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Toluene removal characteristics by a superimposed wire-plate dielectric barrier discharge plasma reactor

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Abstract: A superimposed wire-plate dielectric barrier discharge reactor was used to remove toluene in this study. The effects of oxygen content, gas flow rate, gas initial concentration and with/without catalyst on toluene decomposition were investigated. It was found that an optimal toluene removal was achieved when the oxygen content was about 5%. Under this condition, the highest toluene removal efficiency of 80.8% was achieved when the gas concentration was 80 mg/m^3. The toluene removal efficiency decreased with the increase of the gas flow rate and the initial concentration of toluene. In addition, the ozone concentration decreased with the increase of the initial concentration of toluene. It suggested that combining DBD (dielectric barrier discharge) with Co_3O_4/Al_2O_3/foam nickel catalyst *in-situ* could improve the toluene removal efficiency and suppress ozone formation. Products analysis showed that the main products were CO and CO_2 when oxygen was more than 5%.

Keywords: dielectric barrier discharge(DBD); plasma; oxygen content; catalyst; toluene; product analysis

Introduction

Emission of various volatile organic compounds (VOCs) from refineries, coating and paint industries pollutes the environment seriously. Dielectric barrier discharges(DBDs) process has been considered as one of the most hopeful methods to remove VOCs. DBDs are obtained when high voltage is applied to electrodes that are separated by a gas gap and at least one dielectric barrier. Using typical gap spacings(0.5 mm to 1 cm), ambient gas pressure (100 mbar to 2 bar) and AC applied voltages (typically 500 V to 20 kV at 1 Hz to 1 MHz) will cause a multitude of transient filaments with electron densities of about 1014 to 1015 cm^{-3} and mean electron energies of typically 1—10 eV. It suggests that the DBDs method has some advantages comparing with the traditional catalytic ways. Recently various articles on VOCs decomposition via DBDs were reported, such as the concentration dependence of VOC decomposition by DBDs (Rudolph *et al.*, 2002), CF_2Cl_2 and CF_2ClBr decomposition by DBDs (Hou *et al.*, 1999), oxidative conversion of PFC via plasma processing with DBDs (Yu and Chang, 2001), the removal of acetaldehyde using a barrier type packed-bed plasma reactor (Okubo *et al.*, 2000), toluene decomposition with DBD (Guo *et al.*, 2004) and the catalytic methane oxidation by applying a DBD(Khassin *et al.*, 2004).

In this study, a superimposed wire-plate DBD reactor was applied to evaluate the efficiency for toluene removal from gas streams experimentally. Various operational parameters including applied voltage, oxygen content, gas flow rate, gas concentration, and with/without catalyst were investigated. Gaseous products after DBD processing were monitored and quantified.

1 Materials and methods

1.1 Dielectric barrier discharge reactor

A superimposed wire-plate DBD reactor was used in the reaction(Fig.1). Two pieces of epoxy resin boards (200 mm × 45 mm × 0.8 mm) formed the reactor walls and acted as dielectric barriers (the dielectric constant ε=3.6). The high voltage electrode was made of stainless steel wire, 0.8 mm in diameter. The wire electrode was shaped in a spiral form in order to increase the energy density in the reaction volume. Two grounded copper net electrodes were fixed on the two sides of the middle epoxy resin board. When catalysts were used, two pieