

Non-thermal plasma abatement of trichloroethylene with DC corona discharges

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Abstract

The decomposition of trichloroethylene (TCE) in air by non-thermal plasma was investigated with a multi-pin-to-plate direct current (DC) discharge at atmospheric pressure and room temperature. The effects of various operating parameters on the removal efficiency (RE) were examined. The experiments indicated that for low energy densities higher removal could be obtained with positive corona. For negative corona and 10 % relative humidity (RH) a maximum RE of 99.5 % could be achieved at 1100 J L⁻¹. Formation of by-products was qualitatively analyzed in detail with FT-IR spectroscopy and mass spectrometry. Detected by-products for negative corona operated at 300 J L⁻¹ and 10 % RH include dichloroacetylchloride, trichloroacetaldehyde, phosgene, ozone, HCl, Cl₂, CO and CO₂. The highest RE for TCE was achieved with a relative humidity of 19 %.

Keywords: non-thermal plasma, volatile organic compounds, trichloroethylene, by-products,

1 Introduction

Many organic solvents used in metal, semiconductor and chemical industry have good physical and chemical properties and are therefore useful during the manufacturing process. Despite their good commercial value, most of them have a high volatility causing them to easily evaporate at ambient conditions. As a

result the process waste gases are frequently contaminated with volatile organic compounds (VOCs). Trichloroethylene (TCE) is an example of such a VOC that is widely used for degreasing metal parts and semiconductors. It is also an ingredient in paint removers, adhesives and spot removers. Inhalation of TCE can however cause headaches, lung irritation and dizziness. In more severe cases nerve, kidney and liver damage have been reported. The International Agency for Research on Cancer (IARC) has determined that TCE is “probably carcinogenic”, proving its adverse effects to humans. Due to limitations of traditional methods (incineration, catalytic oxidation and adsorption) for the abatement of low concentrations of VOCs, non-thermal plasma (NTP) generated in atmospheric pressure discharges have been investigated as an energy and cost effective alternative [1-3]. In a NTP, the energy delivered to the system is almost entirely used to accelerate plasma electrons instead of heating up the gas flow like is the case for incineration (750 – 1150 °C) and catalytic oxidation (250 – 500 °C). While the gas stream remains at room temperature, the highly energetic electrons collide with background molecules (e.g. N₂, O₂, H₂O) with formation of active plasma species (ions, radicals,...). These latter species are responsible for the oxidative abatement of VOCs. Kim *et al.* have reviewed NTP techniques for the destruction of air pollutants [4].

In this work, a multi-pin-to-plate electrode configuration is used to generate a DC corona or glow discharge for the abatement of TCE. This electrode geometry was developed by the group of Akishev *et al.* [5-8] and was successfully tested for the removal of SO₂ and NO_x [9]. Vertriest *et al.* applied a large scale laboratory multi-pin-to-plate negative glow discharge for the removal of VOCs and discovered that molecules containing a double carbon bond have the lowest energy requirement for decomposition [2]. A recent review [10] summarizes DC-excited NTPs for VOC abatement. In the present study, a DC corona/glow discharge operated at atmospheric pressure was used for the oxidation of small amounts of TCE in air. The effect of the discharge polarity, initial TCE concentration and water content on the removal efficiency have been investigated. By-products from TCE abatement were qualitatively analyzed with Fourier transform infrared (FT-IR) spectroscopy and mass spectrometry (MS).

2 Experimental

The experimental set-up is illustrated in Figure 1. A compressor delivers ambient air to an air dryer (MSC-Air, Model Compact 10) which controls the relative humidity at approximately 12 %. The humidity of the air can be changed by turning off the air dryer or by using dry air from a cylinder (Air Liquide, Alphagaz 1). A bubbler system is used to set the TCE concentration in the gas stream. The initial TCE concentration is controlled by changing the flow rate (Bronkhorst, EL-FLOW) of air through a 0.5 L bottle containing liquid TCE. The bottle is kept at a temperature of 30.0 ± 0.5 °C in a thermostatic water bath. Experiments are carried out with a total air flow of 2 L min^{-1} and with varying inlet concentrations of TCE (420 – 4000 ppm). The multi-pin-to-plate plasma source is based on the concept of a negative DC glow discharge [7, 9]. It consists

of 5 aligned pins which were positioned 28 mm of each other. The inter-electrode gap in this configuration and the total reactor length are 9 mm and 200 mm respectively. The discharge is powered with a 30 kV/20 mA DC power supply and generated at atmospheric pressure and room temperature. For a total gas flow of 2 L min⁻¹, the gas residence time in the plasma reactor is 2.16 seconds. A high voltage probe (Fluke 80K-40, division ratio 1/1000) measures the voltage applied to the inner electrode. The discharge current is determined by recording the voltage signal across a 100 Ω resistor placed in series between the counter electrode and the ground. Each pin is ballasted with a 1.5 MΩ resistor. The fraction of the total electrical power dissipated in these resistors amounts to 10 % at most.

