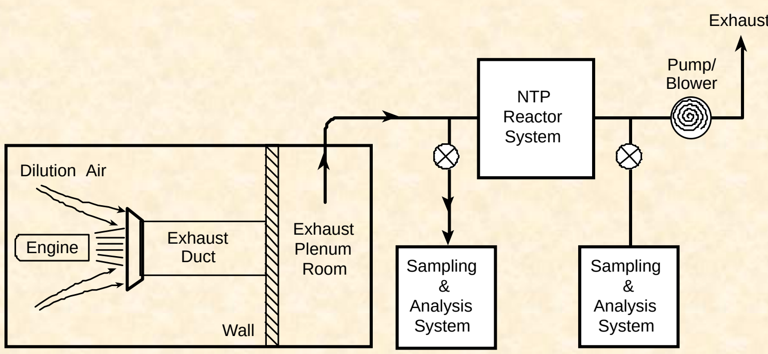
Microdischarge Properties

Parameter	Symbol	Typical value
Channel radius	r	~ 100 µm
Microdischarge duration	t_μ	2-3 ns
Electron density	[e]	~ 10^{14} cm^{-3}
Reduced electric field	E/N	100-200 Td (or 10^{-17} V-cm^2)
Average electron temperature	T_e, D/m	4-5 eV
Current density	J	~ 1 kA/cm^2
Electron drift velocity	v_d	~ 2 x 10^7 cm/sec

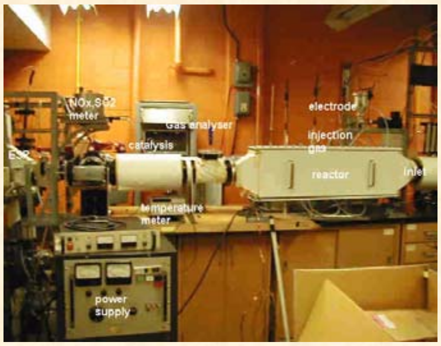
Lab-Scale SDP Reactor Setup

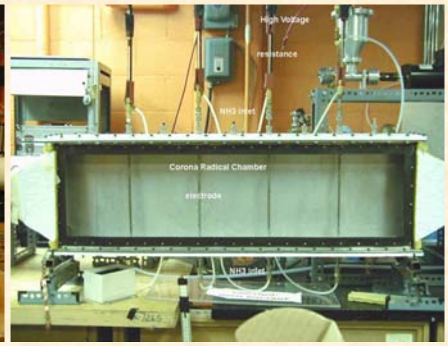


Cruise Missile Engine Test Cell De-NO_x Demo at Tinker AFB Employing CRS System

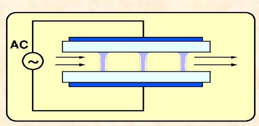


Corona Radical Shower (CRS) Lab-Scale Prototype at McMaster University





Environmental restoration field-pilot demonstration at McClellan AFB



Silent discharge (dielectric-barrier discharge)

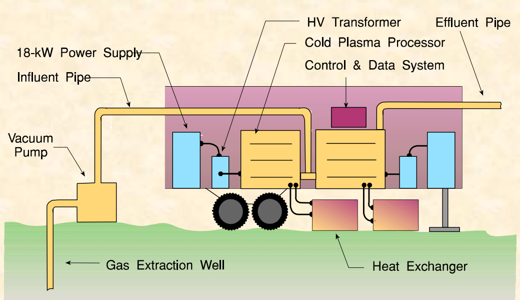
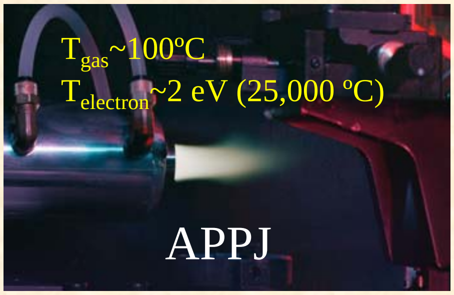
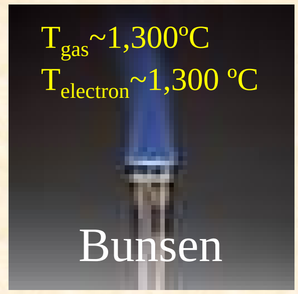


Illustration of mobile dielectric-barrier NTP reactor system employed for VOC decomposition tests at McClellan AFB. Each plasma reactor tank operated at up to 10 kW of plasma power.

