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Plasma-Based Depollution of Exhausters: Principles, State of the Art and Future Prospects

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1. Introduction

Nowadays non-thermal plasma technologies are state of the art for the generation of ozone as an important oxidant for water cleaning or bleaching, the incineration of waste gases or for the removal of dust from flue gases in electrostatic precipitators. Furthermore their possibilities of gas depollution are well known. Plasmas contain reactive species, in particular ions, radicals or other oxidizing compounds, which can decompose pollutant molecules, organic particulate matter or soot. Electron beam flue gas treatment is another plasma-based technology which has been successfully demonstrated on industrial scale coal fired power plants. This chapter aims a comprehensive description of plasma-based air remediation technologies. The possibilities of exhaust air pollution control by means of non-thermal plasmas generated by gas discharges and electron beams will be summarized. Therefore plasma as the 4th state of matter, its role in technology and the principle of plasma-based depollution of gases will be described. After an overview on plasma-based depollution technologies the main important techniques, namely electron beam flue gas treatment, gas discharge generated plasmas including plasma-enhanced catalysis and injection methods will be described in separate sections. In these sections selected examples of commercially available or nearly commercialised processes for flue gas treatment or the removal of volatile organic compounds and deodorization will be described, too. Current trends and concepts will be discussed.

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2. Plasmas and plasma-based depollution technologies

In physics and chemistry, plasma is an ionised gas containing free electrons, ions and neutral species (atoms and molecules) characterized by collective behaviour. Plasma is often referred as the “4th state of matter” since it has unique physical properties distinct from solids, liquids and gases. In particular, due to the presence of charge carriers plasmas are electrically conductive and respond strongly to electromagnetic fields. It contains chemically reactive media as well as excited species and emits electromagnetic radiation in various wavelength regions. The majority of matter in the visible universe (stars, interplanetary and interstellar medium) is in the plasma state. Lightnings, sparks, St'Elmos fires and the polar aurorae are examples for natural terrestrial plasmas. Furthermore, since more than 150 years plasmas are generated artificially by supplying energy to gases, liquids or solids. Such plasmas are used and under investigation for various applications, e.g. surface modification, chemical conversion, light generation or controlled nuclear fusion. Natural as well as artificial plasmas cover an extremely wide range of parameters like temperatures, particle densities and pressure. Broadly speaking, plasmas can be distinguished into thermal and non-thermal plasmas. In thermal plasmas all present species (electrons, ions and neutral species) are in the local thermal equilibrium, i.e. all species have the same mean free kinetic energy (temperature). Such plasmas are produced in fusion experiments with temperatures higher than $10^4$ K. Contrary, in other situations most of the coupled energy is primarily released to the free electrons which exceed the temperatures of the heavy plasma components (ions, neutrals) by orders of magnitude. Such mixtures of energetic electrons in a relatively cold mass of ions and neutrals are called non-thermal or non-equilibrium plasmas. If the gas temperature stays nearly at or slightly above room temperature the plasma is termed “cold plasma”. Even in non-equilibrium plasmas the gas temperature can increase to some $10^3$ K. In such cases it is called “hot non-thermal plasma” or “translational plasma” since it marks the transition to the thermal regime. In fact cold as well as translational plasmas are used for gas depollution.

The most common method for plasma generation for technological and technical application is by applying an electric field to a neutral gas. If the applied field exceeds a certain threshold (breakdown field strength) a gas discharge and thus plasma is formed. There are many different designs of plasma sources for depollution and the most important will be described in the next two sub-sections. Alternatively by the interaction of an electron beam with gaseous medium plasma can be generated. Such electron beam generated plasmas are used in the so-called electron beam flue gas treatment, which is further described in section 3 of this chapter.

2.1 Plasma-based depollution by means of “hot” plasmas

Plasma pollution control can be done by an increase of the gas enthalpy by means of hot (i.e. thermal or translational) plasmas. Such plasmas are widely used for the incineration of gaseous but also liquid and solid waste. An overview is given in (Hammer, 1999). Typical examples are high-intensity arc or plasma torches. Electric arcs discharges are driven between two electrodes (see fig. 1 a) by high current (10 to 1000 A). Thus in arc plasmas high energy and current densities are reached ($10^7$–$10^9$ J m$^{-3}$; $10^7$–$10^9$A m$^{-2}$). High-current arcs at atmospheric pressure can be characterized as thermal plasmas reaching temperatures in the range 5,000–50,000 K (Kogelschatz, 2004), which makes them very useful for material processing (welding, cutting, spraying) and waste treatment.
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Fig. 1. General schemes of thermal and translational plasmas (a) free burning arc discharges in vertical and horizontal configurations; (b) plasma torch; (c) gliding arc

In plasma torches (also referred to as plasmatrons or plasma guns) the electrical energy is coupled into the working gas inside a nozzle and a high gas flow leads to the expansion outside the nozzle as a plasma jet (fig. 1 b). A large variety of plasma torches has been developed. The majority of commercial torches uses direct current arc, inductively coupled radio frequency discharges or microwave excited plasmas as the heat source and atmospheric-pressure air as working medium. The power consumption of plasma torches is in the range of several kW up to some MW. As a very rough estimation, the energy costs for conversion of noxious compounds is about 20 eV/molecule. This corresponds to 0.1 to 1 kg/kWh, a value which is comparable to that obtained in non-thermal plasmas (Hammer, 1999). Gliding arcs (fig. 1 c) are another example for translational plasmas studied for gas depollution and other applications. They consist of at least two diverging electrodes which are passed by a gas flow. The discharge starts at nearest distance between the electrodes, is spreading by gliding along the electrodes in the direction of the gas flow which leads to cooling of the plasma.

Microwave driven plasma torches at atmospheric pressure are typical examples for translational plasmas (non-thermal plasmas at elevated gas temperatures up to 4,000 K). However the gas temperature is high enough to decompose stable organic molecules. In particular nozzle-type microwave plasma source (MPS) (see e.g. Jasinski et al., 2002) has been used for the destruction of gaseous pollutants - mainly vapours of organic solvents - of relatively high concentration, up to tens of vol.%. The nozzle-type MPSs first appeared as structures based on microwave coaxial line components (see e.g. Cobine & Wilbur, 1951) where the microwave plasma was induced in the form of a plasma “flame” at the open end of a rigid coaxial line, at the tip of its inner conductor. The power-handling capability of coaxial-line-based microwave discharges is generally limited to much less than 1 kW due to the low thermal strength of the coaxial line components. Parallel with the coaxial-line-based nozzle-type MPSs so-called waveguide-based nozzle-type MPSs have been developed (e.g. Yamamoto & Murayama, 1967; Moisan et al., 1994, 2001). In these applicators the microwave plasma is also induced in the form of a plasma flame at the tip of a field-shaping structure that is similar to that of the coaxial line based MPSs. However, the microwave power is fed into this structure from a waveguide, usually rectangular at 2.45 GHz. In advanced devices, the microwave power is delivered to the field-shaping structure in form of a conductor with a conical nozzle through a waveguide with a reduced-height section (fig. 2 a).
Fig. 2. Sketches of the waveguide-based cylinder-type MPS (a) and waveguide-based nozzle-type MPS (b). Dimensions are given in mm.

Since both microwave discharges, the coaxial-line-based and waveguide-based one, are gas flowing systems, they are particularly suitable for processing various gases or materials carried by gases. Recently, a new MPS was developed (e.g. Uhm et al., 2006) based on the rectangular waveguide with a reduced-height section, where the discharge is generated inside of a dielectric cylinder with a swirl flow of the working gas. There are no nozzles in the system (see fig. 2 b). It was successfully used for destruction of refrigerant HFC 134a (Jasinski et al., 2009) with destruction mass rate and corresponding energetic mass yield of up to 34.5 kg h⁻¹ and 34.4 kg per kWh of microwave energy absorbed by the plasma, respectively.

2.2 Plasma-based depollution by means of “cold” non-thermal plasmas
In cold non-thermal plasmas the free energetic electrons are able to produce radicals and other reactive species (e.g. ions) which react with the pollutant molecules or particles. Furthermore, if ions can be extracted from the discharge, fine particles can be charged and thus filtered electrically from the flue gas (Grundmann et al., 2007). Additional a biological decontamination of air due to plasma treatment has been reported (e.g. Müller & Zahn, 2007).

2.2.1 Cold non-thermal plasma sources for the depollution of gases
As already mentioned, non-thermal plasmas in gas streams at atmospheric pressure can be generated in two ways. Either with the injection of a high energetic electron beam (so-called electron beam flue gas treatment, EBFGT) or the generation of a gas discharge by means of a sufficient high voltage applied to two electrodes (gas discharges). In discharge generated plasmas the electrons have lower mean energies than in electron beam produced plasmas. Thus plasma chemical reactions can differ and usually in electron beam generated plasmas the energy efficiency is better. However, discharge generated plasmas give the chance to construct more compact after treatment systems for small and medium size gas streams.
To generate plasmas with electron beams special electron accelerator units are needed. Electrons are produced via thermionic emission from a cathode and accelerated inside the vacuum tube. The electron beam transits from the beam generation environment at vacuum pressure ($10^{-5}$ mbar) into the flue gas stream at atmospheric conditions via a beam window and than through a secondary window (Chmielewski et al., 1995). Due to a beam alignment-steering system the beam will scan across or along the flue gas stream. Beam scanning and
window cooling is necessary to avoid destruction of the titanium windows. The beam acceleration ranges from 0.7 to 1.2 MeV, allowing the beam to penetrate the windows without excessive energy loss. The maximum power per accelerator available nowadays is up to 400 kW, total beam power in installations exceed 1 MW (Department of Energy, 2010). Next generation electron beam techniques use radio frequency cavity systems instead of DC transformers (Edinger, 2008). This enables pulsed driven beams with optimized energy control.

To generate plasmas by gaseous discharges several possibilities exists (Becker et al., 2005; Fridman, 2008; Kogelschatz, 2004). The most common discharge types are dielectric barrier discharges (DBDs) and corona discharges. For both types different configurations and geometries, namely cylindrical and planar, exist as shown in fig. 3. DBDs, also referred to as barrier discharges or silent discharges are characterized by the presence of at least one dielectric layer between the electrodes (Kogelschatz, 2004; Wagner et al., 2003). Typical materials for dielectric barriers are glass, quartz and ceramics. Fig. 3 a shows a so-called volume barrier discharge in cylindrical geometry. The discharge gap is usually in the range of 1 mm. Fig. 3 c is a planar surface barrier discharge, i.e. both electrodes (metal meshes) are in direct contact with the dielectric plates. Another type of DBD is the so-called coplanar discharge where both electrodes are embedded in the dielectric material. Due to the capacitive coupling of the insulating material to the gas gap DBDs can only be driven by alternating feeding voltage or pulsed DC voltages. When a sufficient voltage is applied to the electrodes, electrical breakdown occurs most commonly as number of individual discharge filaments or microdischarges (Kogelschatz, 2002). Microdischarges have a small duration (tens of nanoseconds in air), small size (diameter about 100 µm) (Brandenburg et al., 2005) and are distributed over the whole surface area. Due to the local charging of the dielectric surface after microdischarge inception the local electric field is weakened leading to the extinction of the microdischarge after several ten nanoseconds. Thus the barrier prevents the formation of a spark or arc discharge, keeping the plasma in the non-thermal regime. Despite the numerous applications of DBDs the knowledge on microdischarge development and thus plasma parameters and elementary processes within these microplasmas is not sufficient, although the multitude of subsequent microdischarges determines the efficiency and selectivity of the exhaust gas treatment.

Special feature of DBDs are so-called packed bed reactors, where dielectric or ferroelectric pellets (e.g. alumina oxide Al2O3, titanium oxide, TiO2 or barium titanate BaTiO3) are packed between two electrodes (see fig. 4; Holzer et al., 2005; Yamamoto et al., 1992). Due to spontaneous polarization of the ferroelectric a high electric field at the contact points of the pellets is formed resulting in microdischarge inception. The use of pellets is disadvantageous in terms of pressure drop but lead to uniform distribution of gas flow and plasma in the reactor. Furthermore the pellets can be used as catalyst enabling direct interaction between plasma and catalyst.

Corona discharges are characterized by a non-uniform configuration of the electric field, which is achieved by special electrode geometries, e.g. point-to-plane, wire-to-plane (see fig. 3 d) or coaxial wire-in-cylinder configurations (see fig. 3 b). The non-uniformity of the discharge gap enables breakdown at lower voltages allowing low current, non-thermal plasma channels based on the streamer mechanism. Thus coronas often show a filamentary character like DBDs. The electrode gap can be set to several centimetres, which is favourable for large scale applications and minimizes pressure drops. Corona discharges are usually DC-driven discharges, but for environmental applications they are often driven by high voltage pulses with rapid voltage rise (several kV per ns) and short duration (some tens of ns). This concept also referred to as pulsed corona discharges (PCD).
Fig. 3. Typical configurations of barrier (a, c) and corona discharges (b, d) for gas treatment (a) cylindrical asymmetric volume barrier discharge, (b) cylindrical wire-in-tube corona arrangement, (c) plate-like surface barrier discharge, (d) multineedle-plate-corona arrangement.

Fig. 4. Example of a packed bed reactor with special pellet filling.

DC-driven corona discharges are established in pollution control as electrostatic precipitators (ESP) for dust removal of flue gases. In this application the active plasma is restricted to the region closed around the wire electrode. Between this so-called active zone and the opposite electrode (so-called collecting electrode made as plate or cylinder) a passive zone of low conductivity is formed. Ions generated in the active plasma zone enter the passive zone and drift to the collecting electrode. On their way they charge solid particles or droplets which migrate to the collecting electrode. The charged particles precipitate onto the collecting surfaces, are neutralized, dislodged and removed. Various types of dust, mist, droplet etc. down to submicron size can be removed under dry and wet conditions with high efficiency and low pressure drop (Kogelschatz, 2004). Thus ESP technology uses physical aspects of corona discharge and not the chemical processes, although the promotion of plasma chemistry is possible, too. To overcome the “back corona effect” or to decrease the power consumption pulsed operation was proposed (Mizuno, 2007; H.H. Kim, 2004). The back corona effect is obtained with high resistivity dust (e.g.,...
cement particles), which leads to the formation of insulating dust layers on the collecting electrode which reduces the emissions of ions. Alternatively sulphur trioxide can be injected into the flue gas stream to lower the resistivity of the particles.

An interesting concept of corona discharge is the (corona) radical shower discharge, which was developed in particular for NOx- and later for combined NOx- and SOx-removal (Ohkubo et al., 1996; J.P. Park et al., 1999). The discharge only treats a portion of the total contaminated exhaust flow. The treated gas with plasma generated active species is then injected in the total exhaust gas flow like a shower.

Typically DBD and PCD reactors require different supply waveforms with efficiencies (i.e. overall consumed plug power vs. power dissipated into the plasma) as high as possible. DBD reactors are most often supplied using alternating, sinusoidal voltage while the corona discharge systems are pulsed supplied. In case of DBD in many cases classical 50 or 60 Hz supplies are used with high-voltage transformers (Sasoh et al., 2007; Kostov et al., 2009). Due to operating conditions higher operation frequency is often necessary in order to increase the discharge power. The average power control is critical for the yield of the chemical processes. Modern supply system designs include power amplifiers with high-voltage transformers (Francke et al., 2003; Mok et al., 2008) or many solid-state switch based power electronic converter topologies, often resonant ones (Casauve et al., 2004). Since resonant operation complicates fluent control of the output power, often a time-averaged burst (so-called pulse density modulation - PDM) technique is used (Fujita & Akagi, 1999).

Basic configurations of non-thermal plasma supply systems are depicted in fig. 5.

Fig. 5. Basic configurations of power supplies: low frequency systems (left) and high frequency systems (right).

Generally low frequency or high frequency systems are used. In the case of low frequency primary or secondary transformer side current limiting resistors are sometimes used ($R_p$ or $R_s$), in case of pulsed DC supplies sometimes a reactor current-limiting resistor is implemented ($R_{DC}$). These types of supplies usually have limited efficiency ratings (about 40% for low power systems) and due to low operating frequency large weight/volume consumption. In case of controllable systems an adjustable transformer is sometimes used. High frequency supplies usually use a rectifier as the first power electronic converter. Then different configurations and topologies are used, in many cases a high frequency - high voltage transformer (HF, HV). Sometimes additional pulse forming networks are
implemented in order to shape the output voltage waveform. Considering the supply voltage waveform itself a set of different patterns can be defined. Most common is the use of high voltage, AC, sinusoidal supply. In order to influence the average reactor power pulse density modulation technique is sometimes used. Optimization of effectiveness as well as voltage potential distribution levelling sometimes results in a discontinuous, bipolar waveforms.

Pulsed high voltage power supply systems are constructed in a variety as large as in the case of AC sources. In case of large installations, due to high peak values of voltage (up to several MV) and current (up to 0.5 MA), pulse modulators are constructed implementing pulsed thyristors, gas switches (thyratrons, krytrons) or spark gap switching apparatus. These technologies however, due to the principle of operation allow only a low frequency of operation and a limited lifetime. Classical constructions often implement the so called Marx generator topology (Marx, 1928) and Fitch generator topology (Fitch et al., 1968) in connection with magnetic pulse compression, which reaches efficiency rating of up to 76 %. Solid state technology enables much higher operating frequencies and very long lifetime but have a limitation of maximum allowable blocking voltage and maximal repeatable peak current per single power semiconductor. Typically high voltage MOSFET transistors and HV IGBT transistors are used for power electronic supply systems. In order to overcome single element limitations power switching stacks are produced. Nowadays typical efficiency values of up to 96 % are possible.

New concepts of non-thermal plasma sources for the treatment of gases are fused hollow cathodes (FHC). The FHC cold atmospheric plasma source is based on the simultaneous generation of multiple hollow cathode discharges in an integrated open structure with flowing gas (Barankova & Bardos, 2002; 2003). The hollow cathode discharges are non-thermal because of the population of high energy electrons due to the pendulum motion of accelerated electrons between the repelling space charge sheaths at the opposite walls either in cylindrical or planar configurations. For operation at atmospheric pressure small hollow cathode inner diameters (about 200 to 400 µm) are required. The operational stability of the FHC systems is excellent; the plasma is uniform and does not exhibit streamers. The FHC systems allow generation of cold plasma in both monoatomic and molecular gases and the upstream FHC concept with aerodynamic stabilization was successfully tested for gas conversion. The power consumption of FHC has been reported to be about 1–3 orders lower than for other non-thermal atmospheric plasma sources. The FHC design for conversion experiments is based on experimental results obtained with a tuneable radial cathode slit system and different FHC structures (Barankova & Bardos, 2010). A minimum separation of the cathode walls depends both on the type of the gas (monoatomic or molecular) and on the type of generation (pulsed DC or radio frequency). Beside gas conversion the concept has been successfully used for surface treatment, activation and cleaning of temperature-sensitive materials.

2.2.2 Fundamentals

Chemical processes in non-thermal plasmas are based on non-thermal activation of particles via collisions. The quality and quantity of collisions is determined by the density and the kinetic parameters (e.g. mean velocity, collision frequency). In general three different phases has to be distinguished. The first phase is characterized by the electrical breakdown of the gas (e.g. in form of short-lived microdischarges as described above) where free electrons with high kinetic energies are produced via ionising collisions. These electrons undergo further electron-
molecule collisions, namely ionisation (1, 3), dissociation (2, 3), excitation (4) and electron attachment (7). Furthermore Penning-ionisation and dissociation (5, 6); charge transfer (8) and ion reactions are possible. All mechanisms have quite different reaction rates due to its different energy thresholds. For example for dissociation energies between 3 and 10 eV are sufficient, while ionisation requires energies more than 10 eV and electron attachment happens at energies of some eV or lower. Indeed, the exact values are determined by the electronic configuration of the molecule being considered. The reaction rate further depends on the gas temperature which depends on the vibrational excitation level of molecules. The second stage of non-thermal plasma chemistry is the radical formation and removal stage, where a multitude of anorganic reactions takes place. In particular radicals are generated through direct electron impact molecule dissociation and ionization as well as ion-molecule reactions (10), dissociate recombination of ions and electrons (11), attachment and detachment reactions (12) (Chang, 2008).

| Reaction Type          | Equation                                                                 |
|------------------------|--------------------------------------------------------------------------|
| Ionisation             | \( AB + e^- \rightarrow AB^+ + 2e^- \)                                  |
| Dissociation           | \( AB + e^- \rightarrow A + B + e^- \)                                  |
| Dissociative ionisation| \( AB + e^- \rightarrow A^+ + B + 2e^- \)                              |
| Excitation             | \( AB + e^- \rightarrow AB^* + e^- \)                                   |
| Penning-Ionisation     | \( M^* + A_2 \rightarrow A_2^+ + M \)                                  |
| Penning-Dissociation   | \( M^* + A_2 \rightarrow 2A + M \)                                     |
| Attachment             | \( AB + e^- \rightarrow AB^- \)                                         |
|                        | \( AB + e^- \rightarrow A^- + B \)                                      |
| Charge transfer        | \( AB^+ + C \rightarrow AB + C^+ \)                                     |
| Recombination          | \( AB^+ + e^- \rightarrow AB \)                                         |
|                        | \( A^+ + B^- \rightarrow AB \)                                          |
| Ion-Molecule reaction  | \( I^+ + AB \rightarrow \text{products} \)                              |
| Dissociate recombination| \( AB^+ + e^- \rightarrow \text{products} \)                           |
| Detachment             | \( AB^- \rightarrow A + B + e^- \)                                      |

In air plasmas reactive oxygen species are generated by direct electron collisions (13-16), via Penning-processes (17-19) and charge exchange (20) with subsequent ion-molecule reaction.
(21) from O₂ and H₂O. Furthermore in non-thermal plasmas generated in oxygen containing atmospheres at low gas temperatures ozone, and other a strong oxidizing agents like O, *OH and HO•₂ will be formed.

