Regular Article

Treatment of industrial exhaust gases by a dielectric barrier discharge[*]

Michael Schmidt[1,a], Marcin Hołub[2], Indrek Jõgi[3], and Martin Sikk[4]

[1] Leibniz Institute for Plasma Science and Technology, Felix-Hausdorff-Str. 2, 17489 Greifswald, Germany
[2] West Pomeranian University of Technology, al. Piastów 17, 70-310 Szczecin, Poland
[3] University of Tartu, Institute of Physics, Ravila 14c, 50411 Tartu, Estonia
[4] VKG Oil AS, Järveküla tee 14, 30328 Kohtla-Järve, Estonia

Abstract. Volatile organic compounds (VOCs) in industrial exhaust gases were treated by a dielectric barrier discharge (DBD) operated with two different mobile power supplies. Together with the plasma source various gas diagnostics were used, namely fourier transform infrared (FTIR) spectroscopy, flame ionization detector (FID) and GC-MS. The analysis revealed that some exhaust gases consist of a rather complex mixture of hydrocarbons and inorganic compounds and also vary in pollutants concentration and flow rate. Thus, analysis of removal efficiencies and byproduct concentrations is more demanding than under laboratory conditions. This contribution presents the experimental apparatus used under the harsh conditions of industrial exhaust systems as well as the mobile power source used. Selected results obtained in a shale oil processing plant, a polymer concrete production facility and a yacht hull factory are discussed. In the case of total volatile organic compounds in oil processing units, up to 60% were removed at input energy of 21–37 J/L when the concentrations were below 500 mg/m^3. In the yacht hull factory up to 74% of styrene and methanol were removed at specific input energies around 300 J/L. In the polymer concrete production site 195 ppm of styrene were decomposed with the consumption of 1.8 kJ/L. These results demonstrate the feasibility of plasma assisted methods for treatment of VOCs in the investigated production processes but additional analysis is needed to improve the energy efficiency.

1 Introduction

Industrial processes often are sources of gaseous emissions entering the atmosphere and endangering human health and the environment. State-of-the art industrial exhaust treatment systems for exhaust gases are often efficient for the removal of pollutants [1] but usually require large scale installations and, moreover, suffer from the lack of flexibility in treating exhaust gases, strongly and fast varying in concentrations of pollutants and volumes of gas flow. Non-thermal plasma technology is well known to be useful for the decomposition [2,3] of volatile organic compounds (VOCs) which together with oxides of sulphur and nitrogen (SO_x and NO_x) belong to the pollutants most important regarding the amount of emission and hazardous potential. The literature provides many laboratory results for the successful and efficient removal of hydrocarbons, like toluene, benzene, acetone and formaldehyde

to mention only a little [4–6]. Industrial applications are reported mainly using corona discharges [7,8].

Despite of this, the application of dielectric barrier discharges (DBDs) is also quite promising because of their simple mechanical and electrical setup. For the plasma reactor itself inexpensive materials like stainless steel mesh and phlogopite plates can be used. For electrical operation in the simplest case a net frequency step up transformer is sufficient. One of the most important drawbacks for DBDs, the back pressure, can be limited with proper electrode configuration [9,10].

This contribution reports the use of a DBD reactor for treatment of exhaust gases in industrial processes. The aim of the experiments was to investigate the feasibility of the non-thermal plasma system in rough ambient conditions. The results give evidence that a proper tailored non-thermal plasma device can improve the performance of gas cleaning systems significantly.

2 Experimental

The experiments were performed at different industrial facilities in Estonia and Poland. Therefore, a mobile