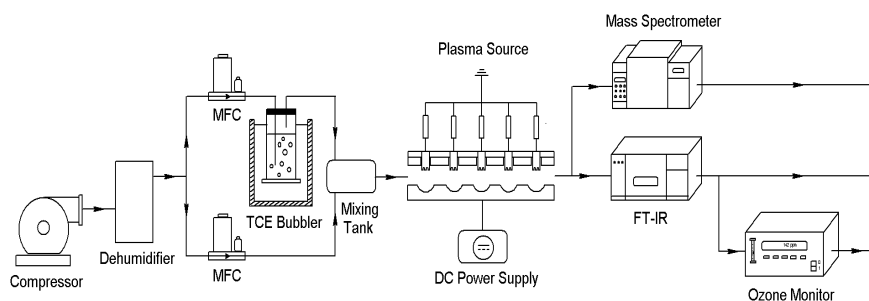


Figure 1: Experimental set-up.

The mass spectrometer used in these experiments is a Quadrupole MS (Omnistar GSD 301 O2 Pfeiffer Vacuum) equipped with a Faraday cup and a SEM Channeltron™ detector. Balzers Quadstar 200 (QMS 200) software (Pfeiffer Vacuum) is applied for collecting and displaying data. Only the maximum peak intensities and the corresponding m/z numbers are collected. The peaks are represented as bar lines over the corresponding m/z . The qualitative identification of the by-products is achieved using Scan Bargraph mode and a SEM voltage of 1600 V in the mass range 0 – 200 m/z and an acquisition rate of 1.5 scan min⁻¹. A resolution of 50 with electron ionization of 60 V was adopted. The decomposition efficiency of TCE and the formation of by-products is also determined with a FT-IR spectrometer (Bruker, Vertex 70). The optical path length of the adjustable gas cell and the resolution of the spectrometer are set at 0.80 m and 4 cm⁻¹ respectively. For each spectrum, 40 samples are averaged from 600 to 4800 cm⁻¹. The mercury-cadmium-telluride (MCT) detector is nitrogen cooled and OPUS (Bruker) software is used to collect and analyze the obtained spectra. Formation of ozone is analyzed by an ozone monitor (Envitec, Model 450). The temperature and the water content of the inlet gas stream are measured with a climate meter (Testo 445).

The RE (%) of TCE is calculated from:

$$RE = \left(1 - \frac{[TCE]_{in}}{[TCE]_{out}}\right) \times 100 \quad (1)$$

where $[TCE]_{in}$ is the concentration of TCE introduced in the reactor and $[TCE]_{out}$ is the TCE concentration in the effluent gas. The energy density ($J L^{-1}$) is calculated as:

$$\varepsilon = \frac{P}{Q} \quad (2)$$

where P is the discharge power (W) and Q the gas flow rate ($L s^{-1}$) through the plasma reactor. The selectivity to CO_2 is defined as:

$$S_{CO_2} = \frac{[CO_2]}{2 \times [TCE]_{in} \times RE} \times 100 \quad (3)$$

where $[CO_2]$ is the concentration of carbon dioxide detected in the effluent gas as a result of total TCE oxidation.

