Environmental Aspects of Plasma Science

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Leibniz Gemeinschaft

FROM THE IDEA TO THE PROTOTYPE

Content

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Plasmas for environmental protection

EU-Project "PlasTEP"

Project with 14 partners from the Baltic Sea Region with the aim of dissemination and fostering of plasma based technological innovation for environment protection in the Baltic Sea Region

- New possibilities fostering of innovative plasma-based exhaust gas and water treatment techniques
- Sustainability analysis of plasma-based environmental protection
- 3 thematic working groups: NOx/SOx; VOCs; polluted water
- www.plastep.eu

Part-financed by the European Union (European Regional Development Fund)

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Plasma Technology = Environmental technology

Waste incineration
- Thermal plasma for burning of solid waste and hazardous gases

Energy and ressource saving technologies
- Substitution of wet chemical processes (surface processing)
- Use of solvent free products due to surface treatment

Depollution technologies
- Decomposition of pollutants
- Filtering of PM (Electrostatic precipitators)

Plasma based generation of active compounds
- Ozone for water treatment or chloride-free bleaching

Efficient lightsources
- Energy saving due to efficient light generation
- Plasma based UV-lightsources for surface processing and curing etc.

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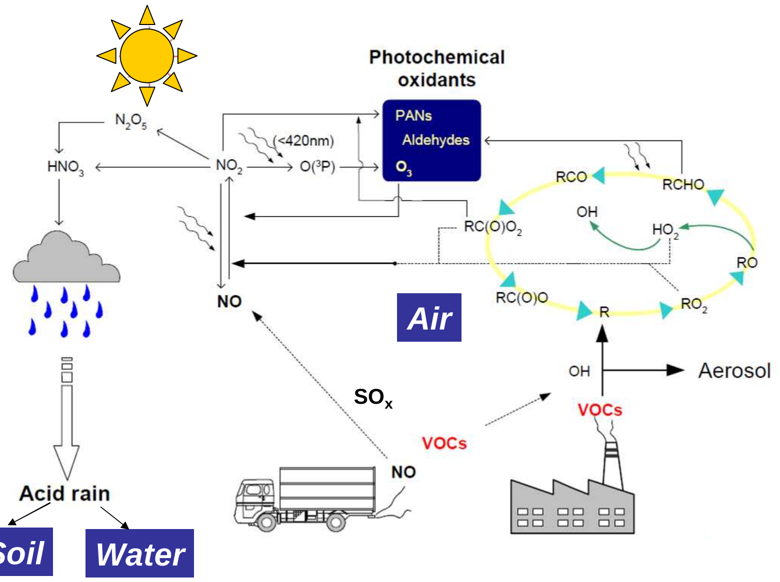
Emission sites and effects



Kim, AIST JPN

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VOC-decomposition and deodorization methods

Thermal Processes

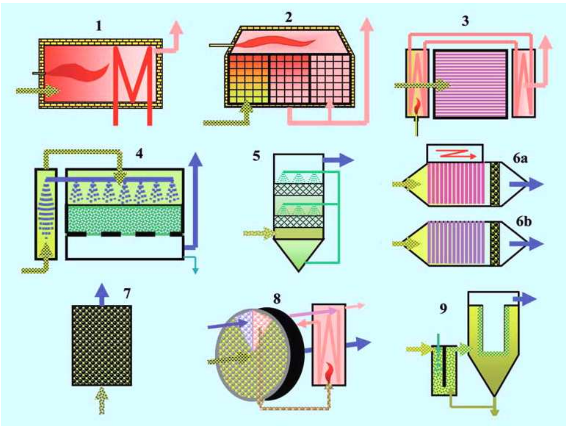
1 TO, Thermal Oxidation
2 RTO, Regenerative Thermal Oxidation
3 Catalytic Oxidation with Recuperation

Filtering/Adsorption

4 Biofilters
5 Scrubber
7 Adsorption Container
8 Concentrator Unit with TO
9 Filtering

Non-thermal Oxidation

6a Electrical Non-thermal oxidation
6b UVS Non-thermal Oxidation



Haus der Technik, Essen/GER

Content

1. Introduction
   - Plasma technology as an environmental technology

2. Exhaust treatment by non-thermal plasmas - Basics
   - Gas discharges for exhaust treatment
   - Discharge physics and plasma chemistry
   - Example for plasma chemistry: Ozone synthesis
   - Hybrid processes
   - Flue gas treatment (NOx and SOx removal)
   - VOC-removal
   - Particulate matter removal

3. Water treatment
   - Advanced Oxidation
   - Electro-hydraulic discharges
   - Antimicrobial treatment by indirect treatment of liquids

4. Summary and Outlook

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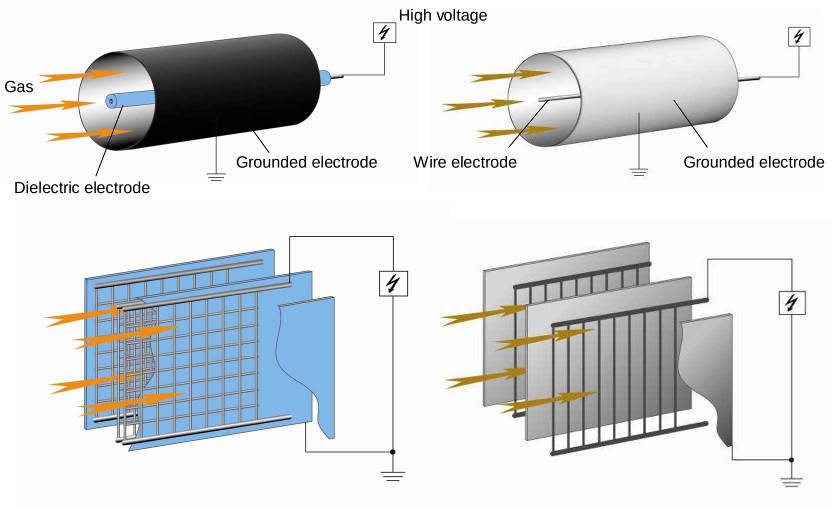
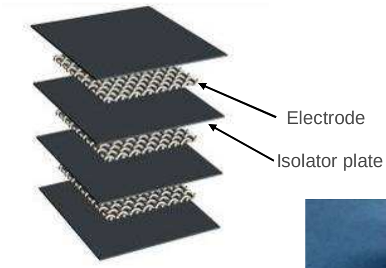
Gas discharges for exhaust treatment

