Corona plasmas: fundamental studies and industrial applications

K. Yan, E.J.M. van Heesch, A.J.M. Pemen, and S. Nair

Abstract

Very important physical and chemical features of corona plasmas are electrons, ions and radicals generation. It is foreseen that the next generation gas cleaning system – called zero emission system, to remove polluting gases, heavy metals, and particles simultaneously, can be developed based on ions and radicals generated by corona plasmas. Potential applications are flue gas cleaning, odour control, inactivation of micro-organisms, wastewater cleaning, synthesis gas cleaning, methane reforming, hydrogen production from fossil fuels, material surface treatment, and nano-particle generation. There are two critical issues to be overcome for large-scale industrial applications. The first one is the capacity and the cost of repetitive pulsed power techniques, and the second is the total energy consumption. This paper discusses the most relevant fundamental investigations and system developments for pollution control and sustainable development.

1 Introduction

With regard to pollution control and electrical discharges in gases, the most popular techniques used to be electrostatic precipitation and ozone generation. Both of them have a history of over a century. In the last 15 years, corona plasma techniques have been widely investigated for pollution control and sustainable development. Investigations have extended from odour treatment, indoor air cleaning, VOCs abatement, flue gas cleaning to methane reforming and hydrogen production [1]. Corona plasmas are often used together with additional techniques in order to control by-products and to increase the efficiency. For
examples, NO, and SO₂ can be converted to NH₄NO₃ and (NH₄)₂SO₄ salts with
NH₃ addition; VOCs can be decomposed to CO₂ and H₂O with catalyst;
Dioxin/furans and Hg can be removed with a corona plasma scrubber; hydrogen
sulphide can be converted to hydrogen and sulphur; under plasma enhanced
catalysis soot and NOₓ can be oxidized to CO₂ and reduced to nitrogen,
respectively. According to available literature, more than 50 types of pollutants
have been investigated for their emission control by using corona plasma
techniques [2]. Table 1 summarizes the state of the art of corona plasma
applications. Although the technique has not been used in industries for radical
generation, it is anticipated that in coming years the technique will play a very
significant role for large volume exhaust gas cleaning. Two critical issues that
should be solved for industrial applications are the capacity and cost of repetitive
pulse power techniques, and the total energy consumption. Pulsed power
switching has become the critical enabling technique for the development.

This paper reviews our recent research and development on various
critical issues of corona plasma techniques in order to bridge the gap between
fundamental investigations and industrial applications.

Table 1. List of potential applications of pulsed corona plasma techniques for
pollution control and sustainable development.

<table>
<thead>
<tr>
<th>Applications</th>
<th>Main functions</th>
<th>Status</th>
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<tbody>
<tr>
<td>Indoor</td>
<td>Bacterial, virus and odour removal</td>
<td>Mature</td>
</tr>
<tr>
<td>Exhaust gas cleaning</td>
<td>To convert NOₓ and SO₂ to NH₄NO₃ and (NH₄)₂SO₄ under NH₃ addition</td>
<td>Industrial demonstration</td>
</tr>
<tr>
<td></td>
<td>To remove gaseous, heavy metals and particles simultaneously</td>
<td>Concept proof</td>
</tr>
<tr>
<td></td>
<td>NOₓ reduction from mobile sources</td>
<td>Concept proof</td>
</tr>
<tr>
<td></td>
<td>Dioxin/furans and Hg removal</td>
<td>Industrial demonstration</td>
</tr>
<tr>
<td>Air cleaning</td>
<td>Odour, VOCs and micro-organisms removal</td>
<td>Industrial demonstration</td>
</tr>
<tr>
<td>Synthesis gas cleaning</td>
<td>Tar cracking, CO to CO₂ conversion, gaseous and heavy metals removal</td>
<td>Concept proof</td>
</tr>
<tr>
<td>Methane reforming</td>
<td>To convert CH₄ to higher hydrocarbons or methanol</td>
<td>Concept proof</td>
</tr>
<tr>
<td>Hydrogen production</td>
<td>To produce H₂ from fossil fuels</td>
<td>Concept proof</td>
</tr>
<tr>
<td>Oil reforming</td>
<td>To upgrade heavy oil to light ones</td>
<td>Concept proof</td>
</tr>
<tr>
<td>Soil cleaning</td>
<td>To remove organic pollutants and micro-organisms</td>
<td>Concept proof</td>
</tr>
<tr>
<td>Water cleaning</td>
<td>To remove organic pollutants and micro-organisms</td>
<td>Concept proof</td>
</tr>
</tbody>
</table>
2 Characteristics of corona plasmas

