DIAGNOSTICS FOR ENVIRONMENTAL ASPECTS OF PULSED ATMOSPHERIC DISCHARGES

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Abstract

Diagnostics for the study of pulsed atmospheric discharges are discussed. To obtain parameters for describing conversion processes of pollutants into harmless products many diagnostic techniques are in use and under development. In this contribution electrical, optical and chemical diagnostics used in air and wastewater remediation are reviewed.

1   Introduction

Pulsed atmospheric discharges create abundant numbers of radicals. In the last decade many applications of non-thermal atmospheric discharges have been investigated for application in pollution control [1]. Streamer like discharges like pulsed corona and dielectric barrier discharges as well as atmospheric glow discharges has been used. In all cases a transition to the spark regime or arc regime is prevented to keep the energy input limited to (fast) electrons in stead of to neutral gas heating. To understand the discharge generation, radical production, chemical reaction kinetics and energy or conversion efficiency many questions must be answered (fig 1). Diagnostic information can deliver parameters for models describing the cleaning processes and for scaling laws of chemical reactors. In this review we discus the diagnostics used in cleaning of flue gas containing NO, SO_2 and in the conversion of phenol dissolved in water.

2   Conversion processes (gas and water cleaning)

Flue gas from combustion contains, among others, NO and SO_2 which form acids in moist air leading to so called "acid rain". With gas discharges an oxidative environment can be created in the flue gas stream in which NO and SO_2 are converted to nitric acid and sulphuric acid. If ammonia is injected in the gas stream solid products like ammonia nitrate and -sulphate will be formed which can be removed from the gas stream in e.g. an electrostatic precipitator. The creation of OH and O radicals as well as Ozone (O_3) has been studied by many groups [1]. The pulsed discharges can also be used to oxidise organic pollutants in water. An example is the conversion of phenol to di- and trihydoxybenzenes. Further oxidation leads to ring opening and the formation of aldehydes and acids. To describe these processes many theoretical calculations and experimental investigations have been performed. Electrical, optical and chemical diagnostics (fig 2) used in experiments and for verification of numerical calculations are discussed.

3   Electrical and plasma parameters

Energy dissipation and the rise time, magnitude and duration of the high voltage pulse are important electrical parameters. High voltage dividers and fast current probes can be used to measure the input power and energy of pulsed discharges like pulsed corona (fig 3, [2,16]). For dielectric barrier discharges produced with an ac power source the energy dissipated during one cycle can also be calculated from a plot of charge versus voltage (Fig 4, [4]). The energy input can than be calculated in Joule/m^3. The efficiency of the cleaning process is usually given in units such as eV per removed molecule, the number of molecules per 100 eV (the so-called G value), in g/kWh or Joule/m^3 /ppm pollutant.

4   Optical diagnostics

The structure of streamer discharges is investigated from numerical calculations as well as from experiments. From the calculations in inhomogeneous fields (point plate geometry) and homogeneous field it is known that streamers are thin filaments with a diameter of less than one mm (Fig 5, [5]) propagating at very high speed of the order of 1 mm/nanosec. This implies that the time and space resolution of diagnostics must be very high. Micro discharges in a dielectric barrier discharge (DBD) are much shorter in length (up to several mm only) but have comparable diameter and propagation velocity. Moreover a surface discharge is formed on the dielectric layer covering the electrode. We start with various optical diagnostics used to better understand these discharges.

