Abatement of trichloroethylene using DBD plasma

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Dielectric barrier discharge plasma was used to oxidize trichloroethylene (TCE) in 21% of O_2 in carriers of N_2 and He. The degradation products of TCE were analyzed using gas chromatography mass spectrometry. TCE was decomposed completely at optimum energy density of 260 and 300 J/l for He and N_2, respectively and its conversion followed zero order reaction. The TCE removal efficiency is decreased in humid air due to interception of reactive intermediates by OH radicals.

Keywords: VOCs; trichloroethylene; DBD plasma.

1. Introduction

Volatile organic compounds (VOCs) are the major pollutants in air, and are harmful to human health and environment. TCE which is halogenated VOCs is widely used as solvent, cleaning agents and extractants in various industrial fields.[1]

Several methods including absorption, adsorption and oxidation (thermally and catalytic) have been used for removal of VOCs. An alternative method for oxidation of VOCs is using electrons, free radicals and ions. This method includes electron beam irradiation, microwave and discharge plasma. Plasma treatment due to its reliability, energy efficiency and possibility of post-processed gas treatments, attracts more

attention. Plasma in its different form such as RF, pulsed corona discharge and dielectric barrier discharge (DBD) can be used for degradation of VOCs at wide range of flow rates and concentrations. Due to its atmospheric pressure and room temperature, and also presence of dielectric barriers which prevent contamination of analyte gas with electrodes, DBD plasma has been used widely for abatement of VOCs.[2]

DBD plasma can generate radicals, ions and activated molecules for decomposition of TCE. The optimum density of these reactive species depends on the plasma conditions such as power, carrier gas and configurative parameters such as dielectric material and gap distance.[3]

2. Experimental

Figure 1 shows the schematic of experimental system. N_2 and He containing 21% O_2 were selected as carrier gases of 1000 ppm TCE. The products of TCE conversion were analyzed using GC/MS. The conversion of TCE was calculated as following:

$$\text{TCE Conversion \%} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are inlet and outlet concentration of TCE, respectively. The DBD plasma reactor consists of a cylindrical quartz tube as a dielectric barrier, a stainless steel rod inner electrode and an external aluminum electrode. A CTP-2000K plasma generator was utilized to transform input AC voltage to applied voltage in the range of 0-10 kV. The power is given by the following equation:

$$P = VI \cos \Phi$$

where V = voltage (kV), I = current (mA) and Φ = phase shift. Specific input energy (SIE) of the discharge was calculated by following relation:
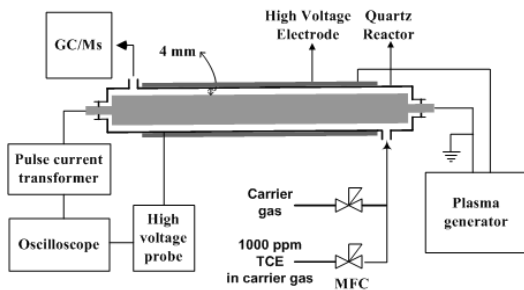SIE (J/l) =power (W)/ gas flow rate (l/s)

Fig. 1. Schematic of experimental set-up for TCE degradation.

3. Results and Discussion

3.1. *Discharge characterization*

Figure 2 shows the effect of input voltage (V) and frequency on applied voltage. The applied voltage depends linearly on the input voltage. For the same input voltage, He has lower slope. One possible reason is that He has lower electron collision cross-section compared to nitrogen and the electron density would be higher accordingly.[3]
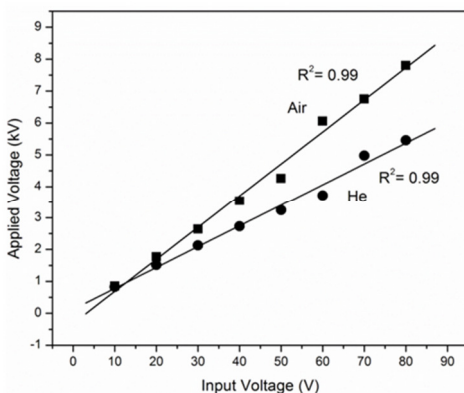
Fig. 2. The relation of input voltage and applied voltage.

