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Non-thermal Plasma as an Innovative Option for the Abatement of Volatile Organic Compounds: a Review

**Marco Schiavon · Vincenzo Torretta ·
Andrea Casazza · Marco Ragazzi**

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Abstract Volatile organic compounds (VOCs) cause global and local impacts, resulting in environmental, health, and economic adverse effects. Industrial and waste management activities are the main anthropogenic stationary sources of VOCs in the atmosphere. The traditional technologies for the treatment of VOC-contaminated air present several limitations when treating effluents with low VOC concentrations, high airflow rate, and with compounds with low solubility in water. However, a novel technology, based on non-thermal plasmas (NTPs) and catalysis, has shown promising results in air purification. In this framework, after an initial overview on NTP-catalysis principles, this review presents and discusses 20 recent papers, with a threefold purpose: evaluating the most recent applications of NTP and NTP-catalysis reactors to the treatment of air-VOC mixtures, analyzing all the parameters that may influence the abatement efficiency and the by-product formation, and providing the reader with insights into the choice of the preferable configurations to use, based on the effluent type and the destination of the treated air. As a result of this review, NTPs may represent a promising option for indoor air treatment, especially because of the lower expected byproduct formation when treating low-concentrated VOC mixtures with relatively low air flow rates. If the target is the abatement of higher VOC concentrations, the higher energy efficiency obtainable in such conditions makes NTP-catalysis a cost-effective option for industrial applications. In addition, the formation of simpler and more soluble by-products makes NTPs a suitable technology for air pretreatment upstream of water-based removal technologies, such as absorption columns and biofilters.

Keywords Dielectric barrier discharge · Corona discharge · Catalysis · Air pollution control · Odor abatement

1 Introduction

Volatile organic compounds (VOCs) are a group of substances that are particularly important for environment, human health and, to a certain extent, for local economy. Indeed, once they are emitted into the atmosphere, VOCs entail non-negligible impacts at different levels: at a global scale, VOCs indirectly contribute to the greenhouse effect, since they are precursor compounds of tropospheric ozone (O_3) (Shao et al. 2016); at a local scale, in addition to favoring O_3 formation, which is a strong oxidant and toxic compound for humans, VOCs can produce adverse effects on human health. Long-term exposure to VOCs in air may increase the risk of developing cancer diseases (Tam and Neumann 2004), since the International Agency for

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M. Schiavon (✉) · M. Ragazzi
Department of Civil, Environmental and Mechanical Engineering, University of Trento, via Mesiano 77, 38123 Trento, Italy
e-mail: marco.schiavon@unitn.it

V. Torretta · A. Casazza
Department of Theoretical and Applied Sciences, University of Insubria, Via G.B. Vico 46, 21100 Varese, Italy

Research on Cancer (IARC) has proven that some VOCs are carcinogenic to humans (IARC 2017). In addition, by definition, such substances are characterized by high volatility, due to their high saturated vapor pressure and their low boiling point. This property, if combined with the low odor thresholds of some of them, makes VOCs easily perceivable by the sense of smell. For this reason, the population that is settled in the vicinity of activities that emit VOCs into the atmosphere may withstand non-negligible odor impacts (Sarkar et al. 2003). In some cases, such processes can even arouse odor nuisance, which may cause negative economic effects, such as the loss of value of terrains or the decline of tourism (Isakson and Ecker 2008). In particularly critical situations, odor nuisance may lead to the closure of the facilities that are responsible for the release of odorants, with the consequent loss of workplaces and the missing economic return of investments (Beloff et al. 2000).

In addition to natural phenomena (e.g., spontaneous releases by arboreal vegetation, forest fires, volcanic activity), VOCs are emitted into the atmosphere by several anthropic activities. Road traffic is one of the main contributors of VOCs in the atmosphere. The reduction of emissions from this sector would require environmental policies on sustainable mobility, improvements on fuel, or on the air treatment technologies of single vehicles to reduce emissions. In addition to the transportation sector, the main VOC sources consist of industrial activities and waste management facilities, such as solvent production and use, pharmaceutical, food and petrochemical industry, civil and industrial wastewater treatment plants and, finally, mechanical-biological treatment of municipal solid waste (Torretta et al. 2014; Luciano et al. 2017). To reduce VOC emissions from these activities, different removal technologies are commonly used: thermal and catalytic combustion, biofiltration, absorption with water or chemical scrubbers, and activated carbon adsorption (Rada et al. 2014). Several studies and real-case applications have been carried out, with different outcomes in terms of abatement efficiency, costs and energy consumption, also depending on the adopted configurations and working conditions (Thakur et al. 2011; Torretta et al. 2013; Torretta et al. 2015; Schiavon et al. 2016a; Schiavon et al. 2016b; Copelli et al. 2012; Torretta et al. 2016).

With reference to the traditional technologies in use, some criticalities can be highlighted: for instance, chemical absorption allows obtaining good abatement efficiencies, but generates waste liquid flows that require additional treatment steps; on the other hand, water absorption may lead to unsatisfying abatement performance when dealing with aromatic VOCs, which are characterized by low solubility in water. Biofilters and the more recent biotrickling filters (BTFs) may represent a valid option, but are particularly sensitive to changes in the waste gas flow rate and contaminant concentrations, since biofiltration relies on the biodegradation operated by microorganisms (Raboni et al. 2016; Raboni et al. 2017). Unsteady conditions of flow rate and inlet concentrations are very common in real situations. In addition, the low water solubility of several VOCs is an obstacle to their diffusion within the microbial biofilm, where biodegradation takes place (Schiavon et al. 2017). Additional VOC removal technologies are based on incineration and activated carbon adsorption. Such processes are suitable for high VOC concentrations and become less efficient and less economically sustainable when dealing with high waste gas flow rates and low concentrations (even < 100 ppm) of gaseous compounds (Ragazzi et al. 2014; Karatoum and Deshusses 2016). Such conditions are typical of activities that are responsible for odor nuisance, which is due to both leaks of untreated air from the compartments of different facilities (e.g., wastewater treatment plants or solid waste mechanical-biological treatment plants) and insufficient abatement of odorant VOCs by the existing air treatment systems.

In addition to the abovementioned traditional removal systems, recent technologies based non-thermal plasmas (NTPs) are gaining growing interest in air pollution control (Xia et al. 2016). Plasma is defined as the so-called "fourth state of matter," i.e., an ionized gas characterized by an equilibrium between ionic charges and electrons (Fridman 2008). Generally, two types of plasma can be distinguished: equilibrium plasmas and non-equilibrium plasmas. In equilibrium plasmas, all charged and neutral particles have the same temperature. This condition occurs when energy, initially accumulated in electrons, is transferred from these to ions and molecules through Joule heating (Schiavon et al. 2016c). For this reason, equilibrium plasmas are commonly named "thermal plasmas," and may reach temperatures in the order of 10^4 K (Fridman 2008). Thermal plasmas are the base-principle of the so-called "plasma torches," which are used in different fields of application, such as gasification of coal (Shin et al. 2013) or of waste in waste-to-energy plants (Mohsenian et al. 2015;

Surov et al. 2017), and surface treatments, including recent applications to cultural heritage (Voltolina et al. 2016). Thermal plasmas are highly energetic and their energy consumption should be adequately taken into consideration in relation to the benefits obtainable by the processes they are applied to and with respect to the duration of their use.