4.1   Photography

With fast photography the streamer discharges can be made visible. In air most light emitted is from the second positive system of Nitrogen which is in the UV. With a CCD camera and a gated image intensifier a spatial resolution of 30 μm. and a time resolution of 1 nanosecond can be obtained [6]. In fig. 6 the exposure time is 100 ns which is longer than the time the streamer needs to cross the gap of 2.5 cm length. It is clear that a large volume is filled when using the point-plate configuration and there is a lot of branching. In the point-wire configuration and observation direction along the wire the filling factor is much less (Figure 6). The streamer diameter is in this case 150 μm which is less than often obtained in numerical calculations.
When the time resolution is decreased to 1 nanosecond a number of small light spots is observed (Fig. 7). This shows that the lights is mostly emitted by the fast propagating streamer head and not from the streamer channel were the electron energy is much lower. With proper time synchronisation, which is not easy because of jitter problems, the streamer velocity can be calculated. On average 0.5 mm/ns is obtained.
The streamer density distribution can also be determined by observing the hot gas channels left behind after the discharge is extinguished. With Schlieren photography the hot gas channels can be made visible (see Fig. 8 taken from [2]), in this case 200 μsec after extinction. The number of hot gas channels is 5-7 per cm wire in a wire-plate configuration. The density perturbation in the gas is small proving that the heat dissipation by the streamer discharge is small. The energy dissipation is higher in a small part near the anode. This is due to the so-called secondary streamer occurring after the primary streamer has crossed the entire gap. The density of micro-discharges in a DBD is usually higher but the length is limited to the gap distance of several mm.

4.2   Interferometry

Interferometry is a widely used technique to measure the electron density and sometimes also the neutral density in arc discharges. Up to now it has not been used for the thin streamer channels but high spatial resolution was demonstrated recently on atmospheric microhollow cathode discharges [7]. A Mach-Zehnder heterodyne interferometer operating at a wavelength of $\lambda = 10.6$ μm was used. One beam passes through the discharge and the second beam is frequency shifted by means of a 40 MHz acousto-optic modulator. The resolution of the interferometer is 0.01 degree corresponding to a line integral electron density of 6.10^{11} cm^{-2}. To separate the contribution from the electrons and neutrals the discharge is switched on and off in a repetitive mode. The fast generation of electrons in a pre-ionised filament was measured at several lateral and radial positions. After Abel inversion the radial density profile of the discharge is obtained (Fig 9) as well as the neutral density or gas temperature profile with a radial resolution of 100 μm and a temporal resolution of 50 nsec.

4.3   Spectroscopy

Emission spectroscopy with high time resolution is used in [8] to measure the hot gas temperature in a self-repetitive streamer discharge in air at atmospheric pressure (repetition rate of 70 μsec. and energy per pulse of 14 μJoule). The variation in the rotational temperature was determined from the spectrum of the nitrogen band at 337 nm. It shows an increase to 380 K during the primary streamer and to 400 K during the secondary streamer 30 nanoseconds later (Fig. 10). The temperature then drops rapidly due to cooling. The effect of gas heating can also be measured from the rotational temperature of OH. A temperature increase of only 30-50 degrees was found [9] for a DBD in argon water gas mixtures.
Absorption spectroscopy is a useful diagnostic for in-situ measurements of pollutants in a gas stream. In [10] the concentration of NO, SO_2 and NH_3 was measured in-situ in flue gas in a pipe of 20 cm diameter. Injecting the gases separately with injection from gas bottles (Fig 12) performed the calibration. The same technique was

applied in a DBD reactor (see Fig 13 from [11]) using a xenon lamp or deuterium continuum lamp and detection with a spectrograph supplied with a CCD camera. Special attention was paid to take background absorption, probably caused by ozone, into account.

Ozone absorption measurements are a relatively easy diagnostic for O_3 concentration measurements. As an example the measured concentration from absorption above water when streamer corona is made in the air in a closed volume gives the ozone production rate [3]. When phenol is dissolved in the water the measured O_3 concentration is lower. From the decrease in rise time of the ozone concentration build-up the reaction rate of ozone with dissolved phenol can be estimated.

Concentration and temperature from NO can also be measured in-situ from laser absorption spectroscopy. This was demonstrated in a DBD [12] from the observation of the NOγ(0,0) band. Because the intensity ratio of some lines within this rotational band have a clear temperature dependence the gas temperature can also be calculated from a relative intensity ratio (see Fig 11). It proves that the temperature rise is not more than 50K.