\[
e^− + O₂ \rightarrow 2 O(^{1}P) + e^− \quad (13)
\]

\[
e^− + O₂ \rightarrow O(^{3}P) + O(^{1}D) + e^− \quad (14)
\]

\[
e^− + O₂ \rightarrow O₂(^{1}Δ) + e^− \quad (15)
\]

\[
e^− + H₂O \rightarrow O^• + •OH + e^− \quad (16)
\]

\[
N(^{2}D, ^{3}P) + O₂ \rightarrow O(^{3}P) + NO
\]

\[
N(^{2}D) + H₂O \rightarrow •OH + NH \quad (17)
\]

\[
O(^{1}D) + H₂O \rightarrow 2 •OH \quad (18)
\]

\[
N₂(A) + H₂O \rightarrow •OH + H + N₂ \quad (19)
\]

\[
M^+ + H₂O \rightarrow M + H₂O^+ \quad (20)
\]

\[
H₂O^+ + H₂O \rightarrow •OH + H₃O^+ \quad (21)
\]

\[
O₃ + •OH \rightarrow HO•₂ + O₂ \quad (22)
\]

\[
H + O₂ + M \rightarrow HO•₂ + M \quad (23)
\]

Many molecules are readily attacked by free radicals. Decomposition of hazardous compounds is archived without heating of the flue or off-gas. Due to the presence of oxygen, water vapour and ozone, oxidizing reactions are dominant. The resulting chemistry is quite complex and depends on the gas mixture itself as well as the temperature. A complete description of all processes is outside the scope of this chapter and only the main important aspects will be discussed in the following. For more detailed and comprehensive information the reader is referred to several books and review papers, e.g. (Fridman, 2008; Penetrante & Schultheiss, 1993; H.H. Kim, 2004; Chang, 2008). Regarding the removal of saturated hydrocarbons (denoted as RH, e.g. alkane), the process start with dehydrogenization reactions (24, 25) followed by the oxidation of the remaining organic radical R• (26). The latter reaction result in the formation of peroxy radicals RO•₂ (26) which are further oxidized down to CO₂ and H₂O (total oxidation) or trigger a radical chain reaction with alkyl hydroperoxide radicals R-OOH (27). In case of unsaturated hydrocarbons additionally radical addition following oxidation, radical chain reaction or polymerisation of hydrocarbons are taking place.

\[
R-H + O^• \rightarrow R^• + •OH \quad (24)
\]
\[ \text{R-H} + \cdot\text{OH} \rightarrow \text{R}^* + \text{H}_2\text{O} \quad (25) \]

\[ \text{R}^* + \text{O}_2 \rightarrow \text{R-OO}^* \quad (26) \]

\[ \text{R}_\gamma\text{-OO}^* + \text{R}_\gamma\text{H} \rightarrow \text{R}_\gamma\text{OOH} + \text{R}_\gamma^* \quad (27) \]

In plasma-based flue gas treatment for NO and SO\textsubscript{2} removal desired reductive reaction paths are of minor importance. Oxidative processes (28 - 30) lead to the formation of NO\textsubscript{2}. The oxidation up to N\textsubscript{2}O\textsubscript{5} is possible (see section 5). If hydrocarbons are present (e.g. ethene, propene, propane) HO\textsuperscript{2} and peroxy radicals become the dominant oxidizers (30, 31) and the energy required to oxidize NO molecule can be reduced. However, to remove NO\textsubscript{x} from the gas a heterogeneous chemical process for NO\textsubscript{2} reduction must follow the plasma treatment. In a similar way SO\textsubscript{2} oxidation to SO\textsubscript{3} by means of plasma treatment is possible, while SO\textsubscript{3} needs to be removed chemically.

\[ \text{NO} + \text{O}^{(3P)} + \text{M} \rightarrow \text{NO}_2 + \text{M} \quad (28) \]

\[ \text{NO} + \text{O}_3 + \text{M} \rightarrow \text{NO}_2 + \text{O}_2 + \text{M} \quad (29) \]

\[ \text{NO} + \text{HO}_2 + \text{M} \rightarrow \text{NO}_2 + \cdot\text{OH} + \text{M} \quad (30) \]

\[ \text{NO} + \text{R-OO}^* \rightarrow \text{NO}_2 + \text{R-O}^* \quad (31) \]

Following the removal stage aerosol particles are formed through reaction of larger radicals with cluster ions and molecules. Aerosol formation is a quite important process since aerosol surface reaction rate is a few orders of magnitude higher then the electronic, ionic and radical reactions. The removal processes are promoted due to heterogeneous reactions. Regarding SO\textsubscript{2} the stimulation of chain oxidation mechanism by plasmas in liquid droplets or ionic clusters at humid gas conditions is known (see Fridman, 2008).

In order to compare different concepts and technologies different aspects must be considered. The main focus is the efficiency evaluation, but costs for investment and operation (warranty intervals, consumption of additives) need to be taken into account, too. Several examples are described, see (Chang, 2008) and references therein. There is no universal parameter for the energy efficiency and the conditions of operation in research and application vary to a great extend. Most widely used parameters are the Specific Input Energy (SIE, or specific energy density SED) and the G-value. The SIE is the dissipated discharge power divided by the gas flow rate \(Q\) (32). In general the gas flow rate \(Q\) relates to standard or normal conditions (Temperature \(T_N=273.15\) K, pressure \(p_N=100\) kPa) and SIE is given in J/sl or kWh/Nm\textsuperscript{3}. The SIE is a reliable scaling parameter and together with the energy efficiency of pollutant removal \(\eta\) (also referred too as energy yield, i.e. mass of removed pollutant \(\Delta m_{\text{Pol}}\) divided by consumed energy of the plasma \(E_{\text{PL}}\)) a good economic evaluation can be done by \(\eta(SIE)\) characteristics (Chang, 2008). It should be mentioned again, that a comprehensive evaluation must consider the efficiency of the power supply transformation, too (i.e. \(P_{\text{tot}} > P_{\text{PL}}\)).
The G-value is adapted from radiolysis and refers to the number of molecules of reactant consumed per 100 eV of energy absorbed (Baird et al., 1990; Penetrante et al., 1996). It is defined as given in (34), where A is removed specie, $\beta_A$ percentage of destroyed contaminants, $p_A$ partial pressure of A, $N_0$ Avogadro constant, E used energy and R gas constant. In plasmas G-value gives the number of radicals generated per 100 eV. Another value to be considered is the chemical selectivity $S_A$ of one possible chemical product A. It is given by the ratio of its concentration (or number density of molecules etc.) and the sum of concentrations of all possible products of one reaction.

