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Decomposition of toluene using non-thermal plasma reactor at room temperature

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Abstract

A non-thermal, atmospheric pressure plasma utilizing a direct-current (DC) back-corona discharge was used to study the abatement of toluene in air at room temperature. Removal efficiency of toluene applying wire-plate geometry increases with increasing applied voltage. Experimental results indicate that about 93% toluene removal efficiency and very small formation of NO_x ($\sim$10 ppm) is achieved for air stream containing 70 ppm toluene concentration. The fact that the negative corona current is larger than that of the positive one at the same applied voltage (polarity effect) is connected with higher efficiency of the plasma reactor at negative discharge polarity.

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Keywords: DC back-corona discharges; Non-thermal plasma; VOC; Toluene decomposition

1. Introduction

Control of volatile organic compounds (VOCs) in the atmosphere is a major environmental problem. Toluene is one of the typical toxic VOCs that is found in gasoline, paints, glues, lacquers, and rubber. Several conventional methods exist for toluene removal like adsorption method [1], thermal or catalytic combustion [2], photocatalytic [3] and biological methods [4]. However, for many applications, particularly in the removal of very dilute concentrations of air pollutant, conventional techniques are not satisfactory. Chemical treatments are often too expensive to treat emissions from high volume, low concentration sources. The most popular catalytic combustion method requires a heat source when the VOC concentration is low.

In recent years, non-thermal plasma (NTP) techniques offer an innovative process to VOC removal from air [5]. NTP in air at atmospheric pressure can be generated either by electron beams [6] or electric discharges [7]. With relation to the growing demand for economic performance, many researchers have been trying to improve the process efficiency to decompose toluene using various plasma reactors with voltage excitation at DC [8–15], at low frequency (50–60 Hz) [16–19] or higher [20,5], from kilohertz to megahertz of even microwave range. Various types of discharges have been investigated, such as corona [14], back-corona [8–12], glow discharge [13], dielectric barrier discharge [20], and surface discharge [17]. NTP is highly non-equilibrium state where the mean electron energy, or temperature is considerably higher than of the bulk-gas molecules which remains close to ambient temperature. The input electrical energy is mainly used to energize electrons (1–10 eV) for ionisation and excitation of gas molecules instead of gas heating. This energy-savings potential is a main reason why NTP technologies are of great advantages and interests. NTP is also an energetic source of active chemical species such as ozone (O_3), oxygen atoms [$O(^1D)$ and $O(^3P)$], hydroxyl radicals, and free electrons, which are known to have destructive effect on hazardous gaseous pollutants. The process efficiency of NTP reaction still can be improved based on two factors, either reducing power consumption, or suppressing the undesired byproduct formation. Nowadays, in order to improve and increase the efficiency of VOC decomposition, an innovative technology has been proposed where a plasma reactor was coupled with a catalytic

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reactor [19–20]. The main objective of this study is to enhance gas-phase toluene decomposition activity using DC back-corona discharge reactor, which is operated at atmospheric pressure and ambient temperature. We demonstrate that using simple and cheep perforated dielectric material (glass fiber fabric) improves the decomposition efficiency.

2. Experimental

Fig. 1a shows a cross-section of a cylindrical laboratory type non-thermal plasma reactor for destruction of toluene in the gas phase. The reactor was constructed using a perspex cylinder (4) with a 80 mm internal diameter in a wire-plane parallel geometry. The passive electrode (3) was made of a metal grid covered with perforated dielectric layer (glass woven fabric) [21]. The application of this layer enabled to develop back-ionisation process on its surface and inside of the pores. The discharge electrode (2) was composed of three metal strings (Cu–Ni alloy wires 0.15 mm), mounted in parallel (Fig. 1b). The total volume of the reactor and electrodes distance was equal 85 cm^3 and 17 mm, respectively. The electrical discharge was ignited by applying DC high voltage in the range 6–18 kV. The gas enters to the plasma reactor from discharge electrode side and after passing the volumetric discharge zone between electrodes diffuses through the surface discharge of perforated dielectric layer and was analyzed with mass spectrometer at the outlet. The discharge phenomena were shown in the Fig. 1 for the corona electrode charged with negative voltage (Fig. 1c) and positive DC voltage (Fig. 1d). The corona discharges were observed as white points along the discharge electrode and back-corona discharge effect as blue afterglow underneath the discharge electrode (2) on the surface on the dielectric layer laying on passive electrode (wire mesh) (3). Some more intense back discharge can be visible in the air channels of empty pores of dielectric layer (Fig. 1d). The experiments were performed at room temperature and atmospheric pressure, and the gaseous toluene (5–200 ppm) was regulated by passing part of air stream from gas cylinder through the pure toluene liquid (>99.5%) which was kept in a water bath ($T = 0$ °C). The gas flow rate, in the range 100–750 sccm, was regulated by mass flow controllers (5850S Brooks). A mass spectrometer QMS-200 OmniStar from Balzers with SEM detectors was used to evaluate the toluene conversion in the discharge and to analyze the reaction products. The toluene conversion C (%), and