Finally two dimensional absorption distributions [13] can give information on the concentration during destruction and production of NO in a reductive or oxidative environment. This also shows the reaction kinetics during the expansion phase of the streamer.

4.4   Laser Induced Fluorescence

Images of NO distributions in streamer discharges have also been obtained from Laser Induced Fluorescence (LIF) [14]. The laser system generates 226 nm radiation (fourth harmonic of Nd YAG laser) in a 7 ns pulse. The beam is focused to a sheet. NO fluorescence is measured at 253 nm to determine the destruction of NO by negative corona discharge with high spatial and temporal resolution. Also in water cleaning LIF diagnostic is a powerful in-situ diagnostic. In [15] destruction of phenol by positive corona discharge above the water was followed with time inside the water by measuring fluorescence at 300 nm. Fluorescence at longer wavelength can be used to follow the build up and destruction of oxidation products (Fig 14).

To identify the OH radical in corona exposed water a fluorescent molecular probe was used in [3]. If the probe molecule CCA (coumarin-3-carboxylic acid) absorbs a hydroxyl radical it becomes strongly fluorescent. In fig 17 the fluorescence spectrum of a 1 mMol CCA solution is shown after different corona-exposure times (10-40 minutes at 100 Hz rep rate). The excitation wavelength is 396 nm. The increase of the fluorescence is almost linear with time. This implies that the production rate of the hydroxyl radicals is about constant.

4.5   Other techniques

Cavity-ringdown spectroscopy can be applied for detection of low concentration radicals. Measurement of the E-field in streamer discharges at atmospheric pressure is difficult. Stark broadening is hampered by pressure broadening. May be the intensity of so-called forbidden lines can be used for estimation of high electric fields in streamer discharges. FTIR spectroscopy is often used for the measurement of the composition of hydrocarbons and other reaction products

5   Chemical diagnostics (Conversion products)

It is in general not sufficient in a study of destruction of VOC's in air or organic molecules in water to measure the reduction in the primary component only because intermediate or final reaction products can be toxic. Gas chromatography and HPLC (high performance liquid chromatography) is often used to determine the composition of pollutants in a treated gas or water stream. As an example in fig 15 were the concentrations of two conversion products are shown as function of time if a 0.27 mMol (25 mg/l) phenol solution is oxidised by a pulsed corona discharge [3]. The concentrations are measured by reverse-phase HPLC using a UV absorption detector. These intermediate products are further oxidised into acids which have been qualitatively identified by Capillary Zone Electroforeses. Ring cleavage products can be separated from polyhydroxybenzenes by Ion-exclusion-chromatography. This is shown in the chromatogram in figure 16 [3,16] in which phenol, polyhydroxybenzenes and acids are clearly separated.

6   Summary and future needs

Pulsed atmospheric discharges are difficult to describe. They consist of two phases: streamer creation and propagation of a thin filament creating exited states, radicals and meta-stable states and a second phase with expansion, cooling and further chemical reactions. Because of the fast time scale and required high spatial resolution diagnosis of these plasmas is very demanding. Electrical, optical and chemical diagnostics have given a wealth of information but e.g. branching of the filaments, concentrations of reaction products and scaling are still difficult to predict. So there is a further need for better diagnostics for the measurement of e.g. E-field and distributions of radicals and reaction products. Also in-situ monitoring for process control and verification of environmental regulations should be further developed (see Fig 18 for some challenges in the diagnostic field).