By working in a way to reduce the time and energy available to the plasma discharge, it is possible to limit the accumulation of energy to electrons only, thus preventing the equilibrium between the latter and the remaining particles. For this reason, such plasmas are defined as non-equilibrium plasmas. In non-equilibrium plasmas, the electron temperature can reach peaks of about 10^5 K, but the average gas temperature remains almost unaltered. For this reason, non-equilibrium plasmas are often known as “non-thermal plasmas” (NTPs) (Fridman 2008). High-energy electrons initiate the so-called “plasma chemistry” by promoting molecular dissociation and generating reactive species and radicals. The latter, on their turn, are able to destroy the molecules initially present in the gas (Ikaunieks et al. 2011; Schiavon et al. 2016c). In spite of the low average temperature of the gas, NTPs are particularly reactive and capable of converting different compounds in secondary products with a simpler chemical structure, until forming the final oxidation products. The latter are carbon dioxide (CO_2) and carbon monoxide (CO), in the case of air containing VOCs (Ragazzi et al. 2014). Atmospheric pressure NTPs may represent a valid option that is alternative to the traditional VOC removal methods, thanks to the relatively low energy consumption for low-concentrated gas streams, to their easy insertion into former waste gas treatment lines and to the possibility of using NTPs for unsteady gas-flow conditions, by adopting modular reactors (Hashim et al. 2016). NTP systems are characterized by good flexibility, since the parameters controlling the discharge can be set on the basis of the type of effluent to treat and of the inlet pollutant loading rate (Yehia 2016).

NTP applications to the treatment of VOC-containing gaseous effluents are often limited to laboratory activities, since their use on a larger scale still requires adequate technical knowledge base and important investments. Intensive studies on NTPs as a treatment option for VOC removal started only at the end of the 1990s, after various experimentations in different scientific fields. Thus, NTPs represent one of the most recent technology for air purification. In the light of this aspect, this review has the purpose of evaluating the applications and the results that NTPs allow obtaining in the removal of VOCs. In addition, this review aims at analyzing all the parameters that may influence the abatement efficiency, depending on the mixture of VOCs that are present in the gaseous effluent to treat. As a matter of novelty, the present work will facilitate the practical choice of the preferable NTP and NTP-catalysis configurations to use, depending on the characteristics of the effluent and on the destination of the treated air (e.g., outdoor or indoor environments).

2 NTP Operation and Typologies

2.1 Generalities on Discharge Formation

Generally, an NTP electric discharge is generated after the formation of a sufficiently strong electric field, i.e., after the application of a sufficiently high voltage between two electrodes (a discharge and a ground electrode), within which the gas flows (Fridman 2008; Yehia 2016). The applied voltage mainly depends on the gap between the electrodes, on the presence (or absence) of dielectric layers and on the gas to treat, but it usually ranges between 10 and 30 kV (Preis et al. 2013). After a sufficiently high voltage is applied, the following processes occurs: ionization, excitation, molecular dissociation, charge transfer, propagation of the streamer, formation of radicals, and their recombination of radicals (Schiorlin et al. 2009).

Depending on the gas composition, plasma chemistry induces the formation of highly reactive species and radicals. Such process ends in a very short time (generally < 1 ms) and this allows limiting the size of NTP reactors (Kim 2004). In the case of VOC-contaminated humid air, which can be frequently found in industrial effluents, the discharge generates hydroxyl (OH) radicals and O_3. OH radicals are formed both by dissociation of water molecules and by a reaction between water and excited oxygen (Yao et al. 2015):

$$e + H_2O \rightarrow H + OH + e \tag{1}$$

$$O(1D) + H_2O \rightarrow 2OH \tag{2}$$

O_3 is generated by reactions between active oxygen (formed by dissociation of oxygen molecules) and molecular oxygen (Yao et al. 2015):

$$e + O_2 \rightarrow 2O + e \tag{3}$$

$$O + O_2 \rightarrow O_3 \tag{4}$$

The success of OH radicals or O_3 in VOC destruction or conversion into simpler compounds depends on the gas composition. For instance, OH radicals are the main actors in the destruction of toluene and isovaleric acid in NTP systems (Schiorlin et al. 2009; Assadi et al. 2015; Ondarts et al. 2017), while O_3 seems to be the main oxidant for acetaldehyde (Thevenet et al. 2008) and benzene (Ascenzi et al. 2006).

An NTP discharge can be generated in different ways, but the most common ones are the corona discharge and the dielectric barrier discharge (DBD) (Kostov et al. 2009; Jo et al. 2016). Further subdivisions can be made on the basis of the type of electric current in use (direct or alternate current), of the presence of catalysts, and of the reactor geometry (planar or cylindrical) (Kim 2004).

2.2 Main Parameters

2.2.1 Design Parameters

The main parameters for the design of an NTP system for air treatment are the gas flow rate and the initial concentration of the incoming contaminants. If keeping the reactor size, the discharge power, and the initial VOC concentration as constant, an increase in the gas flow rate implies a lower residence time of the VOCs in the reactor and, thus, a reduced interaction between active oxidant species and the contaminants, which results in a lower removal efficiency (Van Laer and Bogaerts, 2015; Ma and Lan 2015). A higher flow rate also leads to a higher inlet VOC loading rate and, consequently, to a higher energy consumption to achieve the same removal efficiency. However, the energy efficiency (namely the energy yield, EY) increases with the initial VOC concentration (Vandenbroucke et al. 2011). Such behavior can be explained with the higher probability of contact between active species and contaminants in the gas. The discharge volume is determined by the gap between the electrodes, possibly reduced by the presence of dielectric layers, within which the contaminated gas flows. The gap also determines the discharge behavior: the lower the gap, the more homogeneous the discharge, but the lower the residence time with the same gas flow rate. On the contrary, higher gaps require higher voltages and form a non-homogeneous discharge, with possible local increases in temperature and consequent formation of nitrogen oxides (NO_x) and depletion of O_3. Therefore, a proper compromise should be pursued case by case (Ma and Lan 2015; Kostov et al. 2009). The applied voltage is positively correlated with the conversion of VOCs in the gas (Van Laer and Bogaerts 2015; Tang et al. 2012; Jiang et al. 2013). The applied voltage, together with frequency and the presence of possible dielectric layers (in the case of DBD), determines the energy consumption of the system. Excessive voltage can generate non-homogeneous discharges and can cause the transition from discharge to spark (Fridman et al. 2005).

2.2.2 Performance Parameters

To assess the performance of an NTP system in removing gas-phase contaminants and to compare different cases, some parametrizations turn useful. One of these is the removal efficiency (RE), which is defined as follows:

$$\mathrm{RE}\ [\%] = \frac{C_{in} - C_{out}}{C_{in}} \tag{5}$$

where C_{in} is the initial concentration of the incoming pollutant and C_{out} is its concentration at the outlet of the NTP system. An additional useful parameter is the specific energy density (SED), which is defined as the discharge power (P) normalized to the gas flow rate (Q):

$$\mathrm{SED}\ \left[J\ L^{-1}\right] = \frac{P}{Q} \tag{6}$$

By fixing this parameter, for instance in the correspondence of a target RE, it is possible to quickly formulate considerations on the energy consumption required at different flow rates to ensure the same removal performance. The comparison between different NTP systems in terms of energy efficiency for the abatement of one compound can be more conveniently made by defining EY:

$$\mathrm{EY}\left[g\cdot(\mathrm{kWh})^{-1}\right]=\frac{\mathrm{RE}\cdot C_{in}\cdot M}{\mathrm{SED}\cdot V_m} \quad (7)$$

where M is the molar mass of the contaminant (g mol^{-1}), V_m is the molar volume of the gas (24.04 L mol^{-1} at standard temperature and pressure conditions), and C_in is expressed as parts per million.

The conversion of the initial VOCs in the most desirable carbon-based product (CO_2) is influenced by different factors related to the treated gas and to the adopted type of NTP. A useful parameter that quantifies the degree of mineralization of the initial VOCs into CO_2 is the so-called "CO_2 selectivity" (S_{CO2}), which is generally defined as:

$$S_{\mathrm{CO_2}}\,[\%]=\frac{\left(\mathrm{CO}_{2,out}-\mathrm{CO}_{2,in}\right)}{\sum_{i=1}^{N}x_i\left(\mathrm{VOC}_{i,in}-\mathrm{VOC}_{i,out}\right)} \quad (8)$$

where:

- $CO_{2,\mathrm{out}}$ and $CO_{2,\mathrm{in}}$ (both expressed as ppm) are the CO_2 concentrations at the reactor outlet and inlet, respectively;
- $VOC_{\mathrm{i,in}}$ and $VOC_{\mathrm{i,out}}$ (both expressed as ppm) are respectively the inlet and outlet concentrations of the *i*-th VOC in a mixture composed of N VOCs;
- x_i is the number of carbon atoms given by the *i*-th VOC to form CO_2, in the hypothesis that total oxidation occurs.