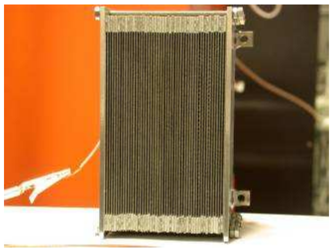
Barrier discharge **Corona**

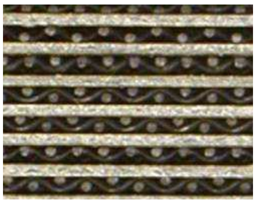


Stack reactor (Barrier discharge)

Stack system with structured electrodes







S. Müller, R.-J. Zahn; Contributions to Plasma Physics 47 (2007) 520-529

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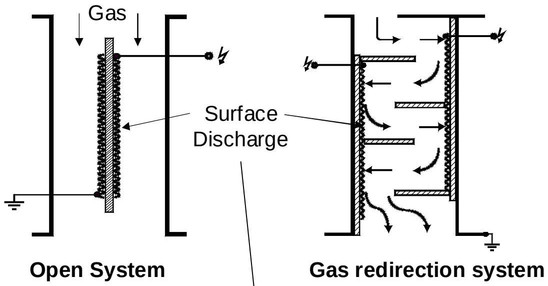
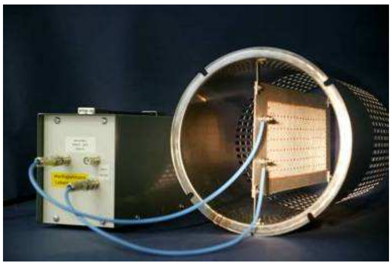
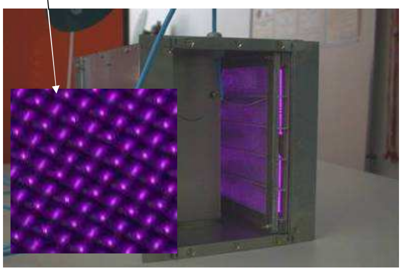
Surface DB with ion-extraction







S. Müller, R.-J. Zahn, J. Grundmann; Plasmas and Polymers 4 (2007) S1004

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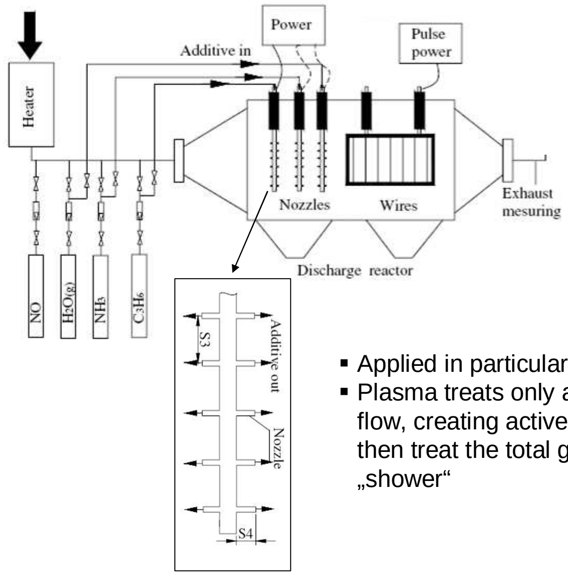
(Corona) radical shower



- Applied in particular to NOx-removal
- Plasma treats only a portion of gas flow, creating active species, which then treat the total gas flow as a „shower“

Chang et al, MacMaster Univ. CAN

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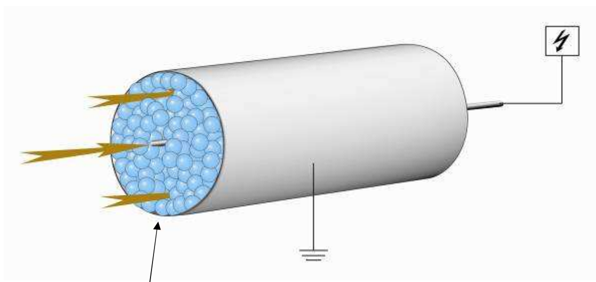
Packed bed reactors



Filling:
- Pellets
- Foams

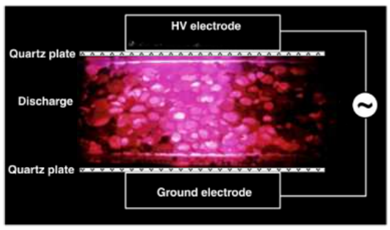


Fig. 2 DBD in the pores of a ceramic foam/schematic electrodes setup.

M. Kraus et al, ABB

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Processes and time scales

Plasma chemistry based on non-thermal activation of particles via collisions

→ quality and quantity determined by kinetic parameters (v_{mean}, ν_{coll})

Plasmaphysics

Plasma chemistry

10^{-12} 10^{-10} 10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-1} 10 time in s

Energy distribution of electrons

Ionisation
Dissociation
Excitation
Attachment

Diffusion

Heat and mass transfer

E/n

Charge exchange

Ion reactions

Reactions of/with active species

Reactions of/with radicals

possible mechanisms with different probability (different energy thresholds)

3 ... 10 eV for dissociation and radical formation

> 10 eV for ionisation

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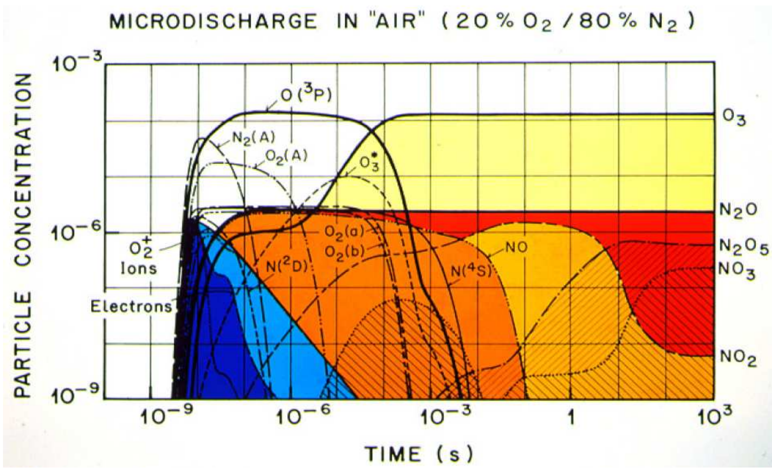
Air chemistry in cold non-thermal plasma



Homogeneous model (143 reactions, 30 reacting species)

U. Kogelschatz, B. Eliasson

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Ozone synthesis

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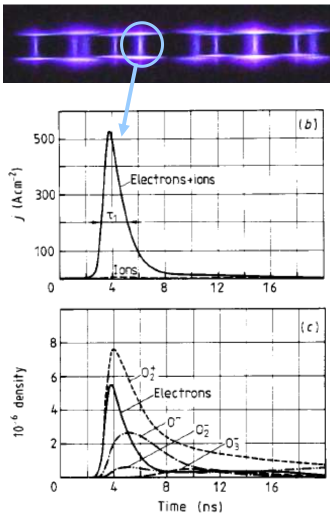

Discharge

Chemistry

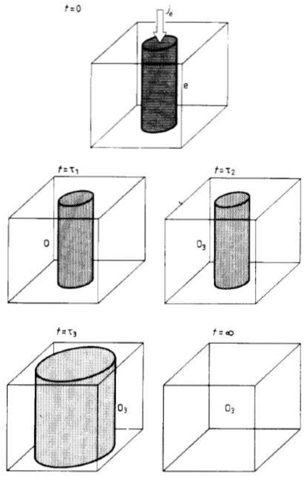

Figure 3. A schematic diagram of the spatial distribution of electrons, oxygen atoms and O_3 molecules at different times.

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Hirth et. al; J. Phys. D. (1986)

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Aerosol particle formation

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Reactions of larger radicals (CHO, CHN) with cluster ions and molecules

Generation of nitric acid (HNO_3) → reaction with radicals

Promotion of VOC removal due to hetero-geneous reaction

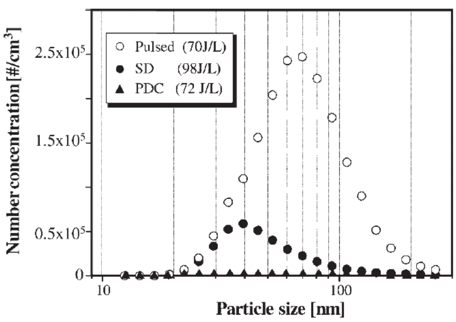

Figure 18. Aerosol formation from the decomposition of benzene (200 ppm benzene, 0.5 vol.-% water vapor). Aerosol was measured by SMPS (TSI Co.).

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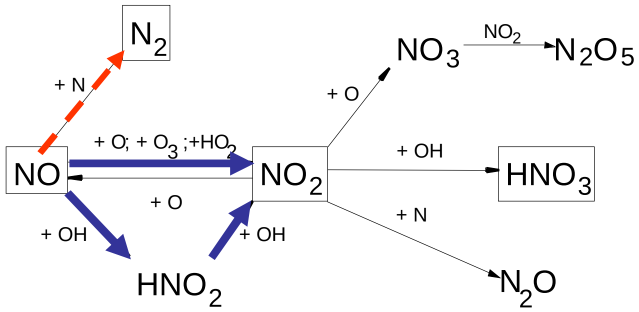
Kim, Plasmas and Polymers 2004

NO_x-conversion



- **Oxidative pathways dominate (espacially in case of humid conditions)**
- **Reduction at (to) high energy input**

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VOC removal reactions

Free electrons: e^- + {O_2, H_2O, ...} → OH, M^+ → HO_2, O_3

10 – 30 eV/OH-radical

→ Saturated Hydrocarbons (e.g. alkane):

Dehydro-	R-H + O → R + OH	
genization	R-H + OH → R + H_2O	R• ... organic radical
Oxidation	R + O_2 → R-O-O	R-O-O ...peroxy radical

Further oxidation to CO_2 and H_2O

Radical chain reaction

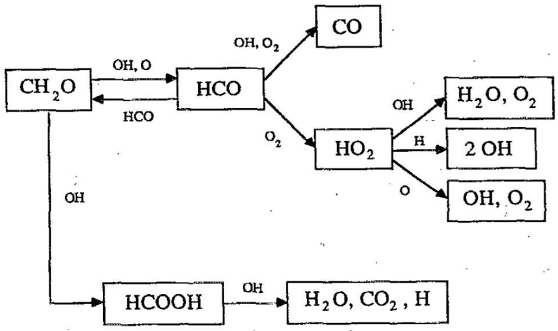
R_a-O-O + R_b-H → R_aOOH + R_b

ROOH ... alkyl hydroperoxide

→ Unsaturated Hydrocarbons (e.g. alkane):
Additionally radical addition following oxidation, radical chain reaction or polymerisation of hydrocarbons

Example: Formaldehyde (CH_2O)

- destruction of CH_2O results dominantly from chemical attack by OH and O radicals
- primary end products: CO, H_2O
- destruction rates typically 2-8 ppm/(1 J/l)



Storch and Kushner, J. Appl. Phys. 1993

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NTP vs. RTO

NTP-VOC removal:

10 – 30 eV/VOC-molecule

Regenerative Thermal Oxidation (RTO):

0.1 eV/molecule

per molecule of air

Lower energy consumption in NTP if VOC-concentration > 0.3 … 1% (3.000 – 10.000 ppm)

Fridman, Drexel University

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Evaluation

- Specific Energy Density (Spec. Input Energy SIE)

  $$\text{SED (J/L)} = P_{dis} / Q$$

  P_{dis} … dissipated plasma power; Q … gas flow

- CO_2-Selectivity S_{CO2}

  $$S_{CO_2}(\%) = \frac{[CO_2]}{[CO_2]+[CO]} \times 100$$

- Carbon balance CB

  $$CB(\%) = \frac{[CO]+[CO_2]+[HCOOH]}{n([VOC]_0-[VOC])} \times 100$$

- Decomposition efficiency η (Destruction and removal efficiency, DRE)

  $$\eta\ (\%) = \frac{[VOC]_0-[VOC]}{[VOC]_0} \times 100$$

  $[VOC]_0$ … inlet concentration;
  n … number of C-atoms

Kim, Plasmas and Polymers 2004

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Energetic efficiency

$$\text{Energy Cost} = \frac{J/L}{\Delta[C]} \times 250\ (\text{eV/molecule})$$

$$G\text{-value} = \frac{\Delta[C]}{J/L} \times 0.4\ (\text{molecules}/100\ \text{eV})$$

$$\text{Energy Yield} = \frac{\Delta[C]m}{J/L} \times 0.15\ (\text{g/kWh})$$

where m is molecular weight of the gas compound. The factors of 250, 0.4 and 0.15 in the equations are the conversion factors at 20 °C and 1 atm.

$\Delta[C]$ … removed amount of molecules in ppm

Kim, Plasmas and Polymers 2004

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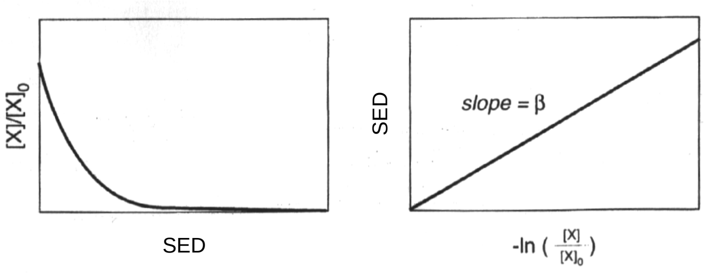
Evaluation: SED-plots



$[VOC] = [VOC]_0 \exp(-SED/\beta)$ $SED = -\beta \ln([VOC]/[VOC]_0$

$1/\beta = k_E$ ... energy constant

$k_E = f($ Temp, gas comp., $[VOC]_0$, ...)

Veldhuizen, TU Eindhoven

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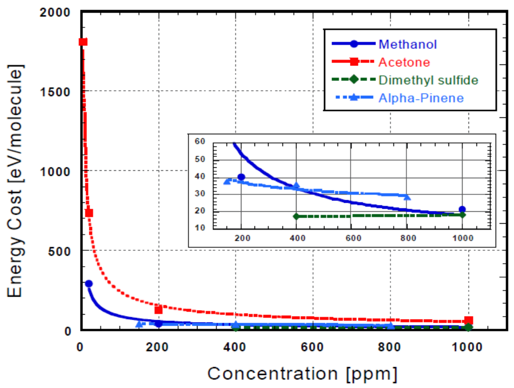
Energy cost



- Energy Price significantly depends on initial concentration
- Few ppm: energy price reaches very high values (not all active species can target VOC molecules)
- Higher concentrations: fraction of energy for removing pollutant molecules higher and energy spent for elimination of each single molecule decreases

Gutsol and Fridman, Drexel University

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Depollution of gases

+ Decomposition of contaminants without heating
+ Wide range of pollutants (Gases ... Particulate Matter PM)
+ Decomposition of organic PM
+ High efficiency for low contamination (e.g. deodorization) ([VOCs] < 1 g C_{org}/m^3)

- High energy cost/molecule → high energy for high concentrations
- Uncompleted conversion and by-products → low selectivity (CO_2)
- Deposition of polymer films in reactors → unstable plasma source

Possibilities

- Indirect treatment (Bypass installations)
- Hybrid methods = combination of plasma with ...
  ... catalysts
  ... scrubbing
  ... adsorbents

Heterogeneous reactions and synergies!

Hybrid NTP / Wet Processes

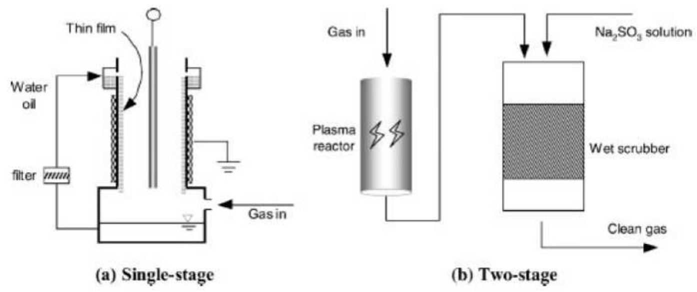

Figure 4. Hybrid NTP reactors combined with a wet process: (a) single stage, (b) two stage.

- Removal of reaction intermediates or final products from gas phase by adsorption and/or chemical reaction
- Gas-phase NTP enhance liquid-phase chemical reactions
- Electrical discharge over a liquid surface → modify mass-transfer characteristics

Kim, AIST JPN

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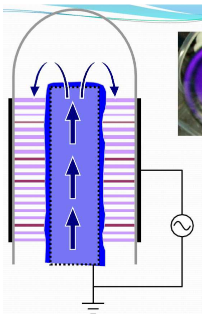
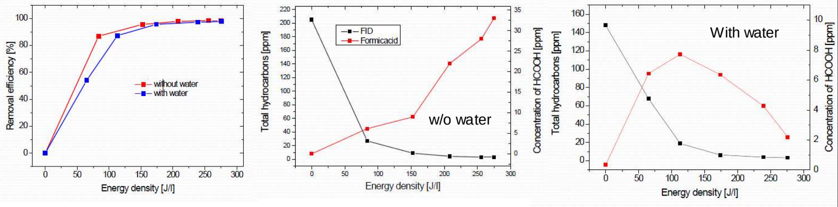
Falling water BD-reactor



Water flows up through vertical hollow cylindrical electrode and flows down making thin water film over high voltage electrode
→ treatment of water (dyes)
→ treatment of gas phase combined with scrubbing

Removal of undecane (non-soluble) → scrubbing of by-product (formic acid)



V. Kovacevic, M. Kuraica; Belgrade University

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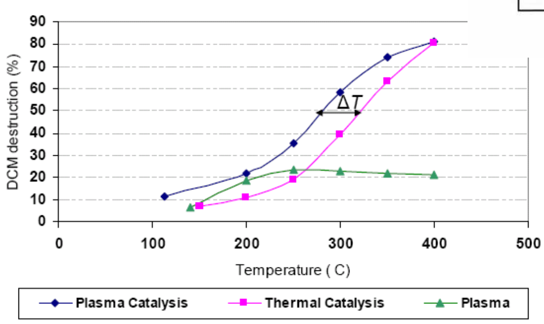
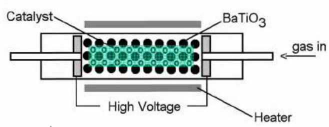
Plasma and catalyst: shift of temperature range

Dichlormethane (DCM) decomposition

DCM with Titanium dioxide





Whitehead et al, Manchester Uni.

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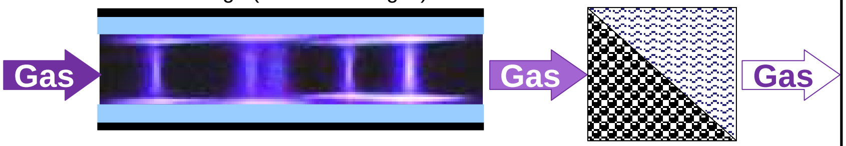
Overall process of plasma based removal

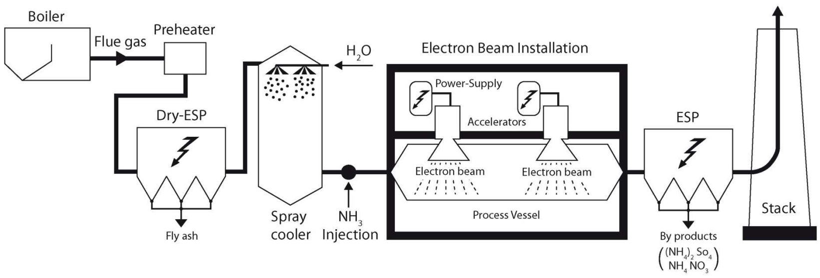


1. Breakdown phase (ps … ns)
- Ionisation, Dissociation, Excitation … → Ions, Electrons & Radicals

2. Reaction phase (µs … ms)
- Recombination and conversion of ions and radicals (primary radicals OH, O → sekundary radicals O_3, HO_2, …)
- Oxidation of pollutants Schadstoffe
- Surface reactions (activation, structural changes)

