Abatement of trichloroethylene using DBD plasma

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Published 13 August 2014

Dielectric barrier discharge plasma was used to oxidize trichloroethylene (TCE) in 21% of O₂ in carriers of N₂ 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 N₂, 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
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.

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.

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 $\Phi$ = phase shift. Specific input energy (SIE) of the discharge was calculated by following relation:

$$\text{SIE (J/l)} = \frac{\text{power (W)}}{\text{gas flow rate (l/s)}}$$

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.

![Fig. 2. The relation of input voltage and applied voltage.](image)

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.](image)

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. CO₂ 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.

Figure 4. Influence of voltage on SIE.

Figure 5 presents TCE conversion % in He and N\textsubscript{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\textsubscript{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\textsubscript{2}.

3.3. Mechanism

During plasma discharge, accelerated electrons impact main constituents of carrier gas:\n
\[ \text{O}_2 + e^- \rightarrow \text{O}_2^+, 2\text{O}^+, (\text{O}_2^+ + e^-) + e^- \]

\[ \text{N}_2 + e^- \rightarrow \text{N}_2^+, 2\text{N}^+, (\text{N}_2^+ + e^-) + e^- \]
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\[ \text{He} + e^- \rightarrow \text{He}^* + e^- \]

Other reactive species which can be produced during discharge plasma are O, O_3, 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.\(^5\)

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

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

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:

\[ \text{C}_2\text{HCl}_3 + \text{O}_3 \rightarrow \text{CHClOO}^- + \text{COCl}_2 \]

TCE also reacts with atomic oxygen:

\[ \text{C}_2\text{HCl}_3 + \text{O} \rightarrow \text{CHOCl} + \text{CCl}_2 \]

The dissociative electron may initiate TCE decomposition as follow:

\[ \text{C}_2\text{HCl}_3 + \text{e} \rightarrow \text{C}_2\text{HCl}_2 + \text{Cl}^- \]

Cl radical can react with TCE:

\[ \text{C}_2\text{HCl}_3 + \text{Cl}^- \rightarrow \text{C}_2\text{HCl}_4 \]

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

\[ \text{C}_2\text{HCl}_4 + \text{O}_2 \rightarrow \text{C}_2\text{HCl}_4\text{OO}^- \]

\[ 2\text{C}_2\text{HCl}_4\text{OO}^- \rightarrow 2(\text{C}_2\text{HCl}_4\text{O}^-) + \text{O}_2 \]
The alkoxy radical may lose a Cl atom to form the DCAC:

\[
C_2HCl_4O \rightarrow CHCl_2COCl + Cl^-
\]

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:

\[
ClO^+ + OH^- \rightarrow O_2 + HCl
\]

### 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.
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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  | 95        | 80             | [6]  |
| Planar electrode, double barrier                  |          |          | Ar/20%O_2   | 25        | >99            |      |
| 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   | 260       | >99            | This |
| Cylindrical electrode, single barrier            |          |          | N_2/21%O_2  | 300       | >99            | 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.
Acknowledgments
The authors acknowledge Dr Wong Ka Lun, Ms TAN Geok Suan and Ms Lim-Ang Ah Buan Angela for their collaborations.

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