The higher the S_{CO2}, the lower the formation of intermediate by-products and CO is. The use of catalysts, high SED values, low initial VOC concentrations, high residence times and, thus, low gas flow rates (at a constant reactor size) are favorable conditions towards high S_{CO2} values (Karuppiah et al. 2012; Ramaraju et al. 2013; Zhu et al. 2015a; Shahna et al. 2017). Humidity has a controversial effect: in the absence of catalysts, its role can be positive for specific VOCs, since water is a source of OH radicals for plasma chemistry (Ma and Lan 2015); in the presence of catalysts, high relative humidity (RH) can lead to catalyst poisoning and limit the availability of active sites for the adsorption of VOCs (Liotta 2010). In addition, due to high electronegativity of water, plasma shows a preference in destroying the water molecule with respect to other species (Locke et al. 2012; Schiavon et al. 2017) and this implies a higher energy consumption for VOC abatement.

2.3 Types of NTPs

2.3.1 Corona Discharge

Corona discharge takes place in the vicinity of sharpened electrodes or filaments, where the short radius of curvature makes the electric field particularly strong. If the maximum of the electric field is located near the cathode or the anode, one can conventionally refer to negative or positive corona, respectively. The most interesting industrial application of corona discharges is represented by electrostatic precipitators (Kogelschatz 2004; Jun et al. 2017), which exploit electrostatic interactions to attract particulate matter towards one electrode. Two kind of geometries are mostly adopted:

1. In the cylindrical geometry (Fig. 1a), the ground electrode consists of an empty cylinder surrounding a metal wire, representing the high-voltage electrode;
2. in the planar geometry (Fig. 1b), the high-voltage electrode consists in metal wires around which the corona effect takes place, while the ground electrodes are composed of parallel metal plates.

The excitement and reaction phenomena occur in the so-called "active volume" region, located close to the electrode where the electric field is the highest. This region may be a very small fraction of the transversal section through which the gas flows. In addition, controlling the discharge may be particularly difficult, since increasing the voltage beyond the value that originates the active volume may lead to the transition from discharge to spark (Fridman et al. 2005). However, this criticality can be overcome by changing the power source and adopting pulsed current. In this case, if the pulse is limited to about 100 ns and the time for achieving the peak is relatively short, it is possible to prevent spark formation and minimize energy dissipation (Kim 2004). This way, a more homogeneous discharge is obtained without the adoption of dielectric layers. In addition, the gap between the electrodes could be enlarged and this would entail obvious advantages in terms of pressure drop (Preis et al. 2013). However, the main

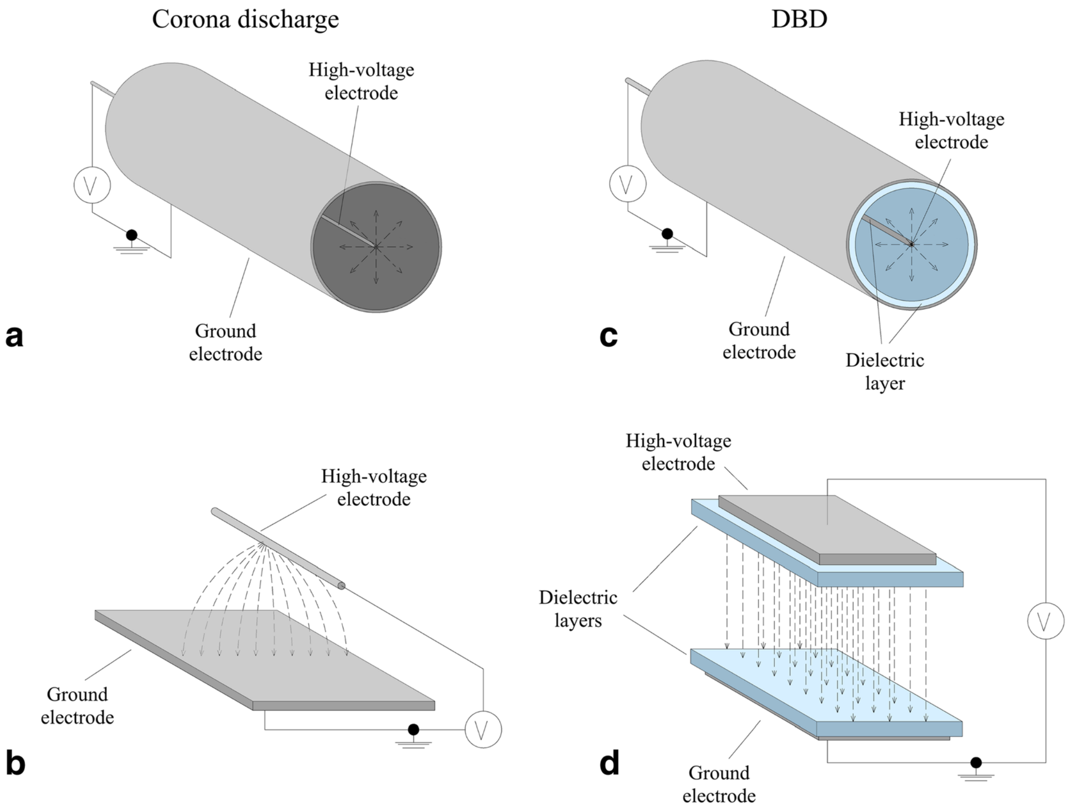

Fig. 1 General schemes of the more common geometries adopted in corona discharge reactors (**a**, **b**) and DBD reactors (**c**, **d**)

limitation of the pulsed corona discharge consists in the need for adopting a pulse generator, whose cost far exceeds that of the power sources commonly adopted for traditional corona discharges.

2.3.2 DBD

DBD is the most studied type of NTP discharges (Ramaraju et al. 2013; Anaghizi et al. 2015). The first experiments concerning the application of a DBD date back to 1857 and were carried out by von Siemens (Kogelschatz 2003). Such experiments led to the commercialization of the first ozonizers, whose main field of application was the production of potable water.

The typical structure of a DBD reactor consists in a couple of electrodes, with at least one electrode coated by one dielectric barrier. The interposed dielectric layer impedes the charge transfer and allows preventing the formation of sparks, spreading the discharge on a wider surface and forming a multitude of micro-filaments, which make the discharge more homogeneous (Fridman et al. 2005; Fang et al. 2007; Ramaraju and Subrahmanyam 2014, Kogelschatz 2003, Yehia 2016). Thanks to this expedient, the probability of contact between the molecules in the gas and the discharge is higher than other types of discharge. In addition, the presence of one or more dielectric layers prolongs the lifetime of the electrodes, since dielectrics act as protective layers preventing possible phenomena of corrosion or deposition of particulate (Nehra et al. 2008). The formation of a multitude of micro-discharge, rather than a few discharges concentrated in few points, reduces the risk of increasing the gas temperature, which could generate undesired by-products and destroy O_3, which decomposes above 100 °C at atmospheric pressure. On the other hand, the interposition of dielectric barriers entails a considerable reduction of energy efficiency (Preis et al. 2013). In addition, due to the interposition of an insulating material, the gap should be limited to a few millimeters to activate the discharge (Hammer 2014). Thus, the gas flow being constant, the residence time would decrease and the pressure drop would increase (Preis et al. 2013).

Typical dielectric materials are glass, quartz, mica, and alumina (Kim 2004). Due to the capacitive coupling of the circuit, DBDs need alternate current or pulsed direct current (Hammer 2014). Typically, the range of adopted frequencies varies between 50 Hz and 500 kHz, while peak voltages of about 10 kV are usually adopted (Fridman et al., 2005). Differently from nano-pulsed corona discharges, the power supply of DBDs is relatively simple and this favors their application to different industrial fields, whose the most common is ozonization.