3 Results and discussion

3.1 Effect of discharge polarity on TCE removal efficiency

Figure 2 presents the experimental results of the effect of the discharge polarity on the RE. The polarity of the DC corona discharge depends on whether the electrode pins are connected to the DC high voltage source (positive corona) or to the ground (negative corona). The mechanism for corona generation differs for both discharges [11]. The discharge of a positive corona consists of thin current filaments, also referred to as streamers. At a certain threshold voltage the streamer-like discharge transitions to an unstable spark discharge regime. For the negative corona, increasing the applied voltage results in the formation of a steady state diffusive glow discharge and in a subsequent sparking [12]. By increasing the energy density, the RE for both negative and positive corona are increased (Figure 2). However, with positive corona and for energy densities up to $330 J L^{-1}$ higher efficiencies are obtained compared to negative corona. Overall, positive corona removes about 17 % more TCE. At higher energy densities ($> 330 J L^{-1}$) sparking occurs for the positive corona and a maximum RE of 80 % is reached. The higher removal obtained with positive corona can be attributed to the fact that streamer discharges have a higher efficiency in the generation of chemical active species that are responsible for the oxidation of TCE [13]. At high energy densities ($> 500 J L^{-1}$) the negative corona shifts to the glow regime which gradually fills the entire gap with active plasma volume. In this mode, almost complete removal of TCE is established at $1100 J L^{-1}$. For both

discharges (negative and positive corona) the selectivity to CO₂ does not exceed 10 %. However, higher CO₂-selectivities are obtained with negative corona.

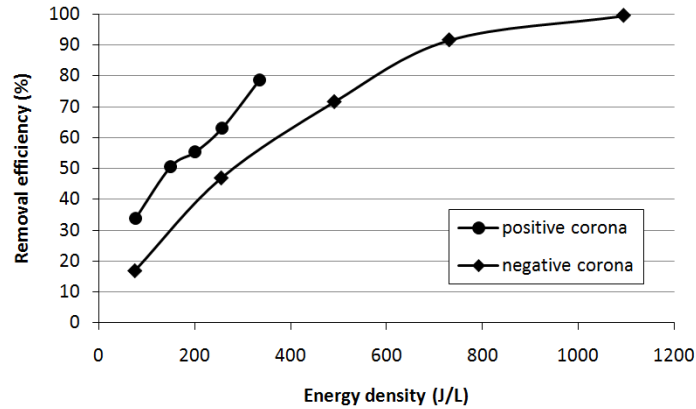
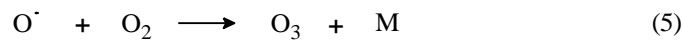


Figure 2: TCE removal efficiency versus energy density (temperature: 20°C, relative humidity: 10%, TCE inlet concentration: 1600 ppm).

3.2 Identification of by-products

For negative corona, by-products are qualitatively analyzed and identified with FT-IR and MS. Table 1 shows the by-products and their IR absorption bands that are detected with FT-IR spectroscopy at an energy density of 300 J L⁻¹. Due to incomplete oxidation, TCE is partially converted to dichloroacetylchloride and phosgene. Hydrogen chloride, carbon monoxide and carbon dioxide are detected as complete oxidation products. Ozone, a typical by-product of NTP treatment, is mainly formed by a three body collision by the following reactions:



MS results additionally confirm the formation of trichloroacetaldehyde and chlorine. After continuous operation of the plasma system, the spherical segments of the anode surface were covered with a brown carbonaceous deposit. The deposit is however not analyzed in the present work. With positive corona and under identical experimental conditions similar by-products were identified. The by-product analysis indicates that TCE is only partially mineralized. This demonstrates one of the shortcomings of NTP which can be improved by catalyst hybridization [14-16].

Table 1: Assignments of the observed infrared frequencies of TCE oxidation (negative corona, energy density: 300 J L⁻¹, relative humidity: 10 %).

Compound	Infrared frequency (cm ⁻¹)
TCE (Cl ₂ C=CHCl)	3169 (C-H); 3099(C-H); 1592, 1560 (C=C); 1253 (CH-Cl); 945, 784, 634 (C-Cl); 850 (C-H)
Dichloroacetylchloride (Cl ₂ CH-COCl)	1822, 1788 (C= ¹⁶ O); 1232 (C-H); 1079, 991 (C-C); 800, 742 (C-Cl ₂); 1783 (C= ¹⁸ O)
Phosgene (COCl ₂)	1832 (C= ¹⁶ O); 1791(C= ¹⁸ O); 1682 [2(C-Cl ₂)]; 852, 662 (C-Cl ₂)
Ozone (O ₃)	1047, 1029 (O=O=O)
Hydrogen chloride (HCl)	3049 – 2732 (H-Cl)
Carbon monoxide (CO)	2178 (C≡ ¹⁶ O); 2114 (C≡ ¹⁸ O)
Carbon dioxide (CO ₂)	2359 (¹⁶ O=C= ¹⁶ O); 2343 (¹⁸ O=C= ¹⁸ O)

3.3 Effect of initial TCE concentration

Figure 3 shows the effect of the initial TCE concentration on the RE for both negative and positive corona. Experimental results indicate that for negative corona the RE of TCE is little influenced by the initial concentration. For positive corona, the RE decreases as the initial concentration of TCE increases. The latter observation is consistent with other studies where the effect of the initial concentration is studied [17-19]. It is believed that higher initial TCE concentration results in less energy available for the decomposition of each TCE molecule which causes a decrease in RE [19].