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Acknowledgement

QUESTIONS

- Energy efficiency, filling factor
- Removal rate (conversion efficiency)
- Time scale chem. kinetics, residence time
- Conversion products (intermediate, final)
- Additives to improve conversion efficiency
- Surface reaction to improve eff. and selectivity
- Theoretical limits, Scaling laws
- Costs (investment, operation, maintenance)
- TASK: FIND PROPER DIAGNOSTICS
         AND INDICATORS

Fig 1

DIAGNOSTICS

• Electrical:	Current,Voltage	Power, ens. conv.eff.
• Optical:	(fast) Photography	Discharge struct.
	Spectroscopy	Plasma parameters
	Interferometry	n_e, N_0, T_e, T_0
	LI Fluorescence	radicals (in water)
• Chemical	rp-HPLC, ICE	Int.+final conv.
	conductrimetry	Products
	TOC (inorg.C)	Oxidation progress
• Biological	ecotoxicity, acidity	Environm. compat.

Fig 2

ELECTRICAL MEASUREMENTS
Pulsed corona discharge

- Fast risetime:
  10^{12} V/s I_o
  = CdV/dt V_1
  = LdI/dt
- Power dissipation in
  Joule/l or
  Joule/l/ppm of poll.
- Energy conversion
  in eV/molecule
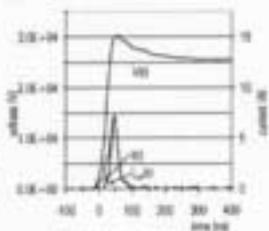
Fig. 3

ELECTRICAL MEASUREMENTS
Dielectric barrier discharge
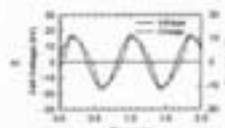
Voltage and charge

versus time
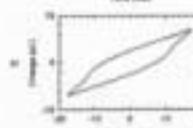
Charge vs voltage

-> Energy per cycle

Rusicha, book:E.M. van Veldhuizen (ed) p 260   Fig 4

STREAMER DISCHARGE
Calculation
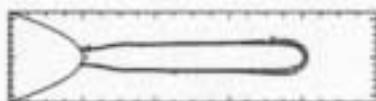
Point-plate (upper) and plate-plate (lower)

A.A. Kulikovski, J. Phys. D: Appl. Phys. 30, 1997) 1515   Fig. 5

Fast photography

CCD camera; exposure time 100 nsec

point-plate   point-wire

E.M. van Veldhuizen, This conference   Fig. 6

75

Fast photography
CCD camera; exposure time 0.8 nsec

E.M. van Veldhuizen, This conference   Fig. 7

Schlieren photography
Wire-plate configuration, delay 200 μs
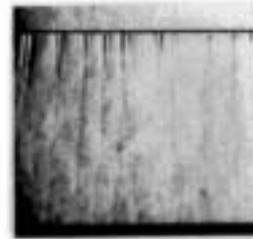
Y.L.M. Creyghton, PhD Thesis, Eindhoven Univ. of Techn.   Fig 8

Interferometry
Microhollow cathode discharge
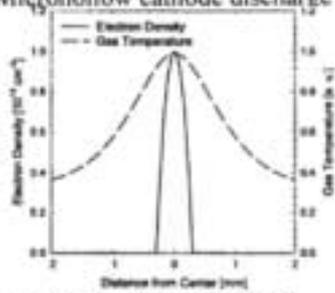
Leipold et al., J. Phys.D. Appl. Phys.33,(2000) 2268-73   Fig 9


Spectroscopy
Repetitive filamentary streamer discharge
Spectrum 335-337 nm, dλ=0.1 nm
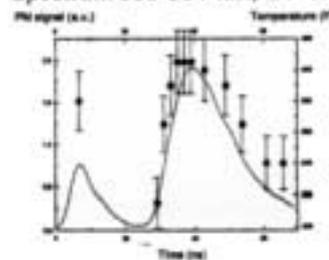
E. Marode et al. J. Adv. Ox. Techn. 4 (1999) 305   Fig.10

