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On-line quantification and human health risk assessment of organic by-products from the removal of toluene in air using non-thermal plasma

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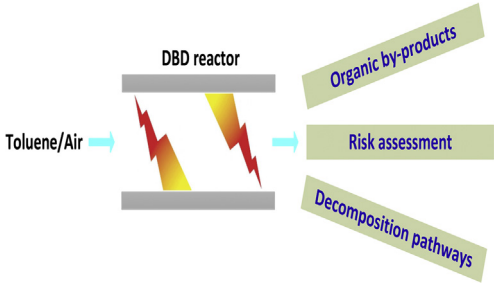
HIGHLIGHTS

- Various organic by-products were produced in DBD removal of toluene in air.
- The organic by-products were qualified and quantified by PTR-TOF-MS.
- The health risk associated with the organic by-products was assessed by health-related index method.
- Acetone is a crucial intermediate for toluene fragmentation by NTP.

GRAPHICAL ABSTRACT



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ABSTRACT

Harmful organic by-products, produced during the removal of volatile organic compounds (VOCs) from the air by treatment with non-thermal plasma (NTP), hinder the practical applications of NTP. An on-line quantification and risk assessment method for the organic by-products produced by the NTP removal of toluene from the air has been developed. Formaldehyde, methanol, ketene, acetaldehyde, formic acid, acetone, acetic acid, benzene, benzaldehyde, and benzoic acid were determined to be the main organic by-products by proton transfer reaction mass spectrometry (PTR-MS), a powerful technique for real-time and on-line measurements of trace levels of VOCs, and a health-related index (HRI) was introduced to assess the health risk of these organic by-products. The discharge power (P) is a key factor affecting the formation of the organic by-products and their HRI values. Higher P leads to a higher removal efficiency (η) and lower HRI. However, higher P also means higher cost and greater production of discharge by-products, such as NO_x and O_3, which are also very dangerous to the environment and human health. In practical applications P, HRI, and η must be balanced, and sometimes the risks posed by the organic by-products are even greater than those of the removed compounds. Our mechanistic study reveals that acetone is a crucial intermediate for the removal of toluene by NTP, and we found that toluene molecules first fragment into acetone molecules, followed by other by-products. These observations will guide the study of the mechanism of aromatic molecule dissociation in plasma.

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1. Introduction

Volatile organic compound (VOC) emissions in the atmosphere are produced by natural and man-made sources. However, since industrialization, man-made VOC emissions have had a considerable impact on human health and the environment. VOCs are the precursors of photochemical smog and ground-level or tropospheric ozone. Some VOCs are toxic and can directly cause a spectrum of maladies, ranging from irritation to cancer. Thus, VOC emissions are controlled by stringent environmental regulations and policies in many countries. Various techniques for VOC removal have been developed, including photocatalysis (Zhao and Yang, 2003), thermal or catalytic oxidation (Hart, 2004), adsorption/absorption (Chiang et al., 2002; Bay et al., 2006), bio-filtration (Estrada et al., 2013), and membrane separation (Liu et al., 2009) etc. However, each technique is only suitable only for a specific type of VOC emission and a universal technology for the removal of all VOC pollutants and working conditions does not exist. Thus, controlling large volumes and low concentrations of VOC emissions in an economical and effective manner remains a challenge.

In the last 20 years, non-thermal plasma (NTP) treatment has been developed as an interesting, novel method for the removal of various air pollutants such as SO_2, NO_x, particulate matter, and VOCs (Futamura et al., 1997; Van Durme et al., 2007; Obradovic et al., 2011; Gao et al., 2017). The non-equilibrium nature of the NTP process allows the feed energy to accelerate electrons to high velocities preferably (gaining 1–10 eV), allowing them to excite and ionise molecules, such as the background gas (for example, N_2, O_2, and H_2O) upon impact while maintaining a gas cold. Under these conditions, many active secondary electrons, photons, ions, and radicals are generated. These active species play a vital role in pollutant removal. Specifically, they can oxidise VOCs to H_2O and CO_2. Thus, NTP is an economical means for the efficient removal of VOCs. However, most research in this field has focused on advanced reactor configurations, including packed bed reactors (Kuwahara et al., 2011; Gandhi et al., 2013; Abd Allah et al., 2014; Jiang et al., 2017b), plasma and catalysts in plasma catalytic reactors (Rahmani et al., 2014; Xu et al., 2014; Feng et al., 2015; Wei et al., 2015; Jo et al., 2016; Bahri et al., 2017; Jiang et al., 2017a), and even micro-plasma reactors with and without catalysts (Chen et al., 2012; Wang et al., 2013; Ge et al., 2015). Each of these configurations has demonstrated an improvement in terms of the removal and energy efficiencies.