3. Post phase (ms … s)
- Diffusion, transport of heat and material, chemical reactions with post reactants
- Aerosol formation
- Adsorption

Electron beam flue gas treatment (EBFGT)



NO → NO_2 → HNO_3 → NH_4NO_3
SO_2 → HSO_3 → H_2SO_4 → $(NH_4)_2SO_4$

- **270.000 Nm^3/h of flue gas**
- **SO_2 removal efficiency above 95%**
- **NO_x removal efficiency above 70%**
- **Dose up to 10 kGy**

A.G. Chmielewski et al; INCT Warschau; Kraftwerk "Pomorzany" Stettin/PL

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EBFGT removal efficiency

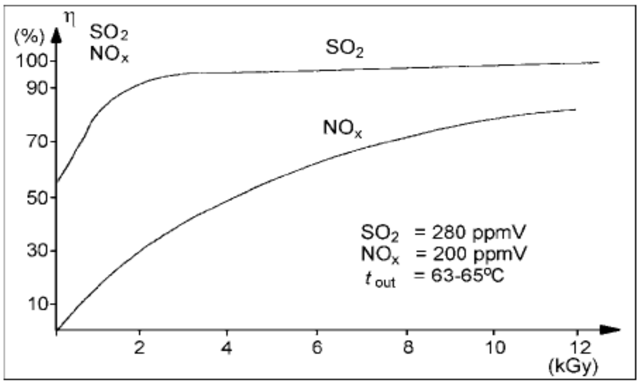

Fig. 1. SO_2 and NO_x removal efficiency *vs*. dose. The results obtained in the pilot plant experiments.

A. Chmielewski et al., ICHTJ Warzsawa

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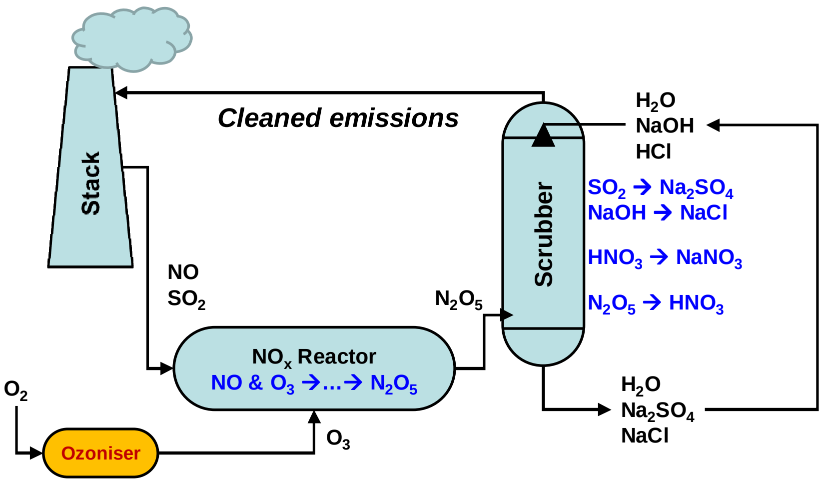
Ozone injection: non-thermal oxidation



E. Stamate et al.; Fuel 2010

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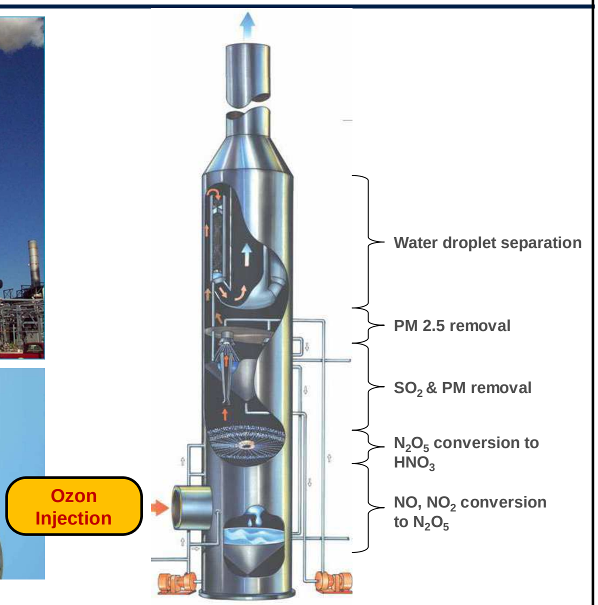
LOTOX (Low Thermal Oxidation) & EDV Scrubbing



Belco/Dupont

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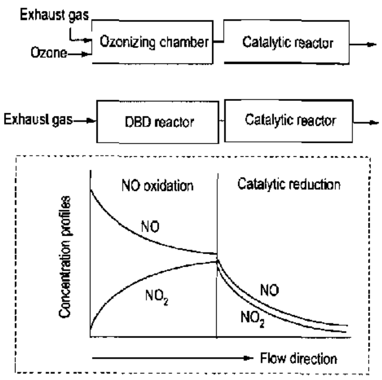
Plasma-unterstützte Katalyse (NH_3-SCR)



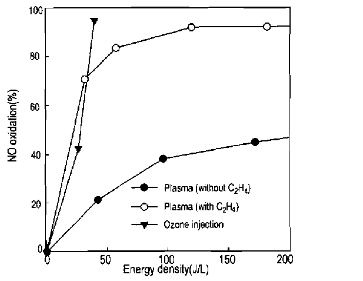


Fig.5 Comparison of the ozone injection method with the direct application of the DBD plasma in terms of the NO oxidation performance (initial NO_x: 300 ppm; temperature: 200 °C)

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O; \quad T \geq 200°C$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O; \quad T \leq 100°C \ \textbf{wenn:} \ [NO] \cong [NO_2]$$

S.M. Young; Plasma Sci. Technol, 2006

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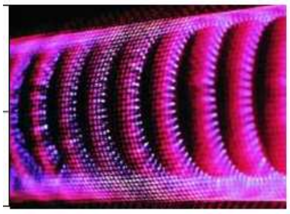
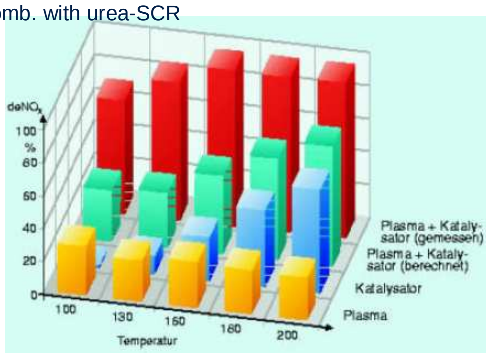
Plasma-enhanced SCR (selective catalytic reduction)

Volume Barrier Discharge comb. with urea-SCR





- up to 85% NOx reduction under cold start and urban driving conditions
- less than 300 W of plasma power applied
- model studies: fuel penalty introduced estimated to be below 2%.