An additional important factor that deserves consideration is the reactor geometry. Analogously to corona reactors, the cylindrical (Fig. 1c) and planar (Fig. 1d) geometries are the most common (Kogelschatz 2004; Nehra et al. 2008). In the cylindrical geometry, the ground electrode is a metal bar, optionally covered by a dielectric layer. The high-voltage electrode usually consists in a cylindrical metal mesh or foil, which is concentric to the ground electrode and internally covered by a dielectric layer. In the planar geometry, the electrodes consist in parallel surfaces (e.g., fine metal meshes) separated by a dielectric layer. Compared to the cylindrical geometry, the advantage of the planar geometry is the possibility of creating a bigger reactor consisting of more parallel DBD units. This allows optimizing the transversal section available to the gas flow and easily scaling the system up (Nehra et al. 2008). This way, pressure drops are minimized: indeed, by packing parallel cylindrical DBDs together, the transversal section would not be completely available to the gas flow, since the regions comprised between the tangential points of the circumferences could not be exploited for the gas treatment.

2.3.3 Plasma-assisted and Plasma-driven Catalysis

One of the drawbacks of NTPs for air cleaning purposes is the potential formation of unwanted by-products, due to the partial conversion of the initial compounds (Kim et al. 2015). The prevention of such by-products is possible by increasing the discharge power, but this would increase the energy consumption. One possible solution to this limitation is the adoption of catalysts.

Catalysts allow reducing the activation energy of chemical processes, inducing alternative and more energy-efficient reaction routes (Trinh and Mok 2016). In addition, several catalyst materials can adsorb molecules on their surface. This allows prolonging the residence time of pollutants and favoring their destruction. In this sense, the catalyst porosity is a very important characteristic. In addition, catalysts can be used to reduce the excess O_3 generated by NTP, which would be released into the atmosphere. Catalysts have shown high efficiency in converting O_3 in atomic oxygen, which is a strong oxidizing agent for VOC decomposition (Subrahmanyam et al. 2010; Trinh and Mok 2015a; Jo et al. 2016). Furthermore, catalysts allow reducing CO formation and moving the carbon balance towards CO_2 (Kim et al. 2015; Jiang et al. 2017a).

The most common catalysts adopted for air cleaning purposes are: aluminum, manganese, and titanium oxides, combined with iron, nickel, platinum, palladium, cobalt, copper, barium, or silver (Chen et al. 2009). Zeolites are also often used in NTP-catalysis (Inoue et al. 2011; Trinh et al. 2014). Due to the abovementioned advantages of adopting catalysts, several studies have been recently carried out on the use of catalysts combined with NTPs, both in single-stage (Subrahmanyam et al. 2007; Magureanu et al. 2007a; Lee et al. 2015; Zhu et al. 2015b; Jo et al. 2016; Patil et al. 2016) and in two-stage combinations (Magureanu et al. 2007b; Nguyen Dinh et al. 2014; Nguyen Dinh et al. 2015; Li et al. 2015).

The single-stage combination is also known as "plasma-driven catalysis" (PDC) or "in-plasma catalysis." The catalyst, which is usually in form of pellets, is directly placed inside the NTP reactor. The latter can be entirely (packed-bed reactor) or partially (hybrid reactor) covered by the catalyst. Alternatively, electrodes made of sintered metal fiber (SMF) can be used. The catalyst can directly influence the plasma properties, can modify the distribution of electrons, and the discharge behavior. On the other hand, the catalyst can be influenced by plasma, which can alter the catalyst properties and its adsorption efficiency (Van Durme et al. 2008).

The two-stage configuration is also known as "plasma-assisted catalysis" (PAC) or "post-plasma catalysis." In this configuration, the catalyst is placed outside the plasma region and is usually in form of pellets. It is preferable to locate the catalyst bed downstream of the plasma region, in order to foster the removal of nitrogen-based byproducts and excess O_3.

The choice of one configuration rather than the other depends on the kind of catalyst and on the target of NTP application: Trinh and Mok (2015b), when treating air contaminated by ethylene with zeolites, observed higher REs in the single-stage configuration, thanks to the more immediate penetration of O_3 inside the pores. In addition, the single-stage configuration allows operating the reactor in a cyclic mode (Vandenbroucke et al. 2011; Kim et al. 2016; Trinh and Mok 2016), i.e., by alternating a phase of adsorption of the pollutants (with no plasma discharge) and a phase of regeneration of the catalyst (by activating the plasma discharge). By analyzing previous experiments on catalysts based on metal oxides, Xiao et al. (2014) confirmed the higher VOC REs when adopting PDC. On the other hand, Chen et al. (2009) documented the higher RE of unwanted by-products and excess O_3 that would be achievable when adopting PAC. For this reason, Chen et al. (2009) suggest the use of PDC when the priority is the achievement of high good REs of the initial VOCs and high-energy efficiency (e.g., industrial applications), while the use of PAC is preferable when air quality and health impacts are the priority target (e.g., indoor air quality).

The choice of the catalyst material is also particularly important, since different materials can be more or less suitable for the removal of the target compounds: manganese oxides (MnO_x), for example, showed high performances in the removal of trichloroethylene (TCE), while silver-anatase (Ag/TiO_2) catalysts are the preferred ones for treating benzene (Vandenbroucke et al. 2011).

3 Recent Experimental Studies on NTP Applied to VOC Removal from Air

In recent years, several studies have been carried out with the common target of seeking the best possible operating conditions for VOC removal with NTPs. Table 1 reports 20 recent laboratory-scale studies on mixtures of compressed or synthetic air and VOCs.

Among the selected studies, 16 experiments focused on the abatement of four single VOCs: toluene (TOL), formaldehyde (FOR), benzene (BZ), and TCE. TOL is one of the most studied VOCs in laboratory-scale NTP applications. BZ, FOR, and TCE are demonstrated carcinogens to humans (IARC 2017) and, thus, are extremely important from the point of view of long-term health effects. TOL, BZ, and TCE are used as additives or solvents in industry. BZ, in particular, is used in printing houses, varnishes and in the chemical industry (Karuppiah et al. 2014; Pangilinan et al. 2016). TCE is one of the most common chlorinated VOCs, which is a category of compounds mainly used as solvents and industrial degreasers (Vandenbroucke et al. 2016; Nguyen Dinh et al. 2015). FOR is formed by incomplete combustion processes (Saulich and Müller 2013). FOR is also a component of the resins used in the wood industry for the production of pressed-wood panels (Wan et al. 2011) and represents one of the most hazardous indoor air pollutants, since it is slowly released by pieces of furniture in houses.

At a laboratory-scale, most of the studies focus on single VOCs rather than VOC mixtures. If, on one hand, the focus on a single VOC facilitates the quantification of the energy required to convert or mineralize the initial contaminant and allows characterizing by-products and reaction mechanisms at different SEDs, on the other hand, it does not allow obtaining useful indications on real effluents, which are often composed of several substances (Schmidt et al. 2015). For this reason, 4 of the 20 selected studies focus on the abatement of VOC mixtures containing at least one VOC among TOL, FOR, BZ, and TCE. The remaining compounds in the four mixtures are: chlorobenzene (CBZ), hexane (HX), cyclohexane (CHX), 1,4-dioxane (DX), *p*-xylene (XYL), and *n*-octane (OCT). In spite of being a rough approximation of real effluents, the study of VOC mixtures allows evaluating possible differences in the reaction mechanisms with respect to single-VOC studies.

4 Critical Discussion of the Experimental Findings

For each of the selected experimental activities, Table 2 reports the maximum RE (RE_{max}), the corresponding SED, the maximum EY (EY_{max}), the maximum S_{CO2} ($S_{CO2,max}$) and the main detected byproducts. When not explicitly reported, SED and $S_{CO2,max}$ were estimated by the graphs presented in the selected studies, and EY_{max} was calculated according to (7) in correspondence of RE_{max}. The list of the main byproducts of the NTP treatments intentionally does not contain O_3 and CO.