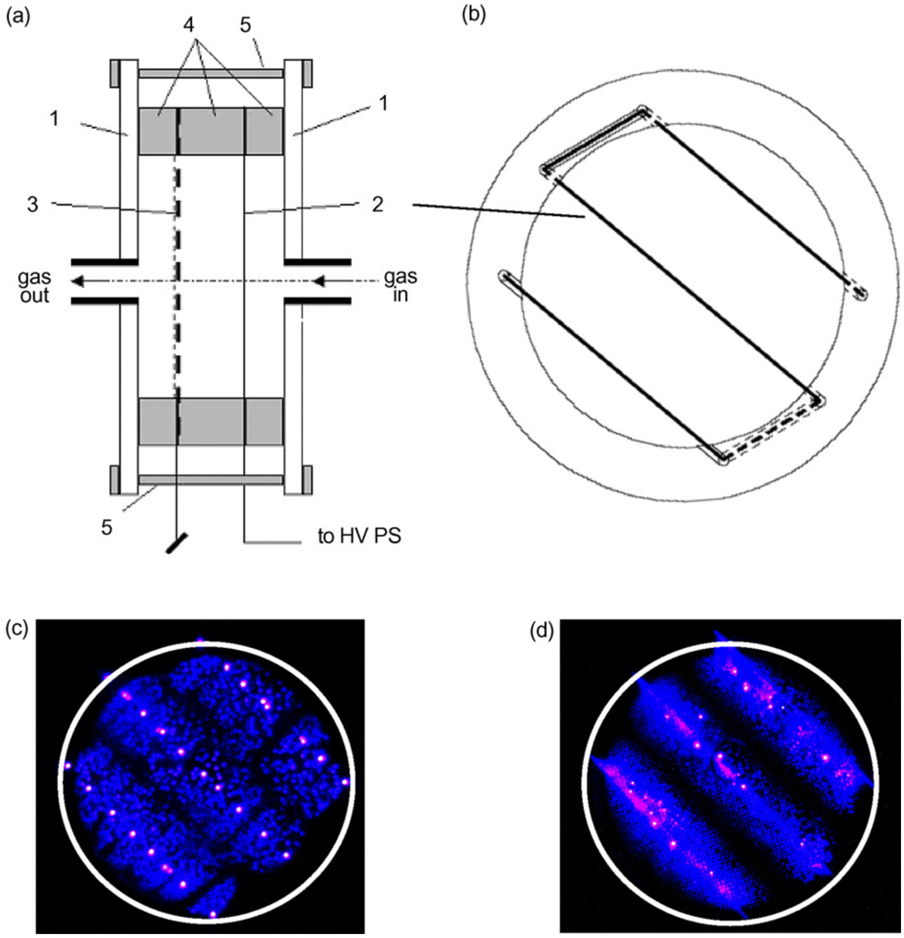

Fig. 1. Scheme of the non-thermal plasma reactor with back-corona discharge using wire-plate electrode geometry (a); cross-section in the plane of discharge electrode (b); discharge images (color online) at DC voltage of 12 kV and different polarity of discharge electrode: negative (c), positive (d). *Illustration*: (1) perspex housing, (2) three metal strings (discharge electrode), (3) passive electrode (metal mesh) covered with perforated dielectric layer [21] (glass woven fabric), (4) dielectric ring system, and (5) set screw.

energy density SED [J/l] in the gas phase were defined as follows:

$$\text{Toluene conversion}: \quad C = (C_o - C_i) \times \frac{100}{C_o}$$

where C_o is the inlet concentration, and C_i the outlet concentration at steady state. Specific energy density: SED [J/l] = discharge power [W] × 60/gas flow rate [l/min].