T. Hammer; Plasma Sources Sci. Technol. 2002

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Multi-stage treatment with molecular sieves

Catalytic supported NTP plant for 10,000 m³/h of waste air

Figure 11: Catalytic supported NTP plant for 10,000 m³/h of waste air behind flavouring processes for food

1. Enrichment of high-molecular compounds in molecular sieve buffer
2. Oxidation of odours with a plasma stage
3. Expellation with desorption air combustion of VOC contingents with catalyst (after sev. months of molecular sieve loading)

R. Rafflenbeul, Envisolve.com; Germany

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Bypass operated plasma plants

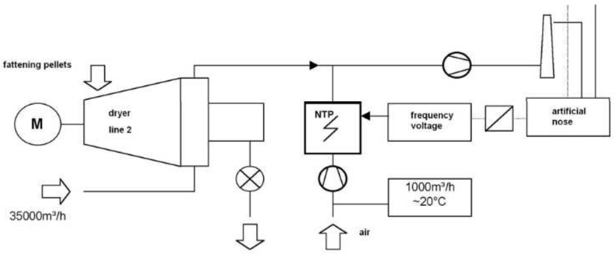

Figure 14: Diagram of a NTP plant for odour reduction in factories for producing fatting food and fish meal (very humid emissions)

- **Indirect plasma treatment of polluted gas by plasma treated gas**

R. Rafflenbeul, Envisolve.com; Germany

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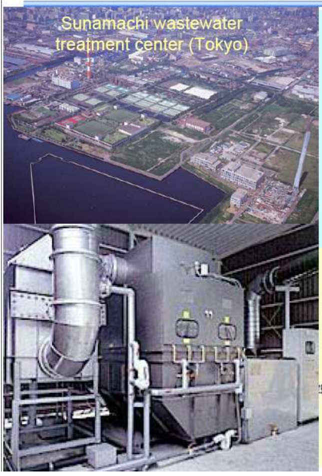
Deodorization unit (commercial)



Plasma-CAT (UTD Co., Swiss)

Two-stage Plasma-Catalyst System

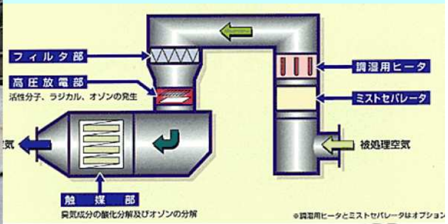
Flow rate = 55,000 Nm^3/hr

Odor concentration =

Removal efficiency = 94%~99%

Specific input energy =

Construction cost = ¥ 140,000,000



Kim, AIST Japan

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PlasmaNorm-Technology

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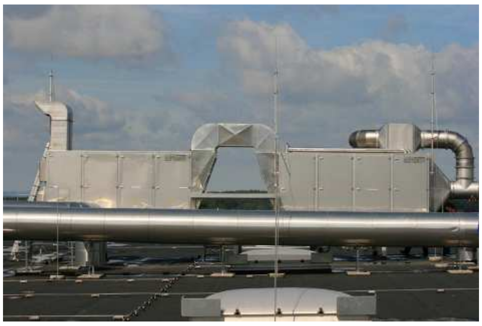

Deodorization of exhaust from ovens for convenience products made of meat (1.5 MW ovens; exhaust stream of 8000 Nm^3/h)

Cooker hoods for large-scale kitchens, gastronomy and private hausholds

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M. Langner; Airtec competence GmbH

Mobile laboratory for paper/pulp mills

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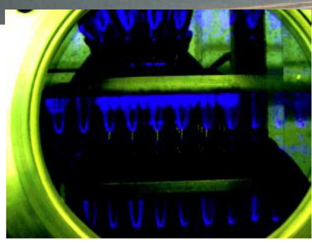
10 kW
750 m^3/h



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A. Fridman, A. Gutsol (Drexel) 2005

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Pilot plant for H_2S removal

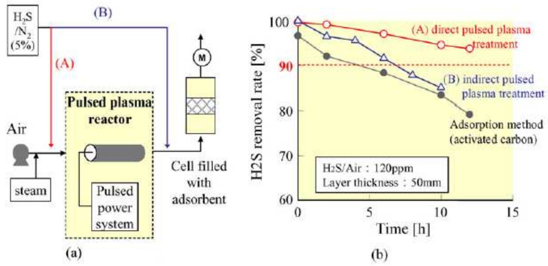

Figure 4. H_2S removal test using the pulsed streamer discharge. (*a*) Test system and (*b*) results.

(a) (b)

A. Mizuno, Plasma Phys. Control. Fusion **49** (2007) A1–A15

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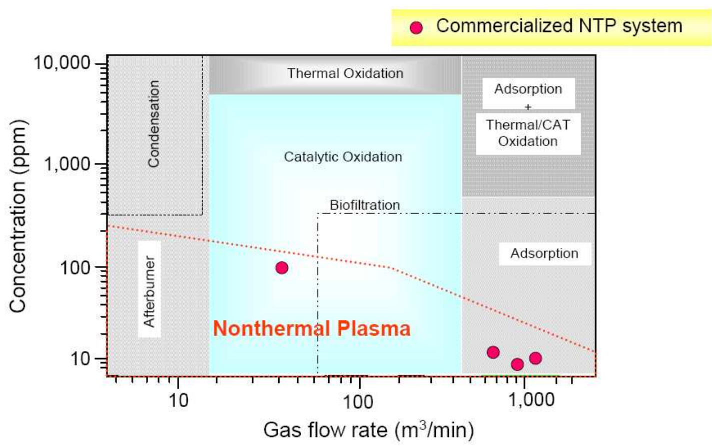
Process features



(Original format from J.A. Dyer, K. Mulholland, *Chem. Eng.*, pp. 4-8, 1994)

Kim, AIST Japan

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Economical benefit

Investment- and running costs

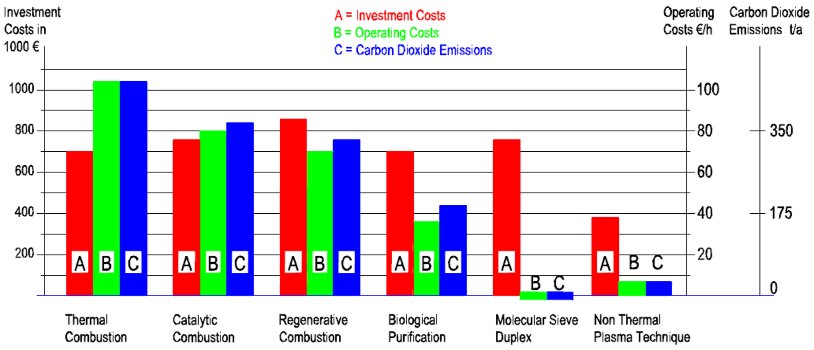

Figure 15: Investment- and running cost comparison of waste air purification processes (50,000 m³N/h) for <100 mg VOC/m³ in the flavour processing industry

R. Rafflenbeul, Envisolve.com; Germany

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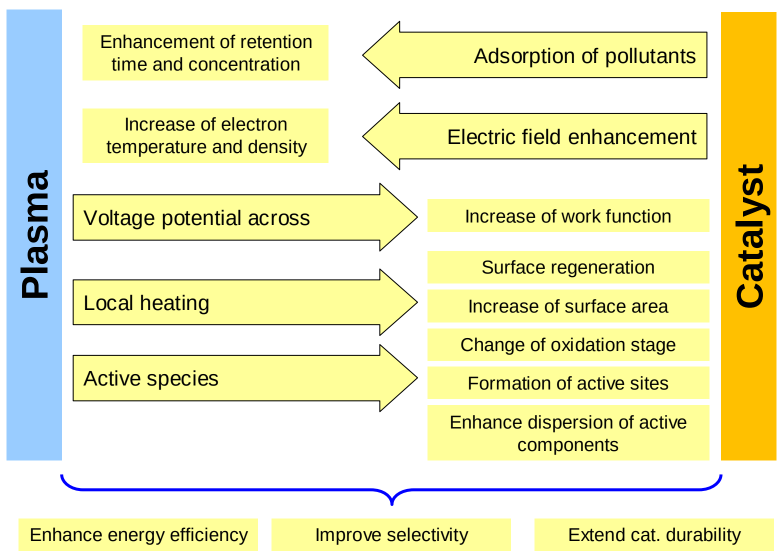
Plasma & Catalyst



Chen et al., Environ. Sc. Technol. 43 (2009) 2216; Van Durne et al., Appl. Catal. B 78 (2008) 324

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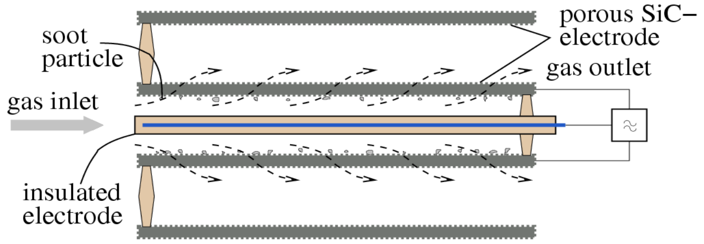
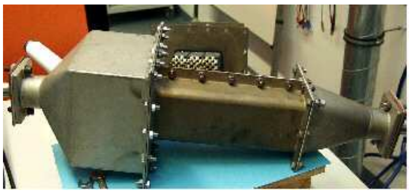
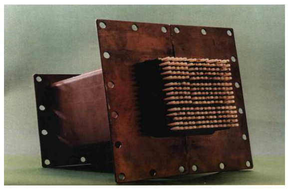
Soot removal

BD-reactor with porous filter electrode







J. Grundmann, S. Müller, R.-J. Zahn; Plasma Chem. Plasma Process. 25 (2005)
Patente WO 2005/028081, DE 197 17 890, ...

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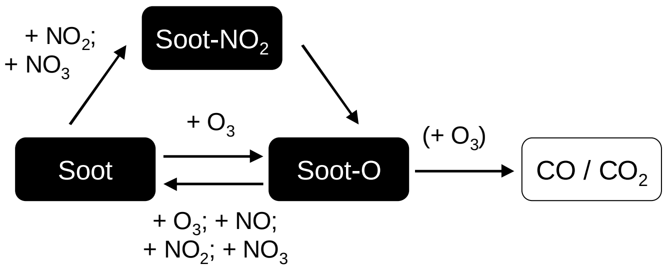
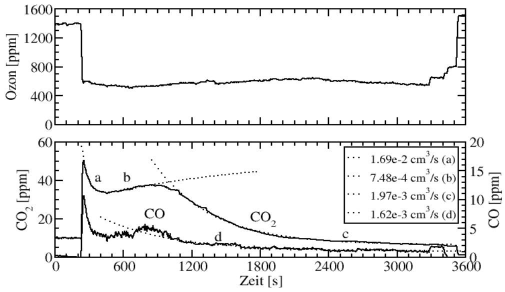
Soot-removal





(1) fast reaction with HC
(2) forming of Soot-O
(3) decomposition of Soot-O

J. Grundmann, S. Müller, R.-J. Zahn; Plasma Chem. Plasma Process. 25 (2005)

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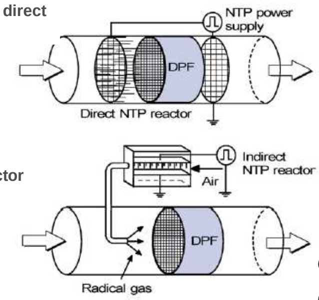
Plasma Regenerated Diesel Particle Filter (DPF)

NO_2 and O_3 incineration with direct NTP reactor (T_g > 200 °C)

NO_2 and O_3 incineration with indirect NTP reactor (T_g > 200 °C)



$$NO + O_3 \rightarrow NO_2 + O_2$$
$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad (T > 200°C)$$
$$C + O_3 \rightarrow CO_2 + \frac{1}{2}O_2 \quad (T > 23°C)$$

Fig. 4 Metal DPF before and after NTP regeneration

M. Okubo et al.; Thin Solid Films, 2006

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Content

1. Introduction
   - Plasma technology as an environmental technology
2. Exhaust treatment by non-thermal plasmas - Basics
   - Gas discharges for exhaust treatment
   - Discharge physics and plasma chemistry
   - Example for plasma chemistry: Ozone synthesis
   - Hybrid processes
   - Flue gas treatment (NOx and SOx removal)
   - VOC-removal
   - Particulate matter removal
3. Water treatment
   - Advanced Oxidation
   - Electro-hydraulic discharges
   - Antimicrobial treatment by indirect treatment of liquids
4. Summary and Outlook

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Water treatment - **Overview**

Water cleaning

- **Physical methods**
  - Sedimentation
  - Filtering
  - Flotation
- **Biological methods**
  - Biochemical Ox.
  - Anaerobic cleaning
- **Chemical methods**
  - Oxidation
  - Disinfection