[a] e-mail: M_Schmidt@inp-greifswald.de
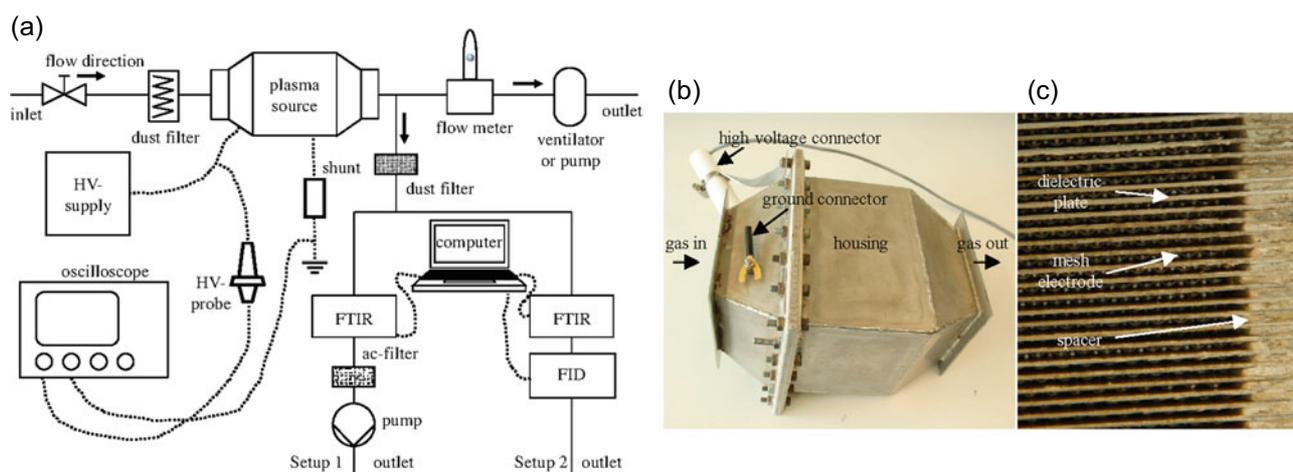
Fig. 1. (a) Experimental setup; (b) photograph of the plasma reactor; (c) detailed electrode configuration.

experimental apparatus applicable in industrial environments was designed. This apparatus mainly consisted of devices for plasma generation and gas diagnostics. The scheme of the used apparatus is depicted in Figure 1a.

As shown, the plasma generation part consisted of the plasma reactor itself, a high voltage power supply, and the electrical diagnostics to measure and control the electrical power input. The plasma reactor was a so-called stacked DBD reactor and consisted of 50 stainless steel mesh electrodes separated by dielectric plates made of phlogopite (magnesium mica) [9] (Fig. 1c). The electrode configuration was mounted in a stainless steel housing with variable gas connections, a high voltage feed-through, and a ground connector (Fig. 1b). For the electrical diagnostic digital oscilloscopes (Tektronix DPO 4104, LeCroy WaveRunner 6100A) and high voltage probes (Tektronix P6015A, LeCroy PPE 20 kV) were used. The high voltage probes were connected directly to the voltage driving the plasma reactor. The current was derived either by reading the voltage drop over a low inductance, current viewing resistor, connected between the grounded electrodes and protected earth, and dividing the obtained value by its resistance of 50 Ω or by a LeCroy CT031 hall effect sensor. These values were recorded by the oscilloscopes. By multiplying and averaging voltage and current for an even number of periods the power input into the plasma reactor was derived [11]. The plasma reactor was energized either with a laboratory programmable power supply (Chroma 61604) with an impedance matched high voltage transformer or by a highly efficient resonant power supply [12].

The topology of the resonant power supply is sketched in Figure 2. The device consisted of a full bridge converter stage and a resonant circuit stage. The initial converter stage transformed the AC-voltage of the supply grid (grid frequency of 50 Hz) into high frequency AC- and finally to DC-voltage. The controllable DC-voltage enabled the output power control. It was transformed back into AC-voltage with the resonance frequency of the power supply – plasma reactor system (around 1 kHz, depending on its capacitance) by means of the secondary resonant unit and

a high voltage transformer. The secondary stage controlled the output voltage highly efficient using the zero-current switching technique.

The gases to be treated and analyzed were sucked by a pump or a ventilator from the industrial process through pipes into a bypass gas channel containing the plasma reactor and the gas analytic devices. The realized gas flow varied between 300 L/h and 10 m^3/h. The temperature of the gases was around room temperature. For gas analysis mainly an FTIR (fourier transform infrared) spectrometer (Bruker Alpha, optical path length 5 m, spectral resolution 1 cm^{-1}, cell temperature 40 °C) was used. For some measurements, an FID (flame ionization detector, Testa 2010T) was used to measure the total amount of hydrocarbons. Furthermore samples were taken with adsorption tubes which were later analyzed by means of GC-MS (gas chromatography coupled with a mass spectrometer detector unit). Filters were used to avoid particulate matter like dust or soot entering the experimental setup.

3 Results and discussion

3.1 Shale oil processing plant

The experiments at the shale oil processing plant in Estonia were performed with setup 1 (see Fig. 1a) and the laboratory power supply. Additional gas samples for the GC-MS analysis were taken simultaneously before and after the plasma reactor. Different measuring points were chosen to investigate the effect of non-thermal plasma on the removal of the gaseous VOC species at several sites in the processing plant. The presented results were taken from absorbers used for exhaust gas cleaning. The plant work was not effected during the experiments which resulted in occasional increases in the VOC concentrations during certain processing states. The composition of the exhaust gas and flow rates also changed during the measurement campaigns.

The GC-MS data obtained at the first two measuring points show, that the composition of the gas was a
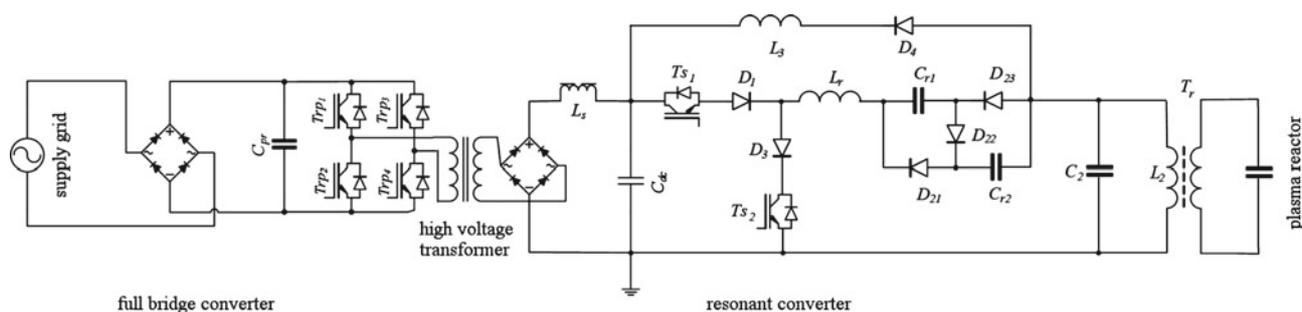
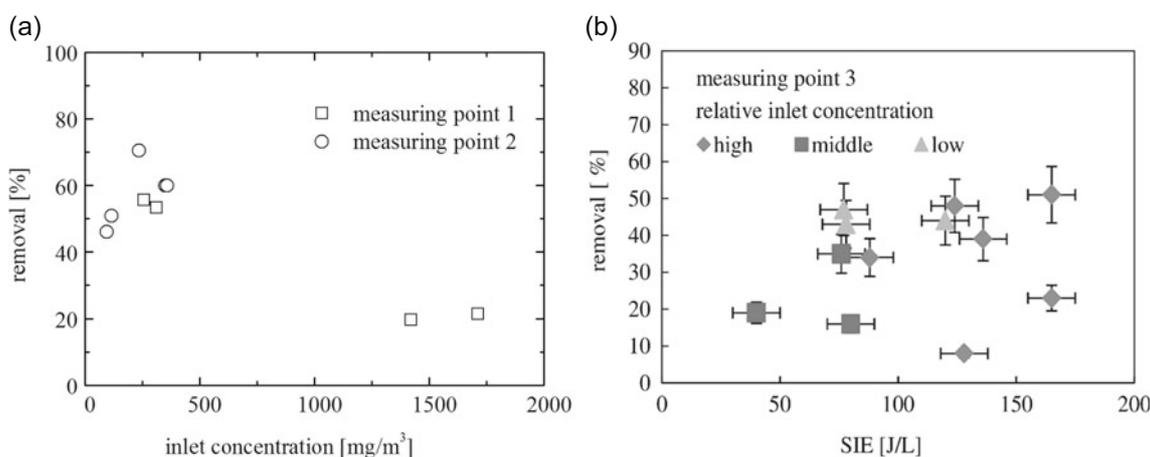**Fig. 2.** Topology of the highly-efficient, resonant power supply.

Fig. 3. (a) Removal efficiency for varying inlet concentrations of VOCs at two different measuring points. SIE was 21–25 J/L for measuring point 1 and 32–37 J/L for measuring point 2; (b) removal efficiency for varying inlet concentrations at measuring point 3 with respect to the applied SIE.

complex mixture of different VOCs, namely various alkanes, alkenes, dienes, aromatic compounds, etc. According to the quantitative results of the GC-MS, aromatic VOCs contributed to about 2–3% of the total amount of VOCs by mass density, whereas the rest of the VOCs were mostly aliphatic. In general, the removal of the total amount of VOCs was more efficient compared to the decomposition of aromatic VOCs alone. The amount of removed VOCs and the removal efficiency (percentage of removed VOCs) as a function of the inlet VOC concentration is shown for these two measuring points in Figure 3a. For these experiments the specific input energy (SIE), calculated according to equation (1) was kept between 21 and 37 J/L.

$$\text{SIE}\left[\frac{J}{L}\right] = \frac{\text{power input[W]} \times 3600}{\text{gas flow}\left[\frac{L}{h}\right]}. \tag{1}$$

The absolute amount of removed VOCs increased with inlet VOC concentration and the removal efficiency was 50–60% when the total VOC concentration remained below 500 mg/m^3. In one case, the removal efficiency reached 70% which is attributable to a somewhat higher SIE value. At higher inlet VOC concentrations, the removal efficiency decreased to 20% even if the SIE was kept at the highest value of about 37 J/L. In the case of aromatic compounds, the removal rate remained smaller

and was 15–40%. The decrease of the removal percentage at high inlet concentration level was at least partially explainable by different compositions of the process gas mixture because the increase in the concentration of VOCs is accompanied by change of the ratio of aromatic to aliphatic compounds.

Figure 3b shows the VOC removal rate for the experiments at a third measuring point where the applied SIE was varied in the range of 40–160 J/L. These data are based on the FTIR measurements. The removal rate increases slightly with increasing SIE and saturates at 100 J/L independent of the relative inlet concentration. FTIR spectra from measuring point 3 are presented in Figure 4. The FTIR-spectra represent the untreated (solid lines) and plasma treated (dashed-dotted lines) process gas. The marked absorption lines regard to methane and the C-H-stretching of compounds lacking of carbon double bonds superimposed with methane absorption lines.

The decrease in concentration of VOCs in general during plasma on condition is clearly observable, although methane is almost not affected. It is known from literature that methane is a rather stable molecule not well affected by plasma treatment [13]. The change in VOC concentration was calculated according to equation (2) where VOC is the area of the analyzed absorption band or the concentration of the corresponding compound, if calibration
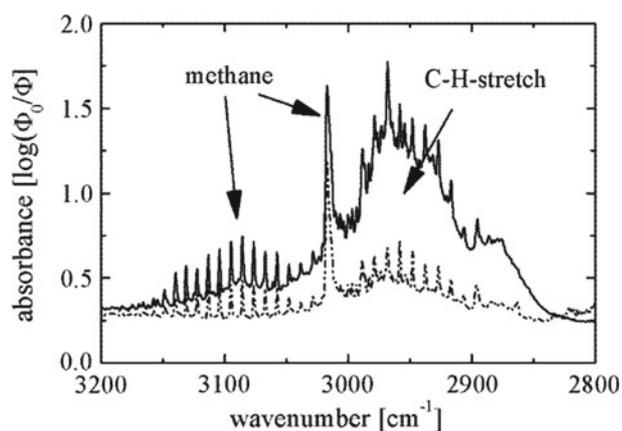
Fig. 4. FTIR-spectra taken at measuring point 3 without plasma (solid line) and with plasma (dashed dotted line).
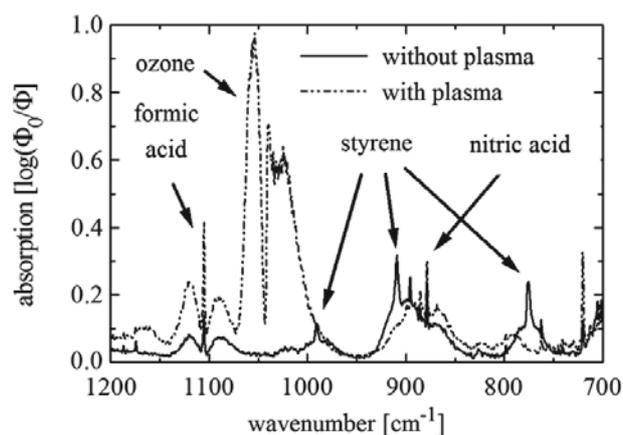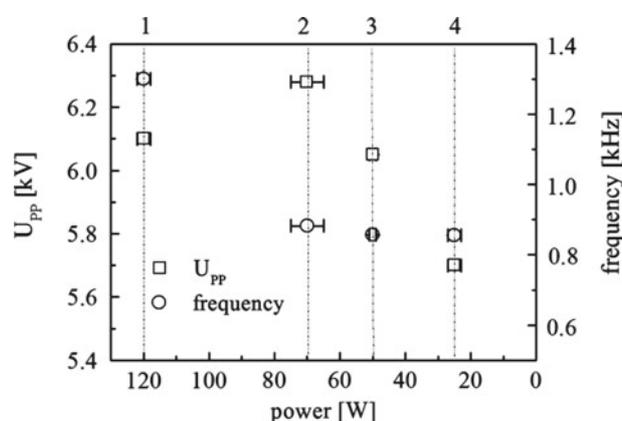
spectra were available.