3. Results and discussion

Corona discharge is a low energy electrical discharge with non-thermal ionisation that takes place in a strong electric field in the vicinity of the discharge electrode with a small radius of curvature. The current–voltage characteristics of the plasma reactor are shown in Fig. 2a. The discharge current increases considerably with voltage increasing, when the back-corona effect appears in comparison with classical corona discharge (without dielectric layers). Moreover, the positive polarity of discharge electrode gives lower current than negative polarity for the same applied voltage. The general advantage of the back-corona discharge is that it operates at lower voltage than the classical streamer corona in the same plasma reactor geometry. The back-corona discharge is observed when the passive electrode is covered with a porous dielectric layer of high resistivity [22]. In such case, the charge emitted from the discharge electrode surface is accumulated on the dielectric surface and intensifies the electric field across the dielectric layer. From some critical point, the breakdown through the dielectric occurs as fine bright discharge channels (microdischarges) inside the pores of perforated dielectric. These bright points on the dielectric surface become a new source of ions of polarity opposite to that of the discharge electrode. The generation of this kind of microdischarges is possible, however, only for back-corona and a specific pore size and discharge power [23]. When porous layer has only very small pores (<1 μm) the discharge developed only on the dielectric surface (surface streamers with typical blue color). On the other hand, when the pore size was too large the flashover took place easily. In general, it can be assumed that the surface discharges on the dielectric layer are also affected by the physical properties, such as the relative permittivity, the resistivity, and the charge relaxation time constant of the dielectric layer.

Fig. 2b shows the behavior of toluene decomposition depending on its initial concentration from 5 to 200 ppm. The proposed NTP reactor showed better performance in treating dilute toluene. The removal rate for treating 200 ppm toluene in air with SED of 400 J/l was 15%, and increased to 98% for 5 ppm. It is well known that the conversion decreases as inlet concentration of VOCs or gas flow rates increases.

Decreasing the gas flow rate, namely increasing the retention time in the reactor, caused that a toluene molecules were submitted to an increasing number of plasma discharges and the probability of collision with electrons and subsequent radical reactions improved, which resulted in a higher toluene removal efficiency.