For each of the selected experiments on single-VOC mixtures, C_{in}, RE_{max}, and the corresponding SED are reported in detail in Fig. 2. The experiments on TCE were carried out with similar values of C_{in}, and RE_{max} values were > 93% in all cases. In spite of this, the SED allowing for such RE_{max} values greatly varied case by case. This appears particularly evident in the studies by Nguyen Dinh et al. (2014), Nguyen Dinh et al. (2015), and Vandenbroucke et al. (2016), which were carried out with the same corona discharge reactor. Such differences might be explained with the different types of

Table 1 Operation parameters and characteristics of the selected experimental activities on VOC abatement

VOCs	Type of NTP reactor	Catalysts (configuration)	C_{in} (ppm) (carrier, RU [%])	Total flow rate (L min^{-1})	Residence time (*s*)	Voltage (kV)	Frequency (Hz)	Reference
TOL	DBD	None	95 (compressed air, 30%)	6.6	0.016	7–10	22	Karatoum and Deshusses (2016)
TOL	DBD	Co-MCM-41 (PDC)	100 (synthetic air, 0%)	0.2	0.22	0–100	50	Xu et al. (2017)
TOL	Photocatalytic DBD	TiO_2/SMF (PDC)	40 (synthetic air, 0%)	1	4	10–40	20	Chen et al. (2016)
TOL	Pulsed DBD	Pd/γ-Al_2O_3 (PDC)	1000 (air, n.d.)	1	1.08	20	10–200	Pham Huu et al. (2017)
FOR	Packed-bed DBD	$NaNO_2$ (PDC)	0.05 (compressed air, 30%)	8.5	0.29	0–20	15,000	Liang et al. (2010)
FOR	DBD	Cu/CeO_2 (PDC)	57.7 (synthetic air, 0%)	1	0.23	0–30	10,000	Zhu et al. (2015a)
FOR	Packed-bed DBD	Ag/CeO_2 (PDC)	276 (synthetic air, 35.5%)	0.605	0.22	0–40	50	Huixian and Zengfeng (2009)
FOR	Corona discharge	MnO_x/Al_2O_3 (PAC)	2.2 (synthetic air, 30%)	6	0.05	0–25	–	Wan et al. (2011)
BZ	DBD	None	95 (compressed air, 30%)	6.6	0.016	7–10	22,000	Karatoum and Deshusses (2016)
BZ	Hybrid DBD	TiO_2/MnO_x/SMF (PDC)	50 (air, 0–100%)	0.5	0.46	14–22	50	Karuppiah et al. (2014)
BZ	Packed-bed DBD	Ag/TiO_2 (PDC)	60–210 (synthetic air, 0%)	4	n.d.	28	100–1500	Kim et al. (2005)
BZ	Packed-bed DBD	$Ag_{0.9}Ce_{0.1}$/γ-Al_2O_3 (PDC)	400 (synthetic air, 0–80%)	0.5	5.8	17–25	50	Jiang et al. (2016a)
TCE	Corona discharge	Pd/$LaMnO_3$ (PAC)	500–560 (compressed air, 18%)	2	2.16	30	–	Vandenbroucke et al. (2016)
TCE	DBD	Au-mesoporous silica (PAC)	430 (compressed air, 0%)	0.51	4	10–25	50	Magureanu et al. (2007b)
TCE	Corona discharge	$LaMnO_{3+\delta}$ (PAC)	510 (synthetic air, 0–18%)	2	2.16	30	–	Nguyen Dinh et al. (2014)
TCE	Corona discharge	$CeMn_4$ (PAC)	360–400 (compressed air, 10%)	2	2.16	30	–	Nguyen Dinh et al. (2015)
Mixture	DBD	AgO_x/MnO_x/SMF (PDC)	50 (CBZ), 100 (BZ), 50 (TOL) (air, 0–85%)	0.250	0.47	14–22	50	Karuppiah et al. (2012)
Mixture	Corona discharge	MnO_x/Al_2O_3 (PAC)	1.5 (BZ), 1.4 (TOL), 1.2 (XYL) (synthetic air, 25%)	6	2.1	25	–	Fan et al. (2009)
Mixture	DBD	MnO_x/SMF (PDC)	100 (HX), 75 (DX), 75 (TOL) (air, 0–100%)	0.300	0.77	14–22	50	Ramaraju and Subrahmanyam (2014)
Mixture	DBD	None	25 (BZ), 164 (TOL), 183 (OCT) (synthetic air, 33%)	0.300	0.98	15	4000	Schiavon et al. (2015)

Table 2 Results of the selected studies in terms of RE_{max}, corresponding SED, EY_{max}, $S_{CO2,max}$, and main byproducts formed during the treatment of VOCs

Reference	RE_{max} (%)	SED ($J\ L^{-1}$)	EY_{max} ($g\ (kWh)^{-1}$)	$S_{CO2,max}$ (%)	Main by-products
Karatoum and Deshusses (2016)	74	360	2.6	n.d.	Benzoic acid crystals
Xu et al. (2017)	100	226	1.69[a]	n.d.	2-Hexanone, 1-methyl-4-nitrobenzene, 4-methyl-2 -nitrophenol
Chen et al. (2016)	~ 92%	~ 210	0.67[a]	> 90%	Formic acid, formaldehyde
Pham Huu et al. (2017)	100	148	17.5[a]	45	Benzene and benzaldehyde
Liang et al. (2010)	93	786	0.47	n.d.	Methanol
Zhu et al. (2015a)	92.9	486	0.14[a]	96.4	Formic acid
Huixian and Zengfeng (2009)	99	108	2.51[a]	86	Not reported
Wan et al. (2011)	87	20	0.12[a]	n.d.	Not reported
Karatoum and Deshusses (2016)	58	360	0.51[a]	n.d.	Not reported
Karuppiah et al. (2014)	95[b]	170	1.00[a]	n.d.	Not reported
Kim et al. (2005)	98	70	2.73[a]	~ 77	Formic acid, phenol, nitrous oxide, NO_x
Jiang et al. (2016a)	100[c]	400	3.00[a]	83.1	Nitrogen dioxide
Vandenbroucke et al. (2016)	96.2	460	4.49[a]	~ 20	Hydrochloric acid, dichloroacetyl chloride, phosgene, chloral
Magureanu et al. (2007b)	100	~ 670	3.50[a]	n.d.	NO_x, octanal, nonanal, decanal, 1-chloro octane, 1-chloro nonane
Nguyen Dinh et al. (2014)	93[c]	460	4.43[a]	n.d.	Hydrochloric acid, chlorine, dichloroacetyl chloride, phosgene, chloral
Nguyen Dinh et al. (2015)	96.9	240	5.50[a]	~ 37	Hydrochloric acid, chlorine, dichloroacetyl chloride, phosgene, chloral
Karuppiah et al. (2012)	100 (CB), 100 (BZ), 100 (TOL)[c]	300	1.08[a] (BZ)	80	NO_x, nitric acid, benzaldehyde, aromatics, and aromatic acids
Fan et al. (2009)	94 (BZ), 97 (TOL), 95 (XYL)	10	2.8 (BZ), 4.2 (TOL), 5.4 (XYL)	~ 100	Formic acid, benzaldehyde, benzyl alcohol
Ramaraju and Subrahmanyam (2014)	100 (TOL), 100 (HX), 100 (DX)[c]	~ 300	0.96[a] (TOL)	~ 88	Not reported
Schiavon et al. (2015)	99.1 (BZ), 100 (TOL), 100 (OCT)	1840	0.51 (BZ)	63	Benzaldehyde, cresols, phenol, benzyl alcohol