3. Electron beam flue gas treatment (EBFGT)

Electron beam flue gas treatment technology is one among the most promising advanced air pollution control techniques. EBFGT is a dry-scrubbing process of simultaneous SO$_2$ and NO$_x$ removal, where no waste (except by-products) is generated. The main components of flue gases are N$_2$, O$_2$, H$_2$O, and CO$_2$, with SO$_x$ and NO$_x$ in much lower concentrations. Ammonia NH$_3$ may be present as an additive to support the removal of SOx and NOx. The electron energy is transferred to the gas components present in the mixture in proportion to their mass fraction. The fast electrons slow down by collisions, secondary electrons are formed which plays an important role in overall energy transfer and the plasma is formed in the flue gas. Then, fast electrons interact with gas creating various ions and radicals, the primary species formed include N$_2^+$, N$^+$, O$_2^+$, O$^+$, H$_2$O$^+$, OH$^+$, H$^+$, CO$_2^+$, CO$^+$, N$_2^*$, O$_2^*$, N, O, H, OH, and CO. In case of high water vapor concentration the oxidizing radicals •OH, HO$_2^*$ and O(3P) as well as excited ions are the most important products. These species take part in a variety of ion-molecule reactions, neutralization reactions, dimerization etc. SO$_2$, NO, NO$_2$, and NH$_3$ cannot compete with the reactions because of very low concentrations, but react with N, O, •OH, and HO$^*$ radicals. After humidification and lowering of the temperature, flue gases are guided to reaction chamber, where irradiation by electron beam takes place. NH$_3$ is injected upstream of the irradiation chamber. There are several pathways of NO oxidation known. In the case of EBFGT the most common are as follows (Tokunaga & Suzuki, 1984):

\[
\text{NO} + \text{O}_2^\text{(3P)} + \text{M} \rightarrow \text{NO}_2 + \text{M} 
\]

\[
\text{O}_2^\text{(3P)} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} 
\]

\[
\text{NO} + \text{O}_3 + \text{M} \rightarrow \text{NO}_2 + \text{O}_2 + \text{M} 
\]

\[
\text{NO} + \text{HO}^* + \text{M} \rightarrow \text{NO}_2 + \text{•OH} + \text{M} 
\]

After the oxidation NO$_2$ is converted to nitric acid in the reaction with •OH according to the reaction (39) and HNO$_3$ aerosol reacts with NH$_3$ giving ammonium nitrate. NO is partly reduced to atmospheric nitrogen.
Plasma-Based Depollution of Exhausts: Principles, State of the Art and Future Prospects

\[
\text{NO}_2 + \cdot \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \tag{39}
\]

\[
\text{HNO}_3 + \text{NH}_3 \rightarrow \text{NH}_4\text{NO}_3 \tag{40}
\]

There can be also several pathways of \(\text{SO}_2\) oxidation depending on the conditions. In the EBFGT process the most important are radio-thermal and thermal reactions. Radio-thermal reactions proceed through radical oxidation of \(\text{SO}_2\) in the reaction \(41\) and \(\text{HSO}_3\) creates ammonium sulphate in the following steps \(42\) and \(43\).

\[
\text{SO}_2 + \cdot \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M} \tag{41}
\]

\[
\text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \tag{42}
\]

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \tag{43}
\]

\[
\text{H}_2\text{SO}_4 + 2\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 \tag{44}
\]

The thermal reaction is based on the following process:

\[
\text{SO}_2 + 2\text{NH}_3 \rightarrow (\text{NH}_3)_2\text{SO}_2 \tag{45}
\]

\[
(\text{NH}_3)_2\text{SO}_2 \xrightarrow{O_2, H_2O} (\text{NH}_4)_2\text{SO}_4 \tag{46}
\]

The total yield of \(\text{SO}_2\) removal consists of the yield of thermal and radio-thermal reactions that can be written as follows (Chmielewski, 1995).

\[
\eta_{\text{SO}_2} = \eta_1(\phi, T) + \eta_2(D, \alpha_{\text{NH}_3}, T) \tag{47}
\]

Where \(\eta, \phi, T, D\) and \(\alpha_{\text{NH}_3}\) are process efficiency, gas humidity, gas temperature, dose deposited (amount of energy transferred to gas by means of irradiation) and ammonia stoichiometry (\(\text{NH}_3\) concentration in relation to stoichiometric value) respectively. The yield of the thermal reaction depends on the temperature and humidity and decreases with the temperature increase. The yield of the radio-thermal reaction depends on the dose, temperature and ammonia stoichiometry. The main parameter in \(\text{NO}_x\) removal is the dose. The rest of parameters play minor role in the process. Nevertheless in real, industrial process, dose distribution and gas flow conditions are important from the technological point of view.

The technology was originally implemented in coal fired power plants but can be applied for the cleaning of off-gases from various combustion processes. A complete EBFGT installation is schematically shown in fig. 6. After the boiler fly ash is removed from the flue gas by an ESP and cooled down and humidified in spray towers. Cooled and humidified gases are then exposed to the electron beam radiation after the injection of ammonia. The high-energetic electrons are forming the plasma and initiate a series of the above listed reactions which lead to the removal of the \(\text{SO}_x\) and \(\text{NO}_x\) by forming ammonium sulphate \((\text{NH}_4)_2\text{SO}_4\) and ammonium nitrate \(\text{NH}_4\text{NO}_3\) respectively. The reacted gas then passes through a particulate removal device (e.g. ESP) to remove the ammonium sulphate and ammonium nitrate which are used as fertilizers. Pilot and industrial installations demonstrated the feasibility of this technology for effective flue gas purification. The process
was implemented in industrial scale in Pomorzany Power Plant (Poland) for total capacity of 270,000 Nm³/h of flue gas. SO₂ removal efficiency above 95 % and NOx removal above 75 % were reported for optimal treatment conditions. A dose of up to 10 kGy (1 kGy = 1 kJ/kg flue gas) is required for NOx removal, while SO₂ can be removed in proper conditions at lower energy consumption. Nowadays most technical problems occurred in the prototype installations has been solved (Chmielewski et al., 2004).

Fig. 6. Scheme of an EBFGT process

In recent investigations the electrical energy consumption could be decreased and the increase of system availability is in progress, too. The new applications concern application of electron beam for flue gases treatment from high sulphur oil fired boiler performed for Saudi Aramco Company (Basfar et al., 2008). In addition the removal of VOCs, dioxins, mercury and other pollutants from flue gases using EBFGT has been investigated. In the case of VOCs, decomposition the process itself is based on the similar principles as primary reactions concerning SO₂ and NOx removal i.e. free radicals attack on organic compounds chains or rings causing VOCs decomposition. For chlorinated aliphatic hydrocarbon decomposition (e.g. chloroethylene), Cl⁻ dissociated secondary electron attachment and Cl⁻, OH radicals reaction with VOCs play very important roles (Sun et al., 2006). The most important development concerns application for the reduction of polychlorinated dibenzodioxins (PCDDs, so-called dioxins) and polychlorinated dibenzofurans (PCDFs) emission from municipal solid waste incinerators (Hirota et al., 2003). Electron beam irradiation demonstrated high levels of mercury oxidation at the bench scale, and the technology might help to improve mercury removal in wet scrubbers or wet ESPs when employed as a primary or secondary mercury oxidation technique (J.C. Kim et al., 2010).

4. Air-depollution by means of discharges generated plasmas and plasma-enhanced catalysis

Several examples on the use of gas discharges for depollution of exhaust air will be discussed in the following. This will cover the removal of volatile organic compounds (VOCs) and deodorization, NOx- and SOx removal and removal of particulate matter (PM), e.g. soot.