CRADAs with the Electric Power Research Institute (EPRI) & High Mesa Technologies (HMT) were an essential part of the development & fielding of this equipment.

The Atmospheric Pressure Plasma Jet: A "Cold flame"





Nonthermal plasma:

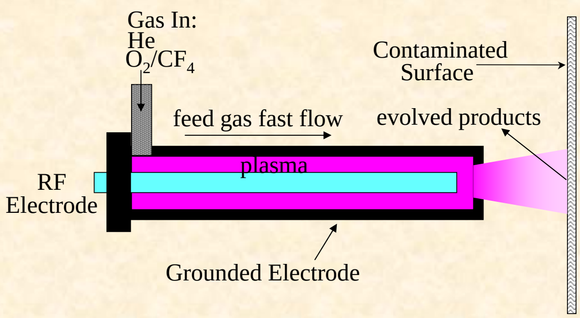
$T_{gas} \sim T_{ion} << T_{electron}$

Thermal plasma:

$T_{gas} \sim T_{ion} \sim T_{electron}$

- Nonthermal operation gives gas temperatures of 50 - 600ºC

Atmospheric Pressure Plasma Jet (APPJ)

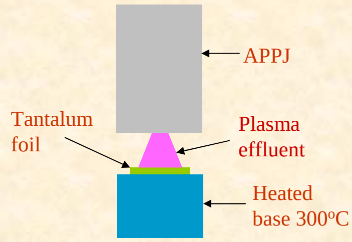


Why He Carrier-Gas?

* Low Breakdown Voltage
⇒ large stable operating window
* Inert
⇒ relatively long reactive species lifetimes
* High Thermal Conductivity
⇒ efficient cooling

- Nonthermal, Uniform-Glow operation requires proper choice of:
  - ⇒ applied EM frequency (e.g. 13.56 MHz)
  - ⇒ electrode geometry (e.g. cylindrical, narrow gap ~ 1.5mm)
  - ⇒ feedgas composition (e.g. 94% He, 2% O_2, 4% CF_4)

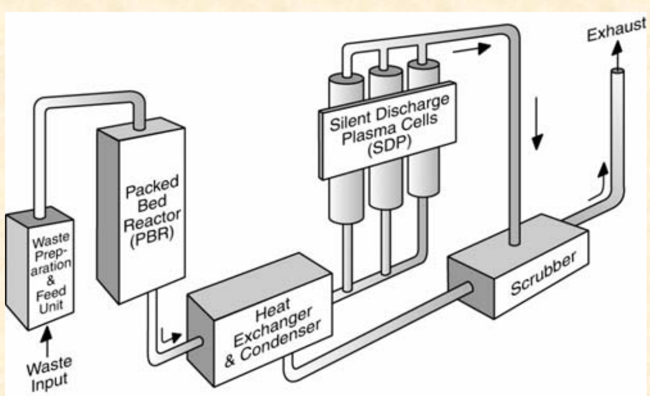
Pu Surrogate Etching Studies



- $Ta(s) + 5F(g) \Rightarrow TaF_5(g)$

- Ta used as surrogate for Pu due to thermodynamic similarities
- Typical etch rates > 10 mg/min over ~ 1.1 cm^2 area
  (equivalent to ~ 5.5 µm/min)

Hybrid PBR/SDP system for specialized LLMW treatment



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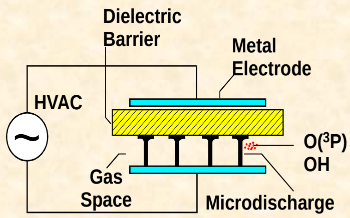