Figure 3 illustrates influence of applied voltage on the power. Increasing voltage at a constant frequency leads to increase of power.
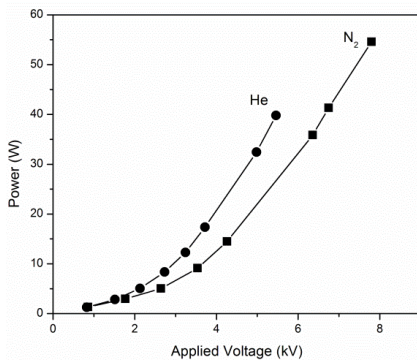
Fig. 3. Influence of voltage on the power.

3.2. *Conversion of TCE*

Figure 4 shows GC spectrums of TCE stream after decomposition in DBD plasma reactor at SIE = 200 J/l. The peak at t= 2.99 min is assigned to TCE. CO_2 and phosgene as final

products, come off at t= 1.30 and t= 1.40 min. The peaks at t= 4.88, t= 5.87, t= 6.55 and t= 6.97 min are attributed to hexanal, heptanal, octanal and nonanal, respectively.
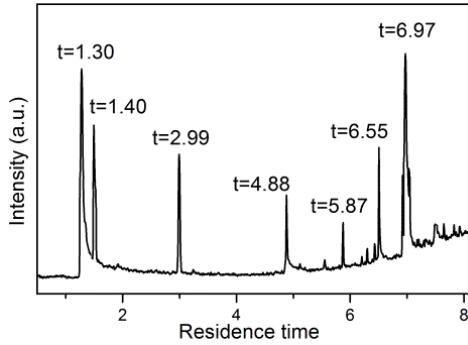

Fig. 4. Influence of voltage on SIE.

Figure 5 presents TCE conversion % in He and N_2 carriers. Conversion is tended to increase as the SIE is increased. The 100% conversion of TCE is achieved at 260 and 300 J/l for He and N_2, respectively. These energies are lower as compared to the energy required during the thermal destruction. This shows that plasma reaction would be energetically feasible for TCE decomposition with low energy consumption.
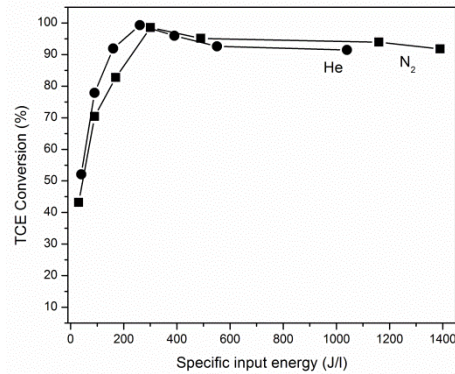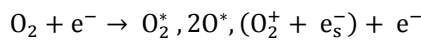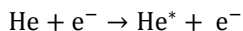

Fig. 5. Conversion of 1000 ppm TCE in gas streams of He and N_2.

3.3. *Mechanism*

During plasma discharge, accelerated electrons impact main constituents of carrier gas[5]:

$$O_2 + e^- \rightarrow O_2^*, 2O^*, (O_2^+ + e_s^-) + e^-$$

$$N_2 + e^- \rightarrow N_2^*, 2N^*, (N_2^+ + e_s^-) + e^-$$

$$He + e^- \rightarrow He^* + e^-$$

Other reactive species which can be produced during discharge plasma are O, O_2^-, N_2^-. Since the electron temperature of the plasma in the discharge chamber is lower than the ionization energy of nitrogen atom (Table 1), then the dissociation species N^+ may not be observed.[5]

Table 1. The required amount of energy for dissociation and ionization of carrier's constituents.

| species	O_2	N_2	O	N	He
Dissociation energy (eV) $(e + AB \rightarrow e + A + B)$	5.15	9.8	-	-	-
Ionization energy (eV) $(e + A \rightarrow e + e + A^+)$	12.1	15.6	13.6	24.3	24.6

Compared to other species, ozone is long-lived species and can make important role in the decomposition process of TCE. It can break double bond of TCE to form phosgene:
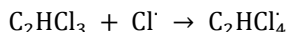
$$C_2HCl_3 + O_3 \rightarrow CHClOO^\cdot + COCl_2$$
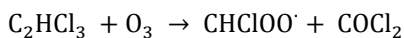
TCE also reacts with atomic oxygen:

$$C_2HCl_3 + O \rightarrow CHOCl + CCl_2$$
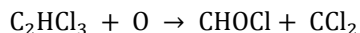
The dissociative electron may initiate TCE decomposition as follow:

$$C_2HCl_3 + e \rightarrow C_2HCl_2^\cdot + Cl^-$$
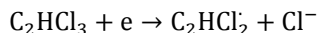
Cl radical can react with TCE:

$$C_2HCl_3 + Cl^\cdot \rightarrow C_2HCl_4^\cdot$$

The resulting alkyl radical reacts with O_2 to form a peroxy radical, which reacts with another peroxyradical to give an alkoxy radical:

$$C_2HCl_4^\cdot + O_2 \rightarrow C_2HCl_4OO^\cdot$$
$$2C_2HCl_4OO^\cdot \rightarrow 2(C_2HCl_4O^\cdot) + O_2$$
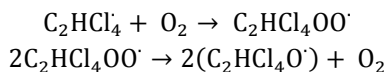
The alkoxy radical may lose a Cl atom to form the DCAC:

$$C_2HCl_4O^{\cdot} \rightarrow CHCl_2COCl + Cl^{\cdot}$$

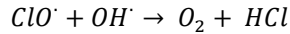DCAC, which was identified as a primary product, should be oxidized further to give CO and CO_2:

$$CHCl_2COCl + O_2 \rightarrow CO + CO_2 + Cl_2 + HCl$$

The TCE removal efficiency is decreased in humid air due to interception of reactive intermediates by OH radicals:

$$ClO^{\cdot} + OH^{\cdot} \rightarrow O_2 + HCl$$

3.4. *Kinetic studies*

Figure 6 presents outlet concentration of TCE at various residence times for two initial TCE concentrations. Concentration of TCE has linear relation with residence time and prolonging the residence time provides longer time for TCE molecules to be attacked by radicals, resulting in higher conversion of VOCs. For modeling the TCE conversion reaction, the DBD reactor may be regarded as an integral plug flow reactor and a simple power-law kinetic model can be used, when interference of reaction products and effect of mass and heat transfer are neglected:

$$(-r_{TCE}) = kC_{TCE}^{n}$$

where $(-r_{TCE})$ is reaction rate of TCE conversion, k is reaction rate constant and C_{TCE} is concentration of TCE.

Assuming n=0, conversion of TCE (x) is as follow:

$$x = \frac{C_0 - C}{C_0} = \frac{k}{C_0}$$

Since temperature of reactor is constant, k which depends only on temperature is also constant and x depends mainly on C_0. In Fig. 6, decreasing C_0 from 1000 ppm (circle) to 700 ppm (square) leads to increase of TCE conversion. This dependency of conversion on initial TCE confirms the assumption of zero order kinetic.[1]
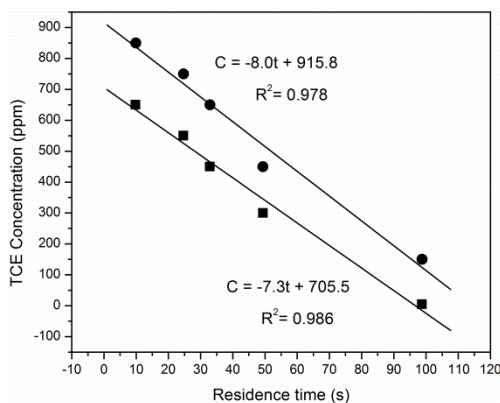
Fig. 6. Destruction of TCE over residence time; two different initial TCE concentrations (circle: 1000 ppm, square: 700 ppm).

Table 2 compares the SIE and conversion % of our DBD plasma reactor with other DBD reactors which have been used for removal of TCE.

Table 2. Overview of published papers on TCE removal with DBD plasma.

Reactor	Gap (mm)	Catalyst	Carrier gas	SIE (J/l)	Conversion (%)	Ref.
Cylindrical electrode, single barrier	3	MnO_x /SMF	air	480	100	[5]
Planar electrode, double barrier	2.5	-	N_2/20%O_2 Ar/20%O_2	95 25	80 >99	[6]
Cylindrical electrode, single barrier	2	-	air	353	100	[7]
Cylindrical electrode, single barrier	1.25	TiO_2/SMF	air	140	>99	[8]
Cylindrical electrode, single barrier	4	-	He/21%O_2 N_2/21%O_2	260 300	>99 >99	This work

4. Conclusion

DBD plasma system was used effectively to decompose 1000 ppm TCE in He and N_2 carriers. Close to 100% removal of TCE was achieved at SIE 260 and 300 J/l for He and N_2 carriers, respectively. CO_2, phosgene, nonanal, octanal, heptanal and hexanal were the major products detected from TCE decomposition in DBD plasma at SIE=100 J/l.

The increase of residence times can increase removal of TCE. But generally high residence time is not favored because it could finally result in decrees of energy efficiency and removal rate.

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