Nevertheless, a major drawback associated with the NTP removal of VOCs is that oxidation does not always result in the production of H_2O and CO_2, and some organic by-products are produced by partial oxidation (Gandhi et al., 2013; Sivachandiran et al., 2013; Abd Allah et al., 2014; Lyulyukin et al., 2016), resulting in low CO_2 selectivity (Karuppiah et al., 2012, 2013; Karatum and Deshusses, 2016). In other words, this plasma-induced chemical reaction is highly non-selective, and the generation of unfavourable organic by-products is inherently difficult to avoid. The organic by-products may be harmful to humans, sometimes even more so than the parent VOCs. Therefore, it is essential to characterise the organic by-products and assess their health risks. To date, few studies have dealt with a qualitative and quantitative analysis of the organic by-products from NTP, and the health risks associated with these organic by-products have not been assessed. This can be partially attributed to the fact that the decomposition pathways and intermediates formed in the gas and solid phases are so complex that there are no effective methods to trace the decomposition processes directly.

In this study, the dielectric barrier discharge (DBD) removal of toluene was investigated, and possible fragmentation pathways are proposed. The generated organic by-products were also characterised and quantified using a laboratory-developed proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) instrument, and the health risks were also assessed using the health-related index (HRI) recommended by the US National Institute for Occupational Safety and Health (NIOSH).

2. Experimental

A schematic diagram is shown in Fig. 1 and provides an overview of the experimental setup used in this study, which comprised a DBD reactor and a PTR-TOF-MS instrument. A standard toluene sample (80 ppm, Shanghai Ji Liang Standard Reference Gases Co., Ltd., China) was introduced into the DBD reactor at a controlled flow rate (100–1000 mL/min). The PTR-TOF-MS instrument was used for the real-time and on-line analysis of the organic by-products, and the NO_x (Ecotech EC9841B, Australia) and O_3 (Ecotech EC9810, Australia) analysers at the outlet of the DBD reactor were used for the analysis of the respective gases. The experiments were performed at ambient temperature and atmospheric pressure.

2.1. DBD reactor

The DBD reactor comprised a stainless-steel wire mesh, two dielectric tubes (quartz and ceramic), and aluminium powder. The quartz tube (i.d., 20 mm; o.d., 25 mm) was wrapped with stainless steel wire mesh, which was used as the external electrode, and was attached to the high-voltage (HV) supply. The ceramic tube (i.d., 10 mm; o.d., 14 mm) was sealed at one end and filled with aluminium powder and used as the inner electrode. The effective discharge length was 50 mm. An AC power supply (CTP-2000k, Nanjing Moersi Electronics Company, China) delivered voltages in the 0–30 kV range and frequencies in the 5–20 kHz range. The applied voltage, current, charge waveform, and discharge frequency were monitored using a digital storage oscilloscope (DSO7052A, Agilent, USA).

A schematic of the electrical circuit of the DBD reactor is shown in Fig. 2. Capacitors C_1 and C_2 constituted a voltage divider with a 1000:1 ratio. The sampling resistor R (50 Ω) at port *a* and capacitor C (0.47 μF) at port *b* were used to detect the output current and power, respectively. The digital oscilloscope recorded the voltage-current waveform when switch *S* was turned to port *a*, and the voltage-charge Lissajous figure was obtained when it was switched to port *b*. The discharge power (*P*) was calculated by multiplying the area of the voltage-charge Lissajous figure *S* by frequency *f*:

$$P = \frac{1}{T}\int_0^T UIdt = \frac{C}{T}\int U\frac{dU_C}{dt}dt = fC\oint UdU_C = fS$$

2.2. PTR-TOF-MS

Proton transfer reaction mass spectrometry (PTR-MS) is widely used for the detection of VOCs in the air. The process involves the chemical ionization of a gas inside the drift tube, usually by proton transfer from H_3O^+. By combining the reaction kinetics with high-resolution mass spectrometry, PTR-MS can be used to qualify and quantify organic gasses in real time with a sensitivity that can extend into the parts-per-trillion by volume (pptv) mixing range (Jordan et al., 2009; Gonzalez-Mendez et al., 2016). In this study, a laboratory-developed PTR-TOF-MS instrument was used for the on-line monitoring of organic by-products derived from the DBD removal of toluene. The PTR-TOF-MS comprised an ion source, a