[a] Calculated on the basis of RE_{max}

[b] Referred to $C_{in} = 60$ ppm

[c] Evaluated at the upper value of the investigated RH range

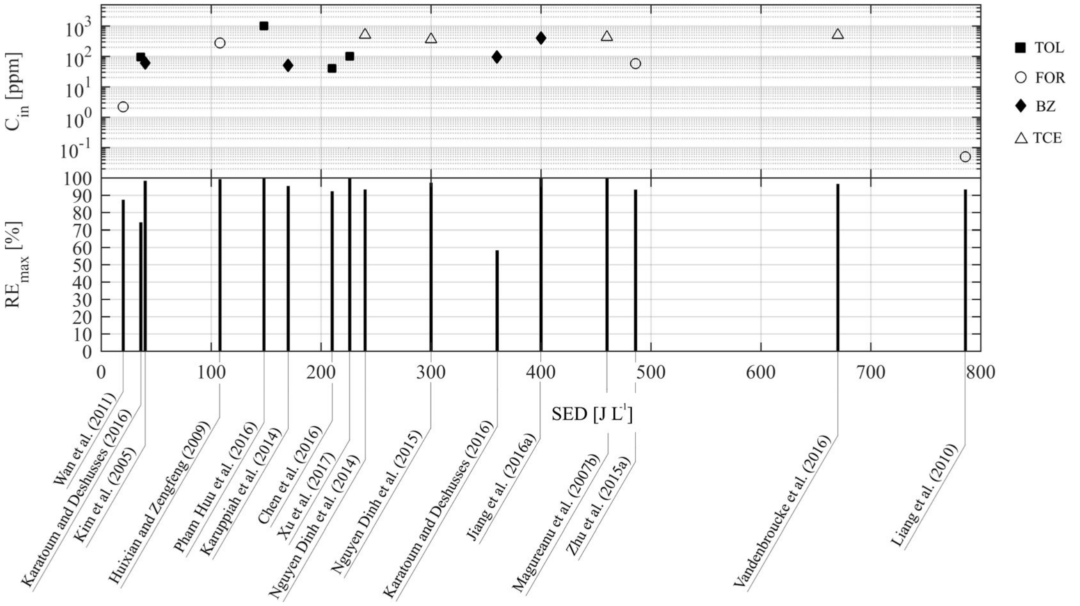

Fig. 2 Results from the selected studied on single-VOC mixtures in terms of C_{in}, RE_{max} and corresponding SED

catalysts adopted. In the light of this, $LaMnO_{3+\delta}$ seems to be the preferable choice with respect to $CeMn_4$ and $Pd/LaMnO_3$. The application of NTP-catalysis to TOL and BZ lead to comparable results in terms of RE_{max} and corresponding SED in relation to the different C_{in} values. A lower performance is reported in Karatoum and Deshusses (2016), which might be explained with the absence of catalysts. Very different results were obtained in the studies on FOR abatement: as reported by Liang et al. (2010), relatively low concentrations (0.05 ppm) were efficiently abated only at relatively high SED (786 J L^{-1}); on the other hand, Wan et al. (2011) obtained an 87% RE at 20 J L^{-1}, starting from a concentration of 2.2 ppm. Possible explanations might be the different types of discharge (packed-bed DBD and corona) and/or the different catalysts adopted.

In general, as observed by Karatoum and Deshusses (2016) in single-VOC experiments, the higher the weight fraction of hydrogen atoms in a VOC, the higher the VOC rate constant, i.e., the lower the SED that is required at the same conditions. Indeed, VOCs with a higher hydrogen weight fraction generally have a higher number of methyl groups and may be more reactive, thanks to their relative ease in losing or gaining a proton at the methyl group (Karatoum and Deschusses 2016). Fan et al. (2009) confirmed such behavior in a mixture of VOCs and observed a higher EY for TOL and XYL compared to BZ.

The surface area of the catalyst has a marked influence on VOC removal (Einaga and Futamura 2004). As a confirmation of this, Xu et al. (2017) studied the effect of the amount of cobalt incorporated onto the zeolite support (MCM-41): surprisingly, beyond an optimum amount, the cobalt doping showed an inhibiting effect on TOL conversion, which is explained with the reduced availability of surface area.

In their experiments, Pham Huu et al. (2017) investigated the effect of temperature on the conversion of TOL when using $Pd/\gamma\text{-}Al_2O_3$ as a catalyst. Interestingly, when the temperature is < 100 °C in the PDC configuration, desorption of TOL occurs from the catalyst. This behavior may be explained with the role of NTP in affecting the adsorption/desorption equilibrium of TOL (Pham Huu et al. 2017). However, when the temperature is > 100 °C, the same authors report enhanced abatement performance of PDC with respect to PAC and NTP alone.

Wan et al. (2011) investigated the different performance of positive and negative corona discharges in removing FOR from synthetic humid air. At the same SED, the positive corona allows for a higher RE of FOR, mainly because of the higher O_3 generation. However, FOR oxidation is more efficiently carried out by OH radicals, as documented by an experiment with RH = 70% on plasma alone (Wan et al. 2011). With

RH = 30%, the introduction of a catalytic stage downstream of the NTP reactor lead to a significant increase in RE: by keeping the SED fixed at 20 J L^{-1}, for instance, the RE increased from 36 to 87%.

Despite the blocking effect of the active sites by water molecules, Nguyen Dinh et al. (2014) observed a positive effect of humidity on both S_{CO2} and TCE decomposition in their experiment carried out with $LaMnO_{3\ +\ \delta}$ (PAC). Reasons for that are the strong oxidation potentials of OH radicals and the role of water as a chlorine scavenger on the catalyst surface. However, TCE abatement generates some unwanted by-products, especially hydrochloric acid and phosgene (Vandenbroucke et al. 2016; Nguyen Dinh et al. 2015).

Karuppiah et al. (2012) applied a DBD with AgO_x/MnO_x/SMF (PDC) both to a mixture of CB, BZ, and TOL, and on the single VOCs. Interestingly, the REs of the single VOCs in the single-component tests were lower than the REs of the respective VOCs obtained when applying NTP to the VOCs in the multi-component mixture at the same SED. One possible explanation for this is the generation of less reactive species in the single-component mixture, implying a lower probability of radical formation (Karuppiah et al. 2012). Conversely, the addition of TOL to a mixture of air and FOR lead to lower FOR removal at the same applied SED, due to competition between these two VOCs (Wan et al. 2011). Ramaraju et al. (2013) and Karuppiah et al. (2012) documented the positive effects of humidity, which increased both S_{CO2} and the VOC REs. According to the results of the experiments on BZ carried out by Jiang et al. (2016a) with $Ag_{0.9}Ce_{0.1}$/γ-Al_2O_3 as a catalyst, RH = 30% seems to be an optimal value to enhance RE and S_{CO2} to 100 and 83.1%, respectively, while higher RH values inhibit the catalytic activity. This appears to be in contrast with the findings of Karuppiah et al. (2014), who observed increased performance on BZ abatement and S_{CO2} when using MnO_x/SMF.

Since the conditions in which EY_{max} and $S_{CO2,max}$ were calculated or estimated widely vary from experiment to experiment, a direct comparison between the selected experiments in terms of these two parameters cannot be made. However, the following general considerations on S_{CO2} can be formulated: among experiments that consider the same single VOC (TOL, FOR, BZ, or TCE), lower C_{in} allows achieving higher values of $S_{CO2,max}$, as confirmed by comparing the results of the studies by Chen et al. (2016) and Pham Huu et al. (2017) on TOL, Zhu et al. (2015a) and Huixian and Zengfeng (2009) on FOR, Kim et al. (2005) and Jiang et al. (2016a) on BZ, and Nguyen Dinh et al. (2015) and Vandenbroucke et al. (2016) on TCE. C_{in} shows a certain influence on EY_{max}: the higher C_{in}, the higher EY_{max}, as confirmed by comparing EY_{max} and C_{in} values among the studies carried out on TOL, FOR, and BZ. In addition, the use of silver in catalysts seems to work in favor of EY (Kim et al. 2005; Huixian and Zengfeng 2009). C_{in} seems not to be a valid parameter for the comparison between the EY values estimated from the studies on TCE removal (Vandenbroucke et al. 2016; Magureanu et al. 2007b; Nguyen Dinh et al. 2014; Nguyen Dinh et al. 2015). Therefore, the higher energy efficiency obtainable when treating higher concentrations of VOCs allows considering NTP-catalysis as an option for industrial applications (Li et al. 2014). When evaluating the operational costs associated with the adoption of NTP-catalytic systems, in addition to NTP power consumption, decision-makers should consider the energy spent for catalyst heating, in order to ensure activation of the catalytic material (Pham Huu et al. 2017).