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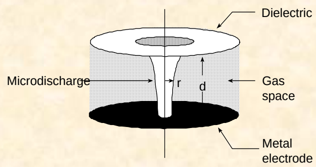
Illustration of Microdischarge



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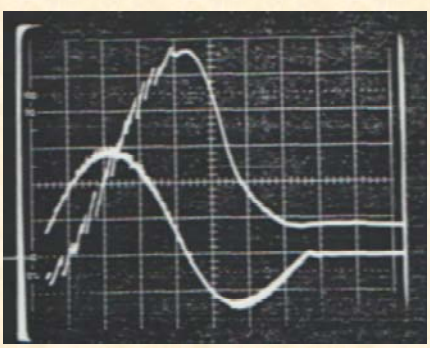
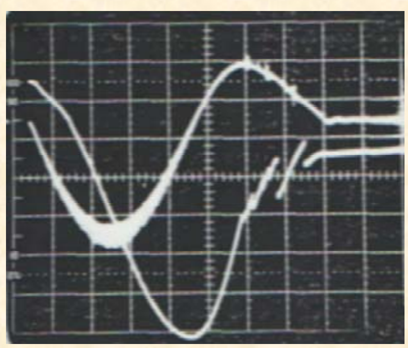
SDP Reactor Current & Voltage Waveforms (Series-Inverter Ozonizer)





Microscopic and macroscopic specific power and energy are expressed in terms of microdischarge properties and operating parameters, respectively

Microscopic

$\overline{P}_\mu = IV / Ad = JN \cdot (E / N)$

$\overline{P}_\mu = q[e]v_d N \cdot (E / N)$

$\overline{E}_\mu = \overline{P}_\mu t_\mu$

Macroscopic

$\overline{P} = P / Ad$

$P_A = P / A$

$\overline{E} = \overline{P}\tau_r = P / Q$

Typical values:

$\overline{P}_\mu$ = 8.6 MW/cm^3

$\overline{E}_\mu$ = 26 mJ/cm^3

P_A = 0.3 W/cm^2

$\overline{P}$ = 1 W/cm^3

$\overline{E}$ = 0.9 J/cm^3 (900 J/lit) ,

For O_2 gas at normal density, a reduced field E/N of 100 Td, an applied power P of 300 W, a cell volume of 300 cm^3, and a flow rate Q of 20 lit/min.

Microdischarge number and area density depend on microscopic and macroscopic discharge parameters

Energy balance: $\dfrac{1/2\,\overline{P}T}{Ad} = n_{1/2}\overline{E}_\mu ad$

Half-cycle discharge number:

$$n_{1/2} = \frac{\overline{P}T}{2\overline{E}_\mu} \cdot \frac{A}{d}$$

Discharge area density:

$$\sigma = \frac{n_{1/2}}{A} = \frac{\overline{P}T}{2\overline{E}_\mu a}$$

Example:

A = 1,000 cm^2 ; r = 100 µm

$\overline{P}$ = 1 W/cm^3

T = 1 ms (f = 1 kHz)

$\overline{E}_\mu$ = 26 mJ/cm^3

$n_{1/2}$ = 62 x 10^3

σ = 62 cm^{-2}

The accumulated microdischarge volume can exceed the reactor active volume

Total number of microdischarges in residence time τ_r***:***

$$N_\mu = 2n_{1/2} \cdot \frac{\tau_r}{T} = 2n_{1/2} f \tau_r$$

Cumulative treated volume ratio:

$$R = \frac{\pi r^2 d N_\mu}{Ad} = \frac{\pi r^2 N_\mu}{A} = \frac{2n_{1/2} f \tau_r}{A}$$

Using parameters from previous example and $\tau_r = 1$ ***sec***

$N_\mu = 1.23 \times 10^8$ and $R = 39$.