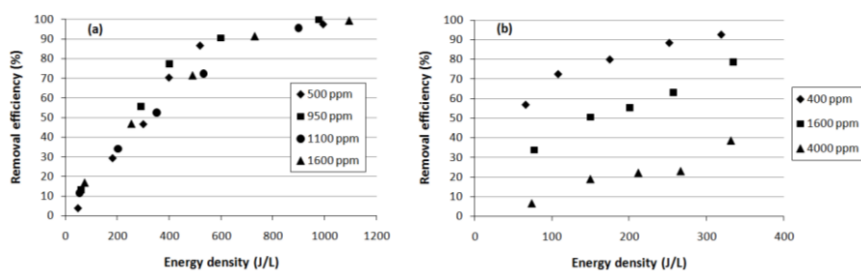


Figure 3: TCE removal efficiency versus energy density for different initial TCE concentrations ((a) negative corona, (b) positive corona, temperature: 20°C, relative humidity: 10%).

3.4 Effect of humidity

The effect of humidity is of great interest for practical applications in industry since process gas consists of ambient air that usually contains water vapour. The influence of relative humidity (RH) on TCE removal is shown in Figure 4. For dry air and 12 % RH the removal of TCE is comparable. However, at 19 % RH the RE is improved with 15 to 20 % over the range of energy densities tested. The water content of the waste gas has opposite effects on the chemical and physical nature of the plasma. Collisions between H₂O and plasma species such as electrons, oxygen radicals and O(¹D) are responsible for the production of OH radicals which act as highly reactive oxidizing agents for VOCs. However, when the relative humidity increases, the electron mean energy is lowered by the electronegative character of water. The subsequent quenching effect of activated chemical species has an adverse effect on the RE [20]. The latter effect was not observed during the present study due to the limited water content of the gas stream. Guo *et al.* determined the concentration of OH radicals during the decomposition of toluene in air with a dielectric barrier discharge operated at atmospheric pressure and with varying RH. The highest toluene RE was achieved at a RH of 20 % which corresponded with the maximum OH yield [21]. Although higher RH were not examined in this study, the RE reached a maximum value at RH of almost 20 %.

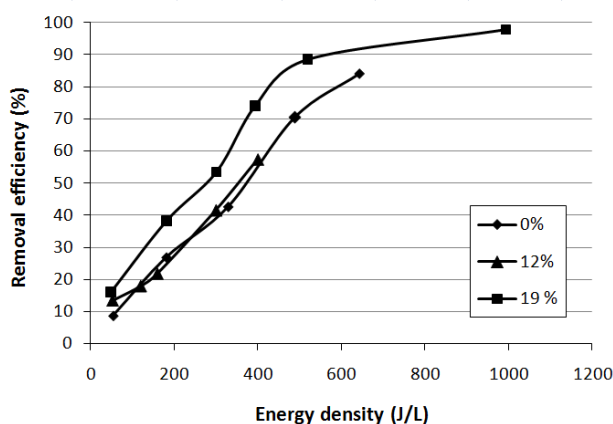


Figure 4: TCE removal efficiency versus energy density for different relative humidities (negative corona, temperature: 20°C, TCE inlet concentration: 500 ppm).

4 Conclusions

In the present study a DC multi-pin-to-plate plasma source was utilized to decompose dilute concentrations of TCE in air. This VOC is often used in industry to degrease metal and semiconductors. The polarity of the plasma

discharge affected the removal efficiency. At low energy densities, higher RE were achieved with positive corona. Degradation products with negative corona include dichloroacetylchloride, trichloroacetaldehyde, phosgene, HCl, Cl₂, CO and CO₂. A maximum RE of 99 % was achieved with negative corona at 1100 J.L⁻¹ and a relative humidity of 19 %.

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