The formation of intermediates and by-products (other than excess O_3) might be a matter of concern. If S_{CO2} is not 100%, CO and other byproducts of VOC conversion are present in the outgoing mixture. CO induces adverse health effects to humans exposed to high concentrations, leading to death in subjects exposed to a concentration of 300 ppm for more than 500 min (Wilbur et al. 2012). For this reason, its emissions from several industrial and power plants are regulated worldwide. Besides CO, the selected experiments report the presence of toxic by-products of incomplete VOC degradation that are particularly important for the chronic effects they may induce to people exposed for long periods at relatively low concentrations. This is the case of benzene, a human carcinogen that may originate at low SED when treating toluene (Pham Huu et al. 2017). A lifetime exposure to concentrations > 0.04–0.13 ppb may induce a cancer risk > 10^{-6} (U.S. Environmental Protection Agency 2015). Nitrogen dioxide (NO_2) is formed in the presence of locally high temperature and is reported as a by-product by Kim et al. (2005) and Karuppiah et al. (2012). NO_2 shows both acute and chronic effects on individuals, which vary from reduced lung development in children to exacerbation of asthma and cardiovascular and respiratory diseases in adults (Kulkarni and Grigg 2015). The compound that showed the highest number of toxic byproducts is TCE, whose NTP-catalytic oxidation generated chlorine, hydrochloric acid, phosgene, and chloral (Vandenbroucke et al. 2016; Magureanu et al. 2007b; Nguyen Dinh et al. 2014; Nguyen Dinh et al. 2015). According to the Agency for Toxic Substances and Disease Registry (ATSDR), short-term exposure to chlorine (1–3 ppm) may cause irritation of the airways, until leading to death (> 430 ppm) (ATSDR 2015). Exposure to phosgene may induce pulmonary edema and lung inflammation, since this compound is hydrolyzed to hydrochloric acid, which damages cells (ATSDR 2014). Chloral is classified as probable carcinogen to humans (IARC 2017). Therefore, apparently, NTP might not be successfully applied to TCE. However, the formation of such by-products is a cost compensated by the removal of a demonstrated carcinogen like TCE.

5 Future Prospects

Following the discussion on the outcomes of the selected literature studies, two fundamental points arise:

1. higher REs are generally achieved by decreasing C_{in} at the same flow rate conditions;
2. the energy efficiency of the NTP-catalysis treatment increases with increasing C_{in} at the same flow rate conditions.

Therefore, based on the first observation, NTP-catalysis seems to be a convenient option if high REs must be granted in case the contaminated effluent is characterized by low VOC concentrations. The convenience further increases if the flow rate decreases, since lower operating costs are expected. In the light of that, indoor air treatment is an interesting field of application. Indeed, the treatment of indoor air generally does not involve high concentrations of contaminants and high volumes of air to be purified. Under such conditions, high REs could be granted at relatively low operational costs. Moreover, high REs are strongly desirable in indoor air treatment, since people spend most of their time in indoor environments (Sarigiannis 2013); consequently, indoor air treatment plays a key role in the reduction of personal exposure to air pollutants. However, to ensure high REs and avoid byproduct formation, the inclusion of a post-plasma catalytic stage is crucial, otherwise the risk of generating byproducts that are more hazardous than the starting VOCs cannot be ruled out, as recently reported in Bahri and Haghighat (2014) and in Luengas et al. (2015). In recent years, several studies were carried out on NTP-catalysis applied to the treatment of indoor air. Van Durme et al. (2007) used a pin-to-mesh corona discharge to remove low concentrations of toluene (0.5 ppm) from dry and humid air (RH = 27%). The SED required to obtain 80% RE with PAC (MnO_2-CuO/TiO_2) was about 20 times and 5 times lower than the SED required by NTP alone, in dry and humid conditions, respectively. At the same SED, the REs obtained with PAC were higher than PDC with a commercial mixture of TiO_2 (> 85%) and aluminum and silicon oxides (< 15%). PAC proved to be the preferred option to abate the main unwanted byproducts of corona oxidation, i.e., O_3 and NO_x. At the same SED, the outlet O_3 concentration in PAC increased with humidity, contrarily to PDC and NTP alone. However, the beneficial effect of PAC in abating O_3 largely compensates the negative effect of humidity. As a result, at the same SED, even with higher RH (45%), the outlet O_3 concentration with PAC was 63–71 and 43–51% lower than NTP alone and PDC, respectively (Van Durme et al. 2007). However, the same authors observed deactivation of the MnO_2-CuO/TiO_2 catalyst after 7 h of continuous operation. This performance decrease is attributable to the blocking effect of the active sites by nitric acid (HNO_3), which is produced by NTP in humid air (Devashasdin et al. 2003; Sano et al. 2006). MnO_2-CuO/TiO_2 in PAC was compared with other catalysts in a following work (Van Durme et al. 2009): MnO_2-CuO/TiO_2 showed higher performance in removing low concentrations of toluene compared with other catalysts like Pd/Al_2O_3 and Fe_2O_3-MnO_2 under humid conditions (RH = 50%); no differences in the O_3 RE were observed among all the investigated catalysts. Even with RH = 74%, the toluene RE turned out to be two times higher if compared with the case of NTP alone (Van Durme et al. 2009). Other investigations on the applicability of NTP-catalysis as an option for indoor air treatment were carried by Assadi et al. (2015). In this case, a DBD was used in combination with TiO_2-based photocatalysis (activated by UV lamps) to remove an initial concentration of butyraldehyde of 40–100 mg m^{-3} in a flow rate of 5–10 $m^3\ h^{-1}$. Among the different configurations that were studied, post-plasma photocatalysis showed the best results in terms of RE and S_{CO2}. However, the maximal S_{CO2} did not exceed

50% and an O_3 concentration of 88.6 ppm was measured at the outlet. The high initial concentration and the high air flow rate may explain such results, which seem to be not promising in view indoor air purification. As highlighted by Bahri and Haghighat (2014), in general, the results obtained in laboratory-scale experiments may not apply to real indoor conditions: indeed, one should consider that VOC concentrations in indoor environments are typically in the order of ppb, while the majority of laboratory-scale studies consider initial concentrations that exceed such levels by one or two orders of magnitude. Furthermore, as pointed out by Futamura et al. (2002), at the same SED, the lower the initial VOC concentration, the higher the negative gap between RE in presence of humid air and RE in dry air: indeed, at the same degree of occupancy of the active sites by water molecules, the probability of interaction between VOC molecules, and catalyst decreases when the initial VOC concentration reduces. An interesting opportunity to remedy this problem is given by adopting hydrophobic materials as zeolites-based catalysts, as those adopted by Inoue et al. (2011); however, the use of dry or humid air was not specified in this study.

To summarize the obtained results, PAC is preferable to reduce unwanted byproducts generated by NTP oxidation of VOCs in air. Although PAC is generally less effective than PDC in removing the starting VOCs, higher removal rates of excess O_3 are observed when placing catalysts downstream of the plasma region. PAC allows for higher removal rates of NO_x compared with PDC. However, two main drawbacks should be considered:

- in PAC, humidity reduces the removal rate of O_3 compared to dry air; however, lower O_3 outlet concentrations are anyway granted by PAC compared with NTP alone;
- deactivation of the catalysts occurs during operation.