4.1 VOC-removal and deodorization
Plasmas have been demonstrated to be able to decompose VOCs and thus odour molecules very efficiently for low decontamination levels (< 1 gCorg/m³) as like in deodorization
issues. Odour emission is a significant problem in the production of food, for farms, in gastronomy and kitchens as well as in waste management. Typical odour molecules are in fact VOCs, namely aldehydes, fatty acids, alkanes, formic acid, amines or esters. VOC contamination is an issue of increasing importance for the depollution of exhaust air, i.e. off-gases from industrial processes. For such problems plasma can be better suited than classical methods like wet scrubbing, adsorption or thermal processes because of lower energy consumption. In (Rafflenbeul, 2008) a plasma based process with an energy consumption of about 35 kWh for 70,000 m³/h exhaust air is described, while an odour reduction of up to 99 % is possible. Due to its compactness plasma devices can be easily integrated in existing systems and processes. Furthermore no waste or waste water is generated. However, the application of non-thermal plasma has to be reckoned for every specific exhaust problem and in fact, in industrial practice plasmas are combined with catalysts, absorbing agents and other methods of depollution. E.g. undesirable by-products can be formed since the plasma-chemical conversion is not selective or influenced by the gas composition and properties, such as residual humidity or temperature. Energetic efficiency has been found to be best at low contamination levels and low gas flows. Special attention must be paid to the geometrical properties of the reactor (length, cross section) since it influences and determines the residence time as well as the back pressure. The residence needs be optimised for a successful treatment (1 to 3 sec are given in literature), while the back pressure should be as low as possible in order to ensure a proper integration in an exhaust air system (Rafflenbeul, 2008; Müller & Zahn, 2007).

For deodorization applications NTP is often enhanced with catalyst or absorption methods. The plasmaNorm process (airtec competence GmbH) comprises a three-stage treatment unit (Müller et al., 2006). In the first stage the polluted gas is stripped of solids, aerosols and particulates by means of a pre-filter. Appropriate filter media such as bag filters for damp or oily air are used according to the air impurities to be removed. A surface DBD serves as the second stage, where pre-filtered air is subjected to reactive radicals and ions initiating oxidation reactions and the decomposition of VOCs and other contaminants. Finally compounds not yet oxidised are retained in an activated carbon bed, which is described as a storage reactor that, among other effects, revert residual ozone to atmospheric oxygen. The economical, long serviceable life of the activated carbon, as it regenerates itself during the process is promoted as one of the main special characteristic of this technology. It is successfully used in gastronomy and kitchens (large scale and private households) as well as food processing industry. E.g. the exhaust from 1.5 MW ovens for convenience products made of meat generating an exhaust stream of 8,000 Nm³/h can be deodorized (Langner, 2009).

In (Rafflenbeul, 1998) a commercial plasma process combined with a biofilter as pre-filter and oxidation catalyst as after-filter is described. Biodegradable compounds in higher concentrations are decomposed in the biofilter, while the subsequent plasma unit partially oxidizes non-biodegradable pollutions which are finally decomposed in the oxidation catalyst section. The same company (Envisolve) describes several commercialised combinations of non-thermal plasmas with catalysts or molecular sieves for waste management facilities, paintshops and other industrial applications generating exhaust streams of up to 300,000 m³/h.

In case of VOC removal different types of power supplies are used in the terms of voltage type and shape, operation frequency, supply system topology. All of the above mentioned parameters can strongly influence overall system performance and an optimum for most cases can be found. Power supply properties may influence the nature of reactor operation
just like the reactor construction itself. First of all the operating frequency influences the breakdown voltage (Valdivia-Barrientos et al. 2006) according to the semi-empirical equation:

$$U_{bd} = 1.4 \left( \frac{C_d}{C_g} \right)^2 \ln(f)$$

(48)

where $U_{bd}$ – reactor breakdown voltage, $C_d$ – dielectric barrier capacitance, $C_g$ – gas gap capacitance, $f$ – supply frequency. Second of all for aimed chemical process often an optimal set of supply parameters can be found yielding in maximal destruction and removal efficiency (Magureanu et al., 2007) or productivity (Buntat et al., 2009) when recalculated into SIE. Such dependencies are often hard to follow in industrial cases, where gas composition is complex and varying with time but nevertheless power supply system parameters play an important role in the VOC removal process.

4.2 Flue gas treatment by means of plasma-enhanced catalysis

Non-thermal plasma has been applied for the treatment of exhausts of varying sizes of diesel engines from small cars, heavy trucks and marines (Miessner et al., 2002; Bröer & Hammer, 2000; Mok & Huh, 2005; Mizuno, 2007; Cha et al., 2007; McAdams et al., 2008). Same technology has also tested for oil fired boilers (Park et al., 2008). Typically the flue gases of these sources contains 200-1,000 ppm NOx, 10-200 ppm hydrocarbons, 200-700 ppm CO, 2-8 % CO2, 1-5 % H2O and 10-18 % O2. The exhaust gas contains also particles with varying sizes.

A great deal of effort was devoted to the treatment of particulate matter in flue gas from diesel engines. In (Müller & Zahn, 2007) a reactor combining a DBD with a wall flow filter for soot reduction is described. In this system one electrode is porous and gas-permeable. The flue gas is let out through the porous electrode, which filters and holds back the soot particles. Thus soot-particles are stored on this electrode which faces to an electrode surrounded by a dielectric material. Toxic and soot-containing harmful substances are decomposed in the plasma. The accumulated soot is decomposed due to cold oxidation process initiated by active plasma species leading to constant regeneration of the filter at low temperatures during all engine operation conditions. In (Yamamoto et al., 2003) the diesel particulate filter (DPF) regeneration for real diesel engine emissions at low temperatures by means of indirect or direct non-thermal plasma treatment was demonstrated. In other studies (Chae et al., 2001, Mok & Huh, 2005) corona and DBD reactors were successfully used for the removal of smoke and particulate matters from diesel engines.

For the reduction of NOx from diesel engine exhausts selective catalytic reduction is used but the catalysts do not work properly at low temperatures below (200-300°C) (Penetrante et al., 1998; Bröer & Hammer, 2000; Tonkyn et al., 2003). For improvement of the reduction efficiency at lower temperatures, plasma enhanced selective catalytic reduction (PE-SCR) has been investigated (Penetrante et al., 1998; Bröer & Hammer, 2000; Tonkyn et al., 2003; Miessner et al., 2002; Mizuno 2007; Mok & Huh, 2005; Cha et al. 2007; McAdams et al., 2008; Hammer et al., 1999). In PE-SCR the plasma serves for the oxidation (NO to higher nitride oxides and hydrocarbons to partially oxidized ones). Oxidation is needed because many NOx-reduction catalysts have a higher activity toward NO2 and thus the removal efficiency at low temperatures is significantly enhanced (Penetrante et al., 1998; Bröer & Hammer,
Further enhancement of NOx reduction on catalyst is achieved by hydrocarbon radicals generated in the plasma (Penetrante et al., 1998; Miessner et al., 2002; Tonkyn et al., 2003). In the oxidizing environment of diesel exhaust, an effective reduction of NOx to N2 on catalyst takes place only when there are enough reducing agents (NH3, hydrocarbons like propene). In the case of optimized burning process, there are usually not enough hydrocarbons in the engine exhaust for efficient reduction of NOx (Tonkyn et al., 2003; Miessner et al., 2002; Cha et al., 2007). Thus it is necessary to inject additional reducing agent to the exhaust gas. When NH3 or urea is used as reducing agent, it has to be carried in a separate tank while hydrocarbons can also be obtained directly from the fuel. Presence of hydrocarbons in the plasma stage enhances the oxidation of NO to NO2 and additionally inhibits the oxidation of SO2 and the formation of HNO3 (Penetrante et al., 1998). The production of HCN can be problematic when hydrocarbons are used (Tonkyn et al., 2003) while the ammonia slip and catalyst poisoning by NH4NO3 have to be considered when ammonia is used (Dors & Mizeraczyk, 2004).