$$\Delta[\text{VOC}] = \left(1 - \frac{[\text{VOC}]}{[\text{VOC}]_0}\right) \times 100\%. \qquad (2)$$

The GC-MS analysis confirmed the FTIR-results and showed that the removal of unsaturated hydrocarbons is much more efficient compared to the removal of saturated hydrocarbons. Both FTIR and GC-MS results obtained from plasma treated gas contained peaks corresponding to partially oxidized species like acetaldehyde and acetone. The FTIR also showed peaks corresponding to ozone and N_2O known as typical products of DBDs operated in air [14]. The concentrations of ozone remained below 200 ppm.

3.2 Polymer concrete production plant

The experiments at the polymer concrete production plant in Poland were performed with setup 1 and the mobile efficient resonant power supply. The flow rate was set to approximately 300 L/h and the power to around 150 W, giving after equation (1) a specific input energy of SIE $\approx$ 1.8 kJ/L. The target pollutant was styrene which is known to be decomposed by dielectric barrier [15] and corona discharges [16]. By the analysis of the FTIR-spectra (samples are presented in Fig. 5) this compound was clearly identified with a concentration of 195 ppm. The solid line in Figure 5 relates to the untreated process gas. The absorption bands of styrene are marked. Additional absorption bands were found and identified as formic acid and nitric acid. The concentration of formic acid increases under plasma on condition, meaning that additional to the already present formic acid, as a polluting compound of the process gas, more formic acid is generated through decomposition of styrene. A change in the concentration of nitric acid by plasma treatment could not be detected, although it is a known by-product of non-thermal plasmas operated in humid air [17]. To summarize the results, a significant effect on styrene as the main pollutant molecule by means of plasma treatment could be measured.

Fig. 5. Samples of FTIR-spectra of the untreated (solid line) and plasma treated (dashed-dotted line) process gas.


Fig. 6. Self adjusting of operational voltage and frequency according to the power settings, at the top of the graph the number of plasma on phase is marked.

The main by-products of plasma treatment are formic acid and ozone, which requires further processes of exhaust gas treatment.

3.3 Yacht hall production factory

For the measurements at the yacht hall production factory in Poland experimental setup 2 with the mobile power supply was used. The target pollutant was styrene but the analysis revealed methanol as an additional pollutant. Due to the quite stable process conditions of the industrial site, different power settings of the power supply could be analyzed. The plasma reactor was switched on four times with decreasing power as shown in Figure 6. The graph shows the self-adjustment of the operational voltage and frequency according to the power settings. The DC-link voltage was controlled using a PI-type controller. On the top of the graph the number of the plasma on phase is marked. Together with the gas flow of around 300 L/h the power settings deliver specific energy inputs between 1.4 kJ/L (phase 1) and 0.3 kJ/L (phase 4).

The concentrations of the pollutants under plasma off and plasma on conditions are given in Figure 7a.
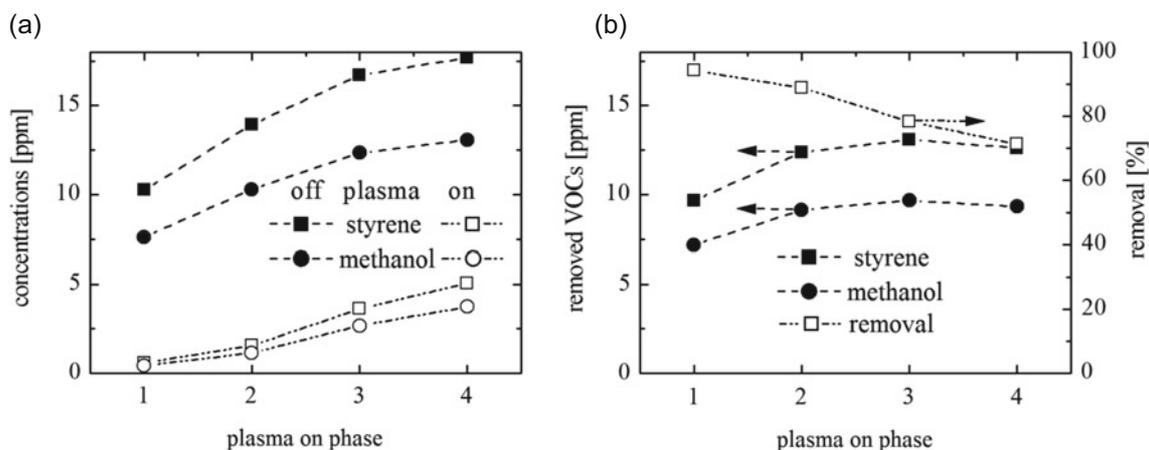
Fig. 7. (a) Concentrations of styrene (boxes) and methanol (circles) without plasma treatment (full symbols) and with plasma treatment (empty symbols); (b) removed amount of styrene (full boxes) and methanol (full circles) together with the percentage overall removal of both VOCs (empty boxes).