Generally speaking, in order to generate streamer corona plasmas while avoiding their evolution into spark breakdown, voltage pulses with short duration and electrode arrangements producing highly non-uniform electric fields are used. The most common electrode arrangements are point-plate, coaxial wire-cylinder, and wire-plate. During time scales of a few tens of nano-seconds, energy transferred to ions is much smaller than energy transferred to electrons. Based on the state of the art of time-resolved and spatial characteristics of streamer propagation [3,4], a positive streamer can be described as: in a non-uniform electric field, a highly ionised plasma, called streamer head, propagates from anode to cathode with a velocity of $10^5$–$3 \times 10^6$ m/s. The size of the plasma region is around 100 μm during the propagation. Between the plasma and the anode, there is an almost dark streamer channel with a diameter similar to the diameter of the streamer head. After the streamer bridging the electrode gap, a current can still flow via the formed streamer channel, the so-called secondary streamer. For a wire-cylinder and/or wire-plate corona reactor, many parallel streamers propagate from the corona wire towards the ground electrode when the applied voltage becomes higher than the inception voltage. The streamer number density per unit length of the corona wire is around 5–10 streamers/cm. The most important issues to evaluate corona plasma characteristics for inducing chemical reactions are active electrons and initial radical production and global chemical kinetics [5].

Figure 1 shows a typical example of the time-resolved SPS(0,0) of N$_2$ and FNS(0,0) of N$_2$+ emission near corona wire in a flue gas. The first peak corresponds to primary streamers, and the later long continuous light emission mainly corresponds to secondary streamers. The intermediate minimum roughly corresponds to the moment at which the primary streamers arrive at the cylinder. In comparison to the first phase during primary streamer propagation, the ratio of the FNS(0,0) emission over the SNS(0,0) emission during the secondary streamer development in the flue gas is about ten times smaller. Because the threshold electron energy for $N_2^+(B^2 \sum_u)$ generation via direct electron impact excitation from the N$_2$ ground state is about 18.7 eV, it is assumed that the stronger the FNS(0,0) emission, the larger the average electron energy. Electron energies during the first phase (primary streamer propagation) are assumed to be much larger than the energy in the second phase (secondary streamer development). Active electrons are mainly produced during primary streamer propagation. However, accurate evaluation of the electron energy is not yet possible because of the complicated processes.

According to the emission spectrum observations, we conclude that in order to efficiently induce chemical reactions, the energy transfer during the secondary streamer developments should be avoided. A secondary streamer is less efficient than a primary streamer, which is similar to the conclusion that onset streamers are more efficient than pre-breakdown streamers [5]. Longer pulses not only lead to a large energy consumption, but also cause significant
energy reflection from the reactor to the source, which lead to damage the pulsed power switch within a very short period. Based on our fundamental investigations on corona plasma generation, optimal specifications of the pulsed power source are listed in Table 2 for the development of industrial corona plasma systems with up to 100 kW average output power. For the time being, there are no reported techniques to develop such pulsed power source and there are no companies that can build the system. One of our recent R&D is to fill this gap by applying our pending patent [6]. Available reported industrial pulsed corona plasma systems were usually designed according to individual empirical experience. Systems are hardly used at optimal conditions.

![Figure 1: Dependence of emission intensities of the SPS(0,0) and the FNS(0,0) near the corona wire in a flue gas. The flue gas temperature and compositions are 384 K, 74.9% of N₂, 14.6% of O₂, 7.0% of H₂O, and 3.5% of CO₂, respectively. The length, inner and outer diameters of the wire-cylinder reactor are 800, 3 and 155 mm, respectively.](image)