For the removal of diesel exhaust, the additional fuel consumption due to plasma treatment should not exceed 5 % which corresponds to SIE of 15-60 J/sl for different diesel engines (Tonkyn et al., 2003; Mizuno 2007). In experiments with synthetic exhaust gas without particles, 80 % of NOx reduction has been achieved with energy input of 27-32 J/sl when hydrocarbons and NH3 were used as reducing agent and temperature was 150 °C (Bröer & Hammer, 2000; Mizuno 2007; Lee et al., 2007). V2O5/TiO2 based catalysts or Co-ZSM5 were used and space velocities were 15,000 and 2,000 h⁻¹. When only hydrocarbons have been used as catalysts, the NOx reduction above 70 % has been achieved in temperature range of 170°C to 260°C with BaY zeolite (space velocity 12,000 h⁻¹) and by using both BaY and γ-Al2O3 the temperature range has been extended to 500 °C (Kwak et al., 2004). For real diesel exhaust gases, the reduction efficiencies are usually smaller because of the presence of particles which reduce NO2 back to NO (Dorai et al., 2000). Diesel exhaust gas of an Multicar M25-10 engine (1,997 cm³, without catalyst) having gas flow of 10 sl/min (space velocity 20,000 h⁻¹) and typically 434 ppm NOx was treated with plasma-enhanced catalysis where catalyst was placed downstream from the plasma reactor (Miessner et al., 2002). Catalyst alone (γ-Al2O3 + oxidation catalyst at 250°C) removed only CO and hydrocarbons (10-50 ppm in the exhaust). The NOx removal by plasma (54 J/sl) and catalyst was only 7 % while the injection of additional propene (1.2 sl/h or 2,000 ppm) increased the NOx reduction to 56 %. Further increase of energy density did not improve NOx removal. For another diesel engine exhaust the NOx reduction of 73 % was achieved at energy densities 43 J/sl and at low temperature of 150 °C (Mizuno 2007). The gas flow rate was of 6 sl/min (space velocity of 36,000 h⁻¹) while inlet gas had about 313 ppm of NOx and 881 ppm acetylene. In this experiment, Pt-Al2O3 pellets were used as catalyst inside the backed bed plasma reactor. For both systems, the estimated additional fuel consumption due to plasma generation was 4-5 % (Miessner et al., 2002; Mizuno 2007). In the second experiment, the removal of particulate matter was determined to be 95 % (5-7 mg/m³).

NH3 as reducing agent was used for a commercial diesel engine from a used truck (Mok & Huh, 2005). Part of the diesel exhaust (10 sl/min) at no load condition with 180 ppm NOx and around 0.6 mg/m³ particulate matters was introduced to the reactor system where monolithic V2O5/TiO2 catalyst was placed downstream of the reactor. The effect of plasma SIE was tested in the temperature range of 100 to 200°C with the ratio of NH3 and inlet NOx concentration set to 0.9. Plasma had strongest effect at 150 °C where the NOx reduction increased from 45 % to 80 % at input energy density of 25 J/sl whereas further increase in
input energy did not improve the reduction. At 200 °C, the reduction was above 65 % already without plasma. Same system was also used for the removal of PM and it was possible to remove 50 % and 80 % of PM at SIE of 20 and 40 J/sl respectively (Mok and Huh, 2005). Up to 85 % of NOx reduction with 2 % of fuel penalty has also been achieved with similar dielectric-barrier discharge/urea-SCR hybrid system applied to VW Passat TDI engine exhaust (cold start and urban driving condition) (Hammer, 2002). An earlier experiment with Hatz 1D30 engine resulted in more than 75 % of NOx reduction with 17 J/sl and at catalyst temperature 170 °C (Hammer et al., 1999).

Plasma-enhanced catalysis has also used to improve the cleaning of marine diesel exhaust at low temperatures below 200 °C where commercial NH3 SCR catalysts do not work properly (Cha et al., 2007). In this study, 1/10th of the exhaust (100 Nm³/h) from 300 hp Yanmar engine was directed to hybrid plasma-catalyst system and the engine load was 25 % (550 ppm NOx, 116 ppm C3H6). The plasma reactor operated properly even after more than 1000 hr of work in highly humid and sooting conditions. The NOx reduction efficiency on catalyst (space velocity of 450,000 h⁻¹) increased from 20 to 80 % at 100 °C and from 55 to 90% at 200 °C at energy density of 40 J/sl with additional C3H6 above 1.5 times the NOx concentration injected to the exhaust and 550 ppm NH3 injected after the plasma reactor. The estimated power consumption of plasma device for the warming period of the engine (500 Nm³/h) was 5-6 kW and this corresponds for about 2 % of the engine power. The plasma reactor reduced also 45 % of the particulate matters (Cha et al., 2007). For larger NOx concentrations of 1,200 ppm, simulated marine diesel exhaust experiments have been carried out (McAdams et al., 2008). At 250°C and with Ag/Al2O3 catalyst, it was possible to obtain 50% of NOx reduction at energy densities of 60 J/sl (with the C3H6:NOx ratio of 2). At 350°C, above 90% of NOx reduction was measured at same energy density values. The catalysts were sulphur tolerant up to the concentrations of 1 %. The fuel penalty of 10 % was estimated for the type of engines simulated in the experiment.

When hydrocarbons are used as reducing agents, some of the NO2 is reduced back to NO on the catalysts and this limits the maximum achievable reduction efficiency (Tonkyn et al., 2003). Use of multiple stages of plasma reactors and catalysts can overcome this limitation and increase of the reduction up to 90 % has been demonstrated in simulated exhaust gases (Tonkyn et al., 2003). Hybrid plasma-catalysis reactor with modular design was recently also tested for removal of NOx in oil-fired boiler (Park et al., 2008). The reactor consisted of four consequent plasma/catalyst modules where catalysts could be either TiO2 or Pd/ZrO2. The hybrid system with two first catalyst modules from Pd/ZrO2 and last two from TiO2 allowed to obtain the best results giving 74 % of NOx reduction with stoichiometric amount of C3H6 at 150 °C and space velocity of 3,300 h⁻¹. Initial NOx concentration was 500 ppm.

In addition to NOx reductions, several examples for large- and full-scale demonstration installations for flue-gas cleaning of SOx, dioxin and some VOCs are given in (H.H. Kim 2004; Mizuno 2007). Most recent review of research on catalytic processes enhanced by non-thermal plasma are presented in (Van Durme et al., 2008).

Pulsed DC-driven FHC discharges with aerodynamic stabilization were used for conversion of NOx in air mixtures. The discharge works as 100% oxidation catalyst, converting NO to NO2, without any additives (Barankova & Bardos 2010). The electrode material plays an important role in the plasma chemical kinetics as it brings about its own material constants, e.g. work function, secondary electron emission coefficient and catalytic activity. Due to an optimized geometry and efficient transfer of power to the electrons in the system, the power consumption for gas conversion is extremely low. Typical specific energy densities within the processing window are around 5 J/sl, i.e. 0.14 kWh/100 Nm³.
5. Injection methods and scrubbing-combined plasma processes

Alternatively to the direct treatment (gas is passing the plasma reactor completely) indirect, remote or so-called injection methods are possible. In this case clean gas will be treated by the plasma and then admixed to the flue gas. The most well known example is the low temperature oxidation (LTO) of NOx by ozone injection. The idea of LTO is to oxidize relatively insoluble NOx to higher oxides such as N2O5 that are highly soluble and can easily be removed in wet scrubbers (Jarvis et al., 2003; Ferrell, 2000).