Spectroscopy
Laser absorption spectroscopy of NO
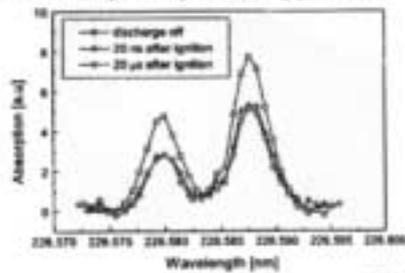
M. Spaan et al. Plasma Sources Sci Technol. 9 (2000) 146   Fig.11


UV-absorption measurements
flue gas
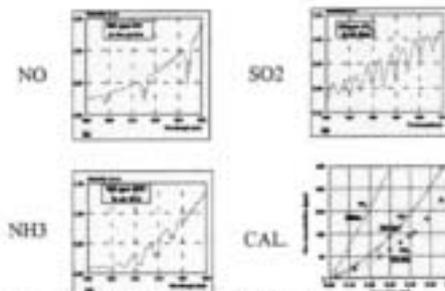
E.M. van Veldhuizen, Proc. Hakone V (1996) 107   Fig 12

76

UV Absorption NO

Flue gas treatment in dielectric barrier reactor
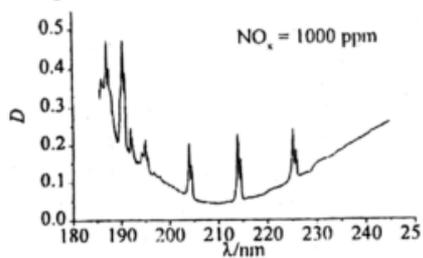
Stefanovic, Wiesemann, Proc 14th ISPC, Praque, p 1039

Fig 13

## IN-SITU MEASUREMENT OF PHENOL AND DHB by LIF
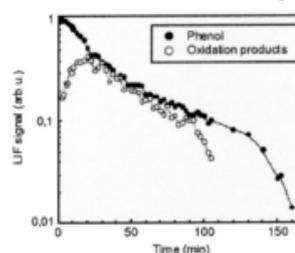
D. Hayashi, J. Phys. D: Appl. Phys. 33 (2000) 1484

Fig 14

CHEMICAL DIAGNOSTICS
Reversed phase HPLC
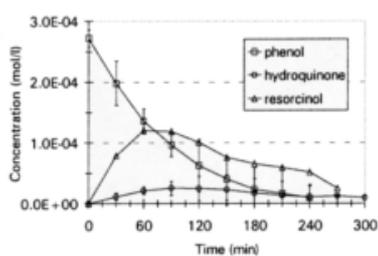
W.F.L.M. Hoeben, PhD Thesis (2000), Eindhoven Un. of Technol.

Fig 15

CHEMICAL DIAGNOSTICS
Phenols and ring cleavage products
from ion-exclusion chromatography
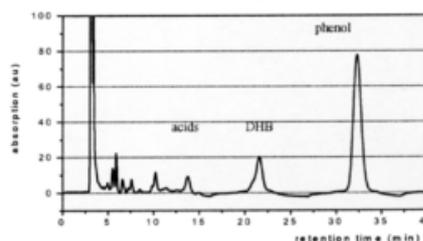
Fig 16

OH RADICALS IN WATER
Coumarin-3-carboxylic acid molecular probe
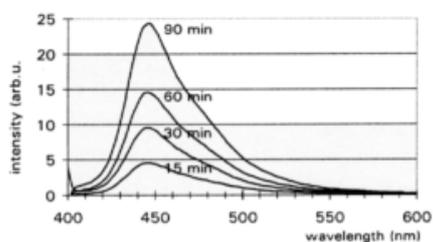
Fig 17

CHALLENGES

- Radical concentrations from cavity ring-down spectroscopy
- Plasma parameters in micro-discharges from Thomson scattering and interferometry
- Decomposition products on-line from LC-MS and in-situ from LIF imaging
- E-field from ? in streamer head and channel
- On-line Dioxins and VOC's

Fig 18