Plasma Chemistry, Kinetics & Electron-Ion Energies

Generalized kinetic equations:

$aA + bB + \ldots \rightarrow pP + qQ + \ldots$

$d[A]/dt = -k[A]^a[B]^b \ldots$

Electron-energy-dependent rate constants are derived from the distribution function:

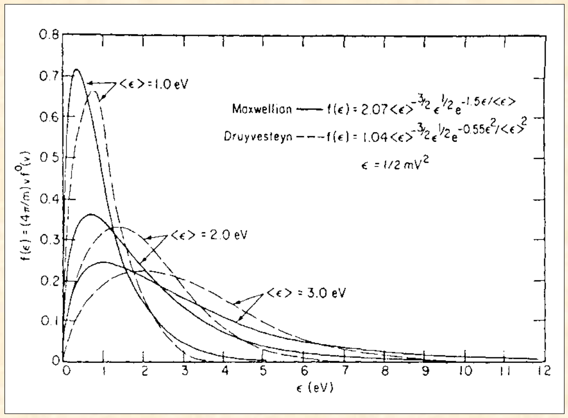
$k_j = \int_0^\infty \sigma_j(\varepsilon)\,(\varepsilon/2m)^{1/2} f(\varepsilon)\,d\varepsilon$, j^{th} process

Maxwellian	**Druyvesteyn**
$f(\varepsilon) = 2.07 <\varepsilon>^{-3/2} \varepsilon^{1/2} \exp(-1.50\, \varepsilon/<\varepsilon>)$	$f(\varepsilon) = 1.04 <\varepsilon>^{-3/2} \varepsilon^{1/2} \exp(-0.55\, \varepsilon^2/<\varepsilon>^2)$

Ion energies are derived from Wannier's relationship:

$\varepsilon_i = 3/2\, KT_i = 1/2\,(m_i + M)\, v_i^2 + 3/2\, KT_g$

Comparison of Maxwellian and Druyvesteyn Distribution Functions



Plasma Chemistry Example: Ozone Synthesis

$e + O_2 \rightarrow 2\,O + e$ $\quad$ **k_1** $= f(T_e)$

$O + 2\,O_2 \rightarrow O_3 + O_2$ $\quad$ **k_2** $= 3.03e\text{-}34\ (T/298)^{-1.36}\ e^{+204\ K/T}$

$O + O_3 \rightarrow 2\,O_2$ $\quad$ **k_3** $= 9.2e\text{-}12\ (T/298)^{0.18}\ e^{-2038\ K/T}$

$d[O]/dt = 2k_1[e][O_2]$

$d[O_3]/dt = k_2[O][O_2]^2 - k_3[O][O_3]$

$d[O_3]/dt\big|_{ss} = 0 \quad \Rightarrow k_2[O][O_2]^2 = k_3[O][O_3]_{ss}$

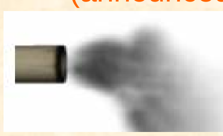
$\Rightarrow [O_3]_{ss} = (k_2/k_3)[O_2]^2$

Motivation for Plasma Combustion Enhancement Research

Prime driver: Path to US energy independence

Specific Issues:

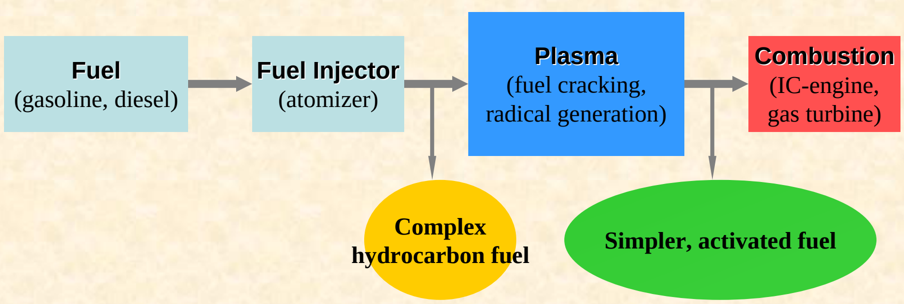
- Internal-combustion & gas-turbine engine efficiency & emissions
- Cost of gasoline (~ $2/gal ! now)
- NO_x/SO_x regulations
  (announced May 2004, in effect 2007)



Fuel- lean burn operation

Main problem with lean-burn operation is combustion stability & energy output.