The concentrations of the pollutants increased during the measurements steadily by a factor of around 2. The concentrations of the pollutants during the plasma on phase increased also showing that saturation of removal is reached. This is depicted in Figure 7b. Although the power driving the plasma reactor decreased to 20% of the power used in the first plasma on phase the amount of removed VOCs stays around 13 ppm and 8 ppm for styrene and methanol, respectively. These results correspond to an overall VOC removal of more than 70%. More detailed information on these experiments can be found in reference [18].

4 Conclusion

The applicability of non-thermal plasma generated by dielectric barrier discharges for the removal of volatile organic compounds from industrial process gases was investigated. The process gases were found to consist of various VOCs like styrene, methane and methanol sometimes accompanied by inorganic compounds like nitrogen oxides, nitric acid and carbon oxide additional to the always present carbon dioxide and water. Polluting VOCs were removed with varying efficiencies, mostly depending on the inlet concentration, specific input energy and the pollutant itself. The decomposition of aromatic compounds was found to be less effective than the decomposition of VOCs in general. The experiments showed that the applicability of a dielectric barrier discharge reactor and sensitive laboratory equipment in industrial processes with proper means of protection is feasible. In general, the results show similar trends as the results found in the literature [6,16] but the consumed energy is higher. This is thought to be due to the more complex gas mixtures found in real exhaust gases. These contain, in contrast to the usually investigated laboratory gas mixtures, significant amounts of carbon dioxide, water and sometimes even particles which are also affected by the plasma and thus, consume energy which is missing for the conversion of the target pollutants.

For further experiments the influence of particulate matter should be taken into account as well as the possibility to combine the plasma reactor with catalysts and/or scrubbers. Since the non-thermal plasma technology is an on-demand technology, usable without significant switching-on time, it is a proper means to assist already installed exhaust cleaning technologies handling pollutions varying strong in concentration and time.

References

1. L.K. Wang et al., *Handbook of Environmental Engineering Volume 1 Air Pollution Control Engineering* (Human Press, Totowa, 2004)
2. H.H. Kim, Plasma Processes Polym. **1**, 91 (2004)
3. A. Fridman, *Plasma Chemistry* (Cambridge University Press, Cambridge, 2008)
4. A. Mizuno, I. J. PEST **3**, 1 (2009)
5. M. Schiorlin et al., Environ. Sci. Technol. **43**, 9386 (2009)
6. A. Vandenbroucke et al., J. Hazard. Mater. **195**, 30 (2011)
7. Y. Kawai et al., *Industrial Plasma Technology* (Wiley VCH, Weinheim, 2010)
8. A. Mizuno, Plasma Phys. Control. Fusion **49**, A1 (2007)
9. S. Müller et al., Contrib. Plasma Phys. **47**, 520 (2008)

10. M. Schmidt et al., Plasma Chem. Plasma Process. **33**, 323 (2013)
11. K.-D. Weltmann et al., Pure Appl. Chem. **82**, 1223 (2010)
12. T. Jakubowski et al., Eur. Phys. J. Appl. Phys. **61**, 24304 (2013)
13. B. Pietruszka et al., Appl. Catal. A **261**, 19 (2004)
14. U. Kogelschatz, Plasma Chem. Plasma Process. **23**, 1 (2003)
15. G.K. Anderson et al., Plasma Chem. Plasma Process. **19**, 131 (1999)
16. X. Zhang et al., IEEE Trans. Plasma Sci. **39**, 1482 (2011)
17. R. Brandenburg et al., Contrib. Plasma Phys. **54**, 202 (2014)
18. M. Schmidt et al., Int. J. Environ. Sci. Technol. (published online) DOI: 10.1007/s13762-015-0814-1