In non-thermal plasmas in oxygen, ozone formation starts by dissociation of O2 via electron impact (49). Resulting oxygen atoms form ozone in three-body collisions (50, M is a third partner), while ozone production is balanced by the decomposition reaction (51) and thermal dissociation (52) at steady state conditions.

\[
\begin{align*}
e^- + \text{O}_2 & \rightarrow 2 \text{O}^{(3P, \; 1D)} \quad (49) \\
\text{O}^{(3P, \; 1D)} + \text{O}_2 + M & \rightarrow \text{O}_3 + M \quad (50) \\
\text{O}^{(3P)} + \text{O}_3 & \rightarrow 2 \text{O}_2 \quad (51) \\
\text{O}^{(3P)} + \text{O}_3 & \rightarrow \text{O}_2 + \text{O} \quad (52)
\end{align*}
\]

For example, exhaust NO can be oxidized by O3 to form NO2, NO3 and, subsequently, N2O5 (53-55). Reaction (54) is the slowest reaction in this chain. Nitric pentoxide (N2O5, anhydride of nitric acid) can be efficiently removed from the exhaust by a washing bottle or scrubbing forming nitric acid (HNO3, 56). In humid exhaust gases, HNO3 may be formed in the exhaust gas itself. It can be used as chemical feedstock or it can be neutralized and used e.g. as fertilizer, similar as in the EBFGT process.

\[
\begin{align*}
\text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2 \quad (53) \\
\text{O}_3 + \text{NO}_2 & \rightarrow \text{NO}_3 + \text{O}_2 \quad (54) \\
\text{NO}_3 + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 \quad (55) \\
\text{O}_3 + 2 \text{NO}_2 & \rightarrow \text{N}_2\text{O}_5 + \text{O}_2 \\
\text{N}_2\text{O}_5(g) + \text{H}_2\text{O} & \rightarrow 2 \text{HNO}_3(aq) \quad (56)
\end{align*}
\]

The deNOx efficiency was found to be maximum at 100 °C and the addition of small water droplets improves the NOx oxidation rate (Stamate et al., 2010). Advantages of LTO NOx is that the plasma discharge is kept clean and the removal rate of NO is higher than direct oxidation methods where the reverse reactions occur to reform NO and NO2 by the O radical (Yoshioka et al., 2003; Eliasson & Kogelschatz, 1991 as cited in Stamate et al., 2010).

A commercial system applying ozone injection is available under the trademark LoTox (Low Temperature Oxidation). The process works within the Electro-dynamic Venturi (EDV) wet scrubbing system in order to achieve a combined reduction of PM, SOx and NOx of stationary emission sources, especially refinery applications (Confuorto & Sexton, 2005).
Ozone is generated on site and on demand and injected after the dry ESP directly into the wet scrubber. N₂O₅ is converted to HNO₃ and finally neutralized by the scrubbers alkali reagent to NaNO₃. Other pollutants such as SO₂ and HCl are removed in the wet scrubbing process simultaneously. There exist a number of commercial installations in the USA and in Asia on different emission sources. NOx removal higher than 90% has been reported. The removal of mercury was demonstrated, too. Several refinery installations have demonstrated LoTox performance and reliability on an applicable scale, the process is available from DuPont BELCO Clean Air Technologies.

There are several advantages combining plasma treatment of gases with scrubbing processes. Gutsol et al. reports on a wet or spray pulsed corona discharges studied for the VOC-removal from paper mill exhaust gases (Fridman, 2008). In case of spray corona water is injected to the corona discharge like a shower, while in wet corona a thin water film rinse on the outer wall electrode. In such arrangement soluble VOCs adsorb on the water droplets or film while non-soluble VOCs can be converted to soluble compounds (e.g. peroxides and peroxide radicals) by means of plasma treatment and subsequently scrubbed within the same arrangement. This results in much lower energy requirements. Furthermore, plasma-stimulated oxidation continuous after adsorption resulting in a larger adsorbing capacity of the water and thus water consumption. However such process is only applicable where already large amounts of polluted water are generated and which requires effective water cleaning.

The ECO (Electro-Catalytic Oxidation) process is another example for a commercialized plasma-assisted depollution process combined with scrubbing (Boyle, 2005). The process is designed for installation downstream of a dry ESP or fabric filter (ash removal). The flue gas is directly exposed to DBD and oxidizes pollutants to soluble or capturable compounds (e.g. NO to NO₂; SO₂ to SO₃; Hg to mercury oxide HgO) and form particulate matter and aerosol mist. SO₂, NO₂ and HgO are removed in a subsequent absorber vessel (two-loop scrubber). Ammonia is added to the scrubber to maintain the pH of the solution for keeping high SO₂ scrubbing rate. NO₂ formed in the ECO reactor is scrubbed by sulphite ions, which are formed by SO₂. Finally (NH₄)₂SO₄ and NH₄NO₃ are formed as well. Several preliminary designs for coal-fired electric utility applications ranging from 175 – 1,000 MW has been developed and long time performance and reliability test were successfully completed. The process is available by the company Powerspan Corporation and has recently combined with post-combustion CO₂ capture technology.

6. Conclusion

To a great extend non-thermal plasma processes were demonstrated for commercial pollution control applications having following peculiarities: The decomposition of contaminants without heating of the gas can be achieved, while a wide range of pollutants (gases and particulate matter/aerosols) can be treated. Organic particles can be decomposed due to oxidation at low temperatures. The best efficiency is reached in low contaminated gases making them well suited for deodorization issues, too. An advantage of plasmas for gas depollution is that the energy consumption of the plasma stage can be regulated easily with the pollutant mass flow by the electrical parameters. However, in all examples the plasma is one part of a complete depollution system, since plasma-chemical conversion is not selective and mainly oxidative Furthermore, energetic efficient treatment is achieved in case of low contaminated exhaust air and the formation of
undesirable by-products has to be taken into account. Plasma processes combined with other treatment processes give synergetic effects. The addition of ammonia-based substances as reducing agents for plasma generated higher nitrogen oxides can be considered as state-of-the-art since it is already used in several processes (EBFGT, LoTox, ECO). Theses process has been successfully demonstrated on an industrial scale, e.g. for the flue gas treatment of coal fired power plants. New developments of EBFGT technology concern the treatment of flue gases from high sulphur oil fired boilers and the removal of (poly)chlorinated VOCs like dioxins from municipal solid waste incinerators. In this context the range of removable contaminants will be extended. Several VOCs, dioxins and mercury are under investigation with promising results at bench scale. The combination of non-thermal plasma with catalysts, absorbing agents or scrubbing techniques are promising approaches.

Hybrid systems and especially plasma-driven catalysis will be one of the major prospects for future developments. Therefore the interaction of plasmas with catalysts has to be investigated more detailed and a profound understanding of the development, physics and chemistry in polluted gases is desired. In this context more efforts on the understanding of the physics of filamentary plasmas consisting of microdischarges is necessary. Furthermore the power supply system parameters play an important role in the removal process and novel topologies with high potential for further improvement are under development.

7. Acknowledgment

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