Novel solution: fuel activation/conversion



Fuel cracking and radical/active-species generation by plasma can promote combustion reactions and efficiency.

Process understanding → Fundamental science → LDRD

Technology development → applications → CRADAs

Basic Plasma Chemistry/Gaseous Electronics of Plasma-Assisted Combustion

Free Radical Generation via Plasma

$e + C_3H_8 \rightarrow C_3H_7\bullet + H\bullet + e$
$e + C_3H_8 \rightarrow C_2H_5\bullet + CH_3\bullet + e$
$e + C_3H_8 \rightarrow 2CH_3\bullet + CH_2: + e$

Other Potential Mechanisms

- Electronic and/or vibrational-rotational excitation
- Ion-molecule reactions

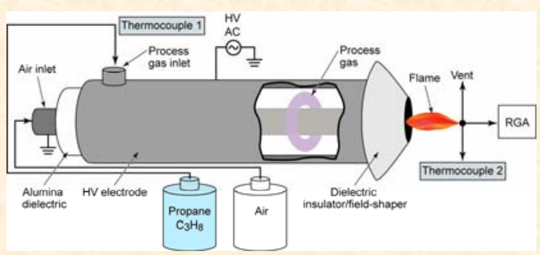
Dissociative Ionization/'Cracking'

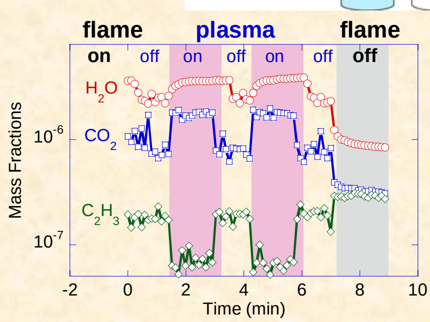
(assuming ion fragments lead to dissociated propane)

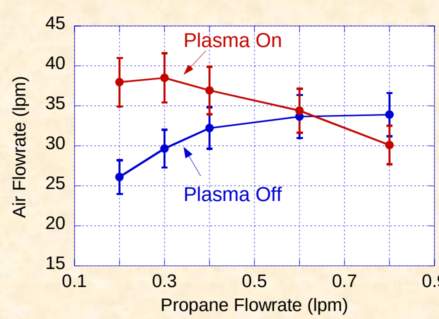
$e + C_3H_8 \rightarrow$ Multiple ions
$C_xH^+_{2x+2} \rightarrow C_mH^+_n + M$

Similar reactions with multiply-charged ions.

Preliminary experiments have proven the NTP combustion enhancement concept







To be continued next Wednesday …

Power conditioning & electrical measurements

Results from experiments & field demos

More chemistry

Scaling relationships

Outline

Overview of Applications of NTPs for Air Pollution Control and Surface Decontamination
Stack emissions (VOCs, NOx/SOx)
Environmental remediation (hazardous chemicals in soil and/or groundwater)
Surface decontamination (actinides, chemical/biological warfare agents)
Combustion enhancement

Applied Electrical Discharge Physics
Streamers/microdischarges (corona and silent electrical discharges)
Atmospheric pressure RF-driven discharges

Plasma Chemistry and Gas-Phase Reaction Chemistry
Electron-energy distribution functions, transport coefficients, and rate coefficients
Active Species (Free Radical) Yields in Electrical-Discharge Driven NTPs
Electron/radical attack mechanisms
Simple reactions/scaling laws

Power Conditioning & Electrical Measurements for NTP Applications
Power supplies/modulators for NTP processing
Voltage and power measurements for corona processing
Voltage and power measurements for silent discharge processing

Example Laboratory and Field Demonstrations
Soil/groundwater remediation
Engine test facility exhaust
Surface decontamination
Combustion enhancement of propane-air flames

Summary and Future Outlook
Regulatory factors
Social/health factors
Energy efficiency