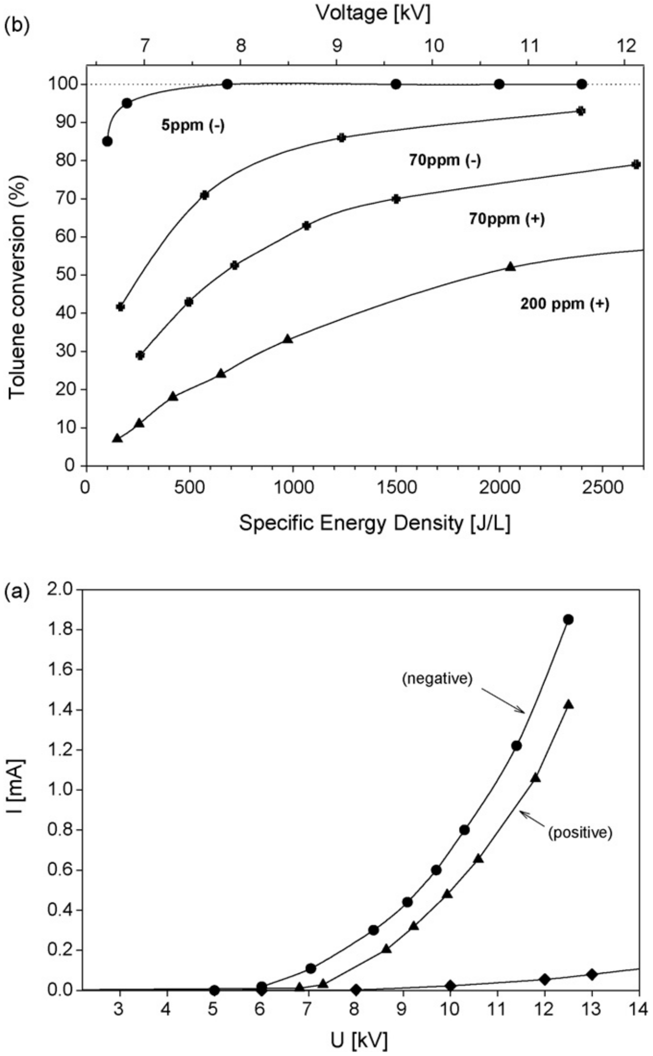

Fig. 2. Electrical and performance characteristics of the plasma reactor in toluene decomposition. Corona current as a function of applied voltage (a) for passive wire mesh electrode covered with perforated dielectric and negative voltage on corona electrode (●), with positive voltage (▲), and without dielectric layer (only corona discharge) (◆). Toluene conversion as a function of the specific energy density for selected toluene input amount = 5, 70, 200 ppm (b); both discharge electrode polarities (positive/negative) and gas flow rate = 250 ml/min.

The results on Fig. 2b indicate also that toluene conversion increases with the increasing of specific energy density and is also dependent on the polarity of discharge electrode (+/−) during back-corona discharge. As shown in Fig. 2b for 70 ppm toluene concentration the removal efficiency for the negative polarity is much higher than for positive one. This means that negative charges on the dielectric layer are more effective in producing surface back-corona discharge than, positive ones. This fact is well correlated with data from Fig. 2a related to the polarity effect on I–V characteristics where the negative corona current is larger than that of the positive one at the same applied voltage.

The main problem of VOC removal in a plasma system is byproduct formation. In a plasma reactor, ions, excited molecules and free radicals are formed initiating sequential chemical reactions. The radicals interact with VOC molecules, but since there is often not enough energy for a complete oxidation, it leads to the formation of byproducts such as CO, O_3, aerosol particles and polymers [24].

Fig. 3 shows the behavior of toluene decomposition and formed gas products (ozone, CO_2, NO, and NO_2) concentration as a function of the SED [J/l] in the proposed non-thermal plasma reactor. The experiments were performed with both polarities of DC current and initial toluene concentration about 70 ppm, and gas flow rate 250 ml/min. As predictably, there is larger toluene decomposition efficiency for negative polarity of discharge electrode.

It is known that non-thermal plasma produces ozone from air via dissociation of oxygen molecule and subsequent reaction of resulted O radicals with O_2 molecule.

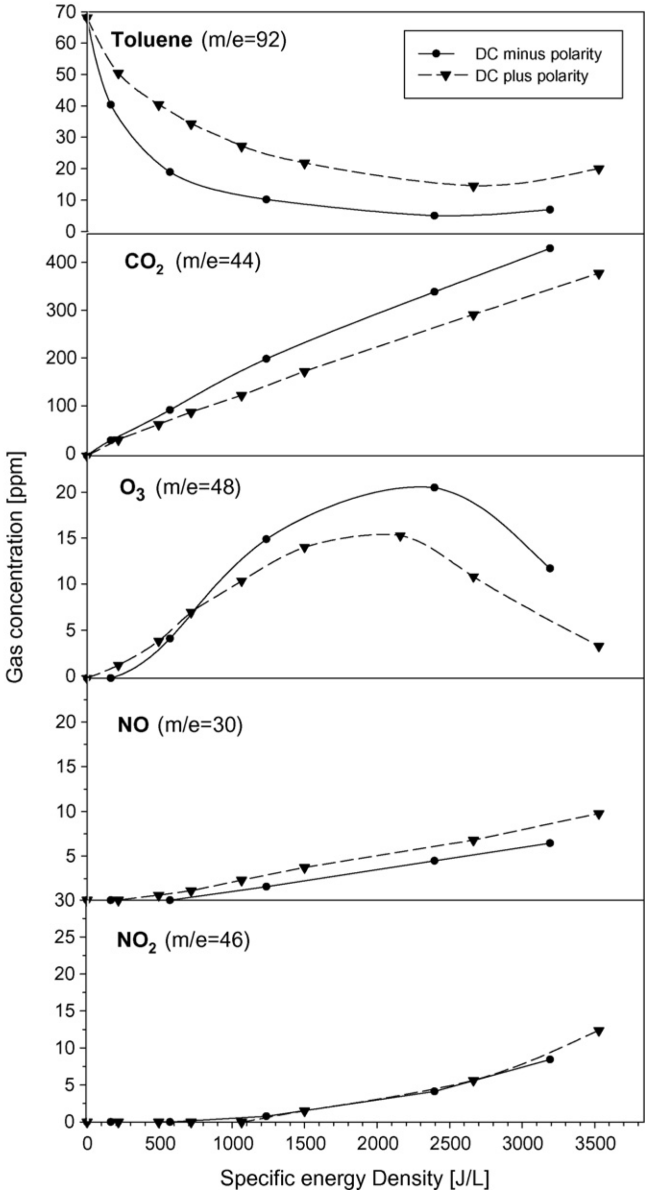

Fig. 3. Toluene decomposition and formed gas products concentration as a function of the SED [J/l] in the proposed non-thermal plasma reactor. Both polarities of DC current and 70 ppm toluene in air, flow rate 250 ml/min.