### Table 2. Specifications of industrial pulsed power sources for corona plasma applications

<table>
<thead>
<tr>
<th>Specifications</th>
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<tbody>
<tr>
<td>Average power (kW)</td>
<td>100</td>
</tr>
<tr>
<td>Peak output current (kA)</td>
<td>20</td>
</tr>
<tr>
<td>Peak output voltage (kV)</td>
<td>100</td>
</tr>
<tr>
<td>Output impedance (Ω)</td>
<td>5</td>
</tr>
<tr>
<td>Peak output power (GW)</td>
<td>2</td>
</tr>
<tr>
<td>Pulse repetition rate (pps)</td>
<td>1000</td>
</tr>
</tbody>
</table>
In order to evaluate the main initial radicals generated by corona plasmas in air and/or in flue gases, systematically experimental investigations on NO to NO₂ conversion in N₂+O₂+CO₂+H₂O+NH₃+NOₓ gas mixtures were carried out [7]. Figure 2 shows typical examples of NO to NO₂ conversion under various gas compositions. Depending on the bulk gas compositions, NO can be either reduced to N₂ by N and NH₂ radicals or oxidized to NO₂ and then to their acid by O, OH and HO₂ radicals. For oxygen rich gases (>3.6%), it can be easily concluded that the N radical generation is almost negligible during corona plasma processing; the main initial radicals are O, OH and H, which is mainly attached to O₂ to form HO₂ via reaction H+O₂+M → HO₂+M. Thus, corona plasma induced chemical reactions in air and/or in exhaust gases are mainly related to O, OH and HO₂ radicals. It is estimated that the ratio of initial radical generation of OH (or H) over O is around 20% to 80%. The energy cost for O radical generation is around 50 eV/O.

A simplified global chemical kinetic model was proposed in order to evaluate the system design [2]. The model includes a radical production process, a pollutant removal reaction, a radical linear termination reaction, and a radical non-linear termination reaction. An energy efficient system should preferably be designed to maintain a linear relationship between the removed amount of the pollutant and the corona energy density. The further research on corona plasma processing is to optimise plasma distribution inside the corona reactor and to develop hybrid corona plasma processing in order to suppress radical terminations. Unfortunately, there is almost no reported work to discuss these issues [5].

![Figure 2: The produced NO₂ via the removed NO in N₂+O₂+NOₓ mixtures.](image-url)
Development of industrial corona plasma systems brings up the following issues: specifications of the pulsed power source; size of the corona reactor; matching between the source and the corona reactor; energy conversion efficiency; radical production efficiency; by-products and cost effectiveness. A general principle for optimising corona energization was proposed in order to improve the initial radical production yield and to increase the energy transfer efficiency. Optimised relationships between the voltage rise-time, the peak voltage, the size of a corona reactor, the output impedance of a voltage pulse generator, the stray capacitance of the corona reactor, and the corona energy density per unit length of the reactor were discussed. Matching a corona plasma reactor to a high-voltage pulse generator becomes even more important when scaling up the system. Based on our 1-10 kW corona plasma system developments, we also conclude that a hybrid pulsed power source (HPPS) shows much more advantages for a large volume corona plasma generation [5].

Figure 3 shows a schematic diagram of HPPS systems with a wire-plate type corona reactor. The HPPS mainly consists of two parts: the high-voltage pulse generator and a resonant capacitive charging unit (or the DC power source). Before applying the high-voltage pulse, the reactor is first charged to a bias voltage $V_{dc}$. By firing the main spark-gap switch $S$, the energies stored in the coupling capacitor $C_{dc}$ and in the high-voltage capacitor $C_h$ are transferred into the reactor simultaneously. After pulsed energization, the reactor and the capacitor $C_{dc}$ are resonantly charged again by the DC source. Corona plasma is generated during the high-voltage pulses. Electrostatic precipitation is realized in-between the pulses.

Figure 4 shows the general method for the optimisation of HPPS corona plasma energization by considering both energy conversion efficiency and corona plasma generation. The optimisation method consists of four logical steps as shown in Fig. 4 with examples of 10 and 30 kW average power at 1000 pps. The symbols $\Delta T$, $Z_{out}$, $C_p$, and $\tau$ are the primary streamer duration, the output impedance of the TLT, the capacitance of the reactor, and the voltage rise time to reach the inception voltage, respectively. The length, inner and outer diameters of the wire-cylinder reactor are 800-3000, 3 and 155-160 mm, respectively. Experimental results are obtained in air under a pulse repetition rate of up to 900 pps. Detailed discussions on the optimisation method were reported in Ref. [5].