To overcome the first drawback, a dehumidification step could be considered. Although humidity is beneficial in the NTP oxidation of some VOCs, higher VOC removal efficiencies can be anyway obtained when applying PAC in dry conditions compared with the sole NTP oxidation in humid conditions (Van Durme et al. 2007). To overcome the second drawback, Van Durme et al., (2007) proposed to simply wash the catalysts with distilled water, which resulted in the successful reactivation of the MnO_2-CuO/TiO_2 catalyst. However, as previously mentioned, the interpretation of laboratory-scale results must consider the higher initial concentrations under study, in comparison with the typical levels expected in indoor environments.

Based on the second observation, NTP-catalysis seems to be a convenient option when the effluent is characterized by higher C_{in} (as in the case of industrial emissions) and when medium REs are required. Thus, NTP seems to be appropriate to pretreat gaseous effluents upstream of other removal technologies. In addition, the presence of a second removal stage downstream of NTP may abate possible unwanted byproducts generated by NTP. If continuously operated, NTP would help reducing the VOC concentrations at the inlet of the removal technology located downstream. This may allow achieving higher overall REs and/or reducing the size of the second removal stage. In the case of absorption columns, bioscrubbers and BTFs, a pretreatment stage may reduce the generation of liquid waste streams by these technologies. In the case of unsteady flow rate, NTP could operate in discontinuous mode and be activated only to abate peaks of concentrations. This mode of operation could be particularly useful if the second removal stage consists in a biological technology, like biofilters, BTFs, or bioscrubbers. Indeed, it is known that biological technologies suffer from discontinuous loading rates of contaminants (Almarcha et al. 2012; Copelli et al. 2012). One of the first extensive study on a practical application of NTP combined with absorption was carried out by Brandenburg et al. (2014), whose work moved from a previous study carried out with the purpose of purifying water through ozonization (Kuraica et al. 2004). Brandenburg et al. (2014) changed the point of view from water treatment to gas treatment, by applying a DBD to a contaminated airflow in presence of distilled water, rather than to contaminated water in presence of clean air. In more detail, NTP oxidation and absorption were combined in one single stage: the ground electrode consists in a cave stainless steel cylinder through which water flows upwards and descends on the outer wall; the high-voltage electrode consists in an alumina foil placed on a cylindrical glass vessel, which contains the ground electrode, the water flow and the mixture of air (Q = 800 L h^{-1}), and undecane (C_{in} = 500 ppm) in a 3-mm gap between the ground electrode and the inner wall of the vessel. The water phase reduced the concentration of by-products in the outgoing air, due to the formation of water-soluble VOCs and HNO_3 from NO_x. However, the presence of the water film in the plasma region lead to a 20% decrease in the energy efficiency of plasma with an applied voltage of 12 kV (Brandenburg et al. 2014). Such findings suggest that separating NTP oxidation and absorption into two stages could allow for higher energy efficiency. Water-soluble by-products would be dissolved in water in the absorption stage. In recent years, a series of studies have been undertaken to investigate the two processes in sequence, with a special focus on biofiltration technologies. Wei et al. (2013) applied a corona discharge (applied voltage: 2 kV) upstream of a bench-scale BTF to pretreat a constant airflow containing dimethyl sulfide (C_{in} = 70–80 mg m^{-3}). The pretreatment allowed increasing the overall RE from 84.4 to 95.4%, thanks both to the conversion of dimethyl sulfide into more soluble compounds (e.g., carbonyl sulfide and methanol) and to the formation of new and diverse microbial communities. Synergies between NTP oxidation and biofiltration are confirmed by Jiang et al. (2016b): in this case, a DBD was adopted to pretreat a mixture of air and chlorobenzene (Q = 4 L h^{-1}; C_{in} = 500 mg m^{-3}) upstream of a BTF. An additional BTF was operated in parallel, as a control reference. The activation of the DBD allowed for a general increase in the overall RE: at the highest empty bed residence time (60 s), RE increased from 57.8% (with no pretreatment) to 94.5% (with pretreatment) at the same SED. Contrarily to the results obtained by Wei et al. (2013), the microbial diversity slightly decreased when using NTP (Jiang et al. 2016b). This behavior may depend on the initial contaminant and on the by-products of NTP oxidation: Wei et al. (2013) documented the formation of additional compounds besides dimethyl sulfide (carbonyl sulfide and methanol), which may favor the growth of new communities, while no by-products were listed by Jiang et al. (2016b) besides hydrochloric acid. In addition, in the latter study, oxidation of biomass by O_3 is considered the reason for a decrease in the total microbial biomass content, while no data on this parameter were presented by Wei et al. (2013). A mild decrease in the biomass content could be beneficial to prevent excess biomass formation or clogging episodes (Mudliar et al. 2010). However, to confirm such statement, longer durations of the experiments would be necessary compared to those reported in the cited works. A decrease in the biomass content was confirmed by Schiavon et al. (2017), who observed a 25% reduction of the microbial biomass after activating a DBD upstream of a biofilter to treat a mixture of air (Q = 150 L h^{-1}) and five VOCs (toluene, *n*-heptane, benzene, ethylbenzene and *p*-xylene, with a total C_{in} of 309–574 ppm) with SED between 128 and 256 J L^{-1}. The decrease in biomass was partly ascribed to O_3 and CO poisoning, the latter being detected downstream of the DBD reactor. In spite of this, the DBD pretreatment played a fundamental role in abating peaks of inlet concentration and in preventing damages to the biomass exposed to sudden changes of VOC concentration. The prevention of by-product formation can be achieved by adopting PAC. In this sense, Jiang et al. (2017b) studied the combination of NTP-catalysis and BTFs applied to a mixture of air and 1,2-dichloroethane in variable concentration (200–800 mg m^{-3}) by using a CuO/MnO_2 catalyst bed. An additional BTF was used as a control reference with no pretreatment. By increasing the inlet concentration, the combined process showed better stability, since the decrease in RE was lower in the combined process than in the control BTF experiment: in the first case, following a concentration increase from 200 to 800 mg m^{-3}, the RE was 85%, while the corresponding RE in the control BTF did not exceed 39%. However, an SED of 3500 J L^{-1} was used in this study, which is about one order of magnitude higher than the ranges of SED adopted in the previously cited studies. Thus, in view of scaling up NTP processes in combination with traditional removal technologies, additional investigation is needed if the aim is to exploit NTP oxidation in a continuative mode. The activation of NTP only in the event of concentration peaks would reduce the operational costs compared to continuous operation.

6 Conclusions

Recent NTP applications to mixtures of air and VOCs were reviewed in this paper. In particular, catalysis coupled with NTP offers enhanced removal performance and higher S_{CO2} compared with NTP alone. However, application of low SED may result in the formation of unwanted byproducts and further research is needed to avoid such situations when treating chlorinated VOCs like TCE.

In the light of the considerations expressed in the previous section, NTPs, especially if coupled with catalysis, may represent a promising option if the target is the abatement of low-concentrated VOC mixtures with relatively low air flow rates, due to the lower energy efficiency and thanks to the higher expected S_{CO2} (i.e., to the reduced formation of by-products). Therefore, indoor air treatment represents an interesting field of application, due to the generally low concentrations of the typical VOCs encountered in indoor environments. In spite of their low concentrations, long-term exposure to carcinogenic compounds (e.g., FOR and BZ) may induce cancer, if such VOCs are not efficiently removed. If the target is the abatement of higher VOC concentrations, the higher energy efficiency obtainable in such conditions makes NTP-catalysis a cost-effective option for industrial applications. NTP may be proficiently applied as a pretreatment stage upstream of consolidated removal technologies that have shown limited performance when dealing with unsteady VOC loading rates or with compounds characterized by low solubility in water: this is the case, for instance, of absorption columns and, especially, biofiltration systems. However, both fields of application require further research to confirm adequacy and convenience of NTP and NTP-catalysis. In particular, NTP-catalysis to indoor air treatment requires additional tests with lower initial concentrations of VOCs to validate the conclusions on its applicability in such context; similarly, long-term tests should be carried out on combinations of NTP and NTP-catalysis with biofiltration systems to demonstrate the advantages showed in the available laboratory-scale studies.

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