Plasma

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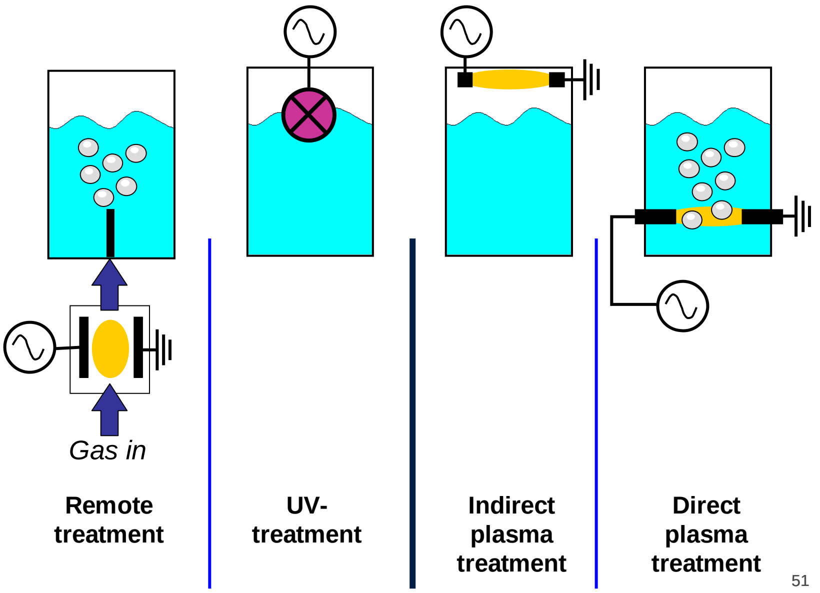
Water treatment - **Overview on plasma methods**



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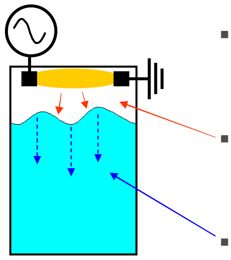
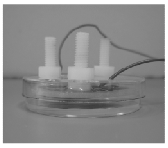
Indirect plasma treatment



- Use of “classical gas discharge” for water treatment, no special efforts (power supply, independent on water conditions, …)
- Indirect interaction of atmospheric pressure plasma with liquids mainly based on reactions at gas/plasma-liquid interface
- Bulk effects based on diffusion processes
- Biological (bactericidal) effects of plasma treatment mainly based on changes of liquid: resulting in generation of more or less stable reactive species



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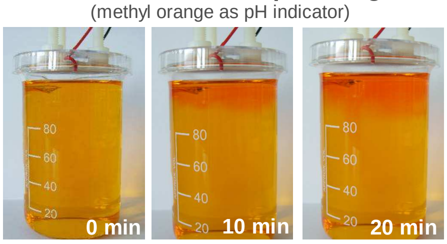
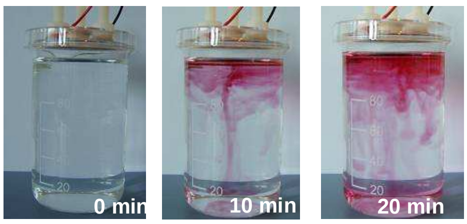
5. Water treatment

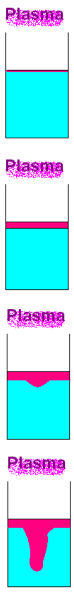
Bulk effects by indirect treatment

Generation of $H^+ \rightarrow$ pH change
(methyl orange as pH indicator)



Generation of nitrite
(Spectroquant® – nitrite test)





Phases of spreading:

surface reaction
directed gas phase-liquid interaction

spreading phase
formation of a diffusion front

Diffusion influenced by gradients
e. g. temperature, magnetic fields

⇩

„Drop and structure formation“

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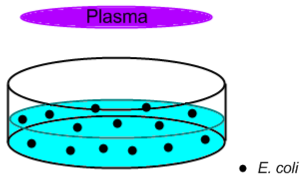
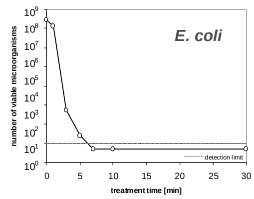
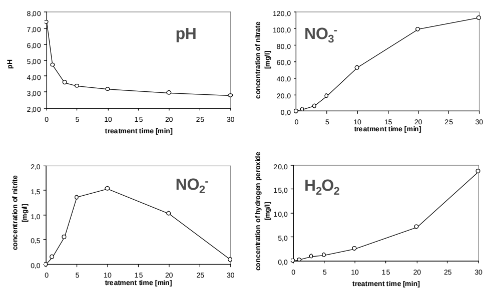
Indirect treatment of non-buffered liquid

Inactivation of suspended vegetative microorganisms





Acidification and generation of nitrate, nitrite (peroxynitride) and hydrogen peroxide



K. Oehmigen et al., Plasma Process. Polym. 7 (2010) 250-257

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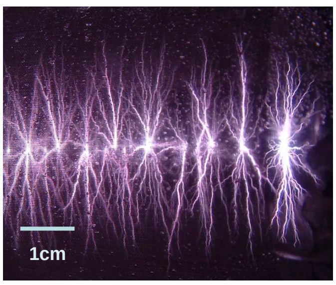
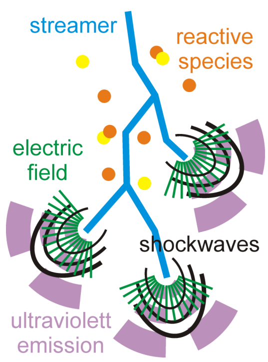
Plasmas in Water

High but pulsed electric field strenght and pulsed discharge in water enable fast and efficient biological and chemical decontamination without additional chemistry

- Effects due to electric field, radiation (UV), radicals and schock waves
- Dependent on puls parameters: temporal inactivation or killing





J. Kolb, INP Greifswald/ODU Norfolk

Summary and Outlook

- Plasma technolgy is (already) an environmental technology at all!
- NOx, SOx, VOCs and other gaseous contaminants can be decomposed in non-thermal plasmas (NTPs) via „radical based“ plasma chemistry.
- Exhaust treatment by means of NTP is especially suited for low concentrations in small and medium gas flows.
- Applicability/feasibility is determined by the specific situation (type and amount of contaminants, properties of gas flow) and has to consider effectivity and selectivity.
- There is a large potential for hybrid/catalytic/heterogenous methods.
- Generation of plasma at or in water is possible and leads to antimicrobial and chemical effects.

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The participation and accomodation for summer school students is free of charge!

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http://www.plastep.eu/english/newsdetails/einzelansicht/article/60/

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