According to the optimisation method, the coupling capacitor $C_{dc}$ and output $Z_{out}$ impedance of the TLT of our mobile 10-30 kW HPPS system are designed to be 14 nF and 20 $\Omega$, respectively. Figure 5 shows the system layout. A set of 16 parallel wire-cylinder reactors in the middle of Fig.5 is used. The length and outer diameter of each reactor are 1000 and 160 mm, respectively. The reactor wall and gas temperatures can be controlled individually. For gas to aerosol and/or solid conversion, the wall temperature can be operated below the gas temperature (or the dew point). For corona plasma induced decomposition processing, a wall at a higher temperature will improve the processing efficiency.
Figure 3: A schematic diagram of a hybrid pulsed power system and a wire-plate corona reactor. The inductor L, the capacitor C, and the resistor R form the LCR trigger circuit. The two-stage TLT is constructed with two-types of magnetic cores, where $Z_{out} = 2 \cdot Z_0$. The A-type core refers to either metglas or micro-gap ferrite. The B-type core is a ring ferrite.

Figure 4: Corona plasma optimisation for a hybrid pulsed power source at 1000 pps. The peak pulse voltage and the total voltage are 75 and 110 kV, respectively.
Figure 5: A schematic diagram of a mobile 10-30 kW hybrid pulsed power source and wire-cylinder type corona plasma system.
4 Future perspectives

In coming years, corona plasma techniques can be widely applied in many industries after very reliable corona plasma systems are further developed. The mobile system shown in Fig.5 will be used for various kinds of industrial demonstrations in order to evaluate both technical and economical feasibilities. Integrating corona plasma techniques with other available techniques, such as electrostatic precipitator, can lead to develop a zero emission system for low concentration emission abatement. Long-term industrial demonstrations would become very important in coming years for promoting industrial applications. A few examples of potential applications are discussed in the following.

4.1 Odour emission control

Complaints about odour nuisance are an important problem for today’s livestock and poultry industries. With the development of the standardization of odour concentration measurement, lawfully imposed counter-measures would become general practice. Available odour control techniques include ventilation, wet-scrubbing, dry-scrubbing, chemical cleaning, active carbon absorption, dilution, condensation, masking, combustion, electrostatic precipitation, bio-filter and/or reactor, UV irradiation, ozone deodorization, and advanced oxidation technologies, such as UV+O_3, UV+O_3+H_2O_2. For industries, such as animal farmers and meat producers, our industrial tests with gas flow rates of up to 5000 Nm$^3$/h indicated that a corona energy density of around 0.2-0.4 Wh/Nm$^3$ is sufficient to realize a satisfactory deodorization. The treatment time ranges from a few ms to a few seconds. The low energy consumption can lead corona plasma processing to become one of the most promising techniques for deodorization. With the HPPS system shown in Fig.5, up to 20,000-50,000 Nm$^3$/h of odour gas can be deodorized for industrial applications.

4.2 Exhaust gas cleaning

As one of the post-combustion cleaning techniques to remove NO$_x$ and SO$_2$ from exhaust gases, corona plasma techniques have demonstrated their technical and economical feasibilities in contrast to commercially available techniques [1]. Moreover, corona plasma is also very efficient for low concentration NO$_x$ gas cleaning (<25 ppm), such as NO to NO$_2$ and then to HNO$_3$ conversion and dust collection in highway tunnels, where the NO$_x$ concentration is in the order of 1-10 ppm. For such low initial concentration, radical terminations or the so-called NO$_x$ cycle are not very significant [2]. With the HPPS system up to 10,000 Nm$^3$/h gas in the tunnel can be cleaned for industrial applications.

Industrial demonstrations on exhaust gas cleaning from municipal incinerator are anticipated in coming years to removal NO$_x$, SO$_2$, Hg, HCl, dioxin/furans, and dusts simultaneously.
4.3 VOCs emission control

For most of the commercial pollution control techniques, such as catalytic and thermal incineration, adsorption and absorption, the lower the concentration, the higher the cost per ton removed [8]. For corona plasma techniques, the lower the concentration, the lower the cost. When the corona energy density is only around a few Wh/Nm³, the global kinetics shows insignificant radical terminations. Such unique characteristics of corona plasma processing can lead to a wide range of industrial applications to convert low concentration (less than 50 ppm) VOCs to aerosol, which then can be collected by a precipitator. For high concentration VOCs emission control, corona plasma assisted catalysis can be used to reduce the reaction temperature, to increase the removal efficiency and to regenerate the catalyst.

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References