The ozone formation increased with SED [J/l] up to about 1800 J/l (Fig. 3) and then decreased with further increase of SED probably due to the temperature increase inside of the reactor which leading to decomposition of ozone or oxidation of NO molecules to NO_2. There is no direct correlation between the amount of ozone formed and the observed conversion of VOC during its oxidation in plasma. The concentration of CO_2 produced increased with the increasing input power, as shown also in Fig. 3. The main reaction products detected are CO_2 and H_2O but additionally a deactivation process is started which is connected with aerosol particles formation [13] and covering of the discharge electrode and dielectric layer with a thin polymeric film (brown residues) during plasma discharges [24]. It is suggested [13], that at low input power mostly condensed products (polymeric species) were formed. In general decomposition of toluene and polymeric species competes with polymer formation. Above certain level ($>$1200 J/l), polymer decomposition may become the predominant reaction, and hence polymer deposition rates decrease with increasing discharge power. Machala et al. [13] suggested that possible aerosols including a peroxy-acetyl-nitrates species (PANs) during plasma discharges may be formed by a mechanism similar to the formation of photochemical smog in the atmosphere. Unfortunately a carbon balance was not attempted due to the nature of the setup which makes it difficult to collect the carbonaceous solid deposit generated inside of the reactor.

As long as the plasma reactor is operated in air-like mixtures, the formation of nitrogen oxides (NO_x, HNO_2, HNO_3), which are also dangerous air pollutants, is unavoidable. Fig. 3 shows the formation of NO and NO_2 as the function of input power in the reactor. The formation of NO_x showed a nearly linear relation to the SED [J/l] and reached the level of about 10 ppm. Therefore, maximum available value for input power in the plasma reactor will be determined not only by the toluene decomposition efficiency but also by the formation of NO_x.

The optimization of reactor geometry and operating conditions is still one of the largest challenges since mechanisms for VOC decomposition and byproduct formation have not yet been fully understood. For comparison of the presented method with other NTP process we calculate the energy yield parameter EY [g/kWh] as proposed by Kim et al. [25]. For example, when 70 ppm toluene was decomposed at the SED range ($\leq$200 J/l), the energy yield was 2.5 g/kWh. The optimized reaction conditions in air at room temperature with good yield of CO_2 are initial toluene concentration below 100 ppm and flow rate below 100 ml/min with the average power dissipated in the discharge above 10 W. For high-applied voltage it was possible to selectively destroy the toluene to CO_2 without observing carbon-based deposit in plasma reactor with back-corona discharge.

4. Conclusions

This experimental study shows the possibility of oxidation of toluene with air at room temperature and atmospheric pressure in non-thermal plasma reactor with back-corona, especially for highly diluted mixtures (<100 ppm), where thermal and catalytic techniques are not economically attractive. We proposed new type of non-thermal plasma reactor with parallel wire-mesh geometry where the perforated dielectric layer (glass woven fabric) was situated on the mesh electrode. The results of the investigations showed that:

- Decomposition of toluene was mostly determined by the SED [J/l] and depended on its initial concentration and the polarity of the discharge electrode. Destruction efficiency of toluene decreases with increasing gas flow rate (or decreasing residence time) of VOCs in a plasma reactor.
- The energy yield of toluene removals can be achieved up to 2.5 g/kWh.
- The major toluene destruction byproducts are CO_2, H_2O, polymeric species, and no significant O_3 and NO_x are observed. Condensed polymeric species can be successively oxidized to CO_2 only at higher SED.
- Application of the back-corona phenomenon, especially with negative polarity of discharge electrode, allows reaching much higher current densities and finally the higher efficiency of the toluene conversion if compared with typical DC streamer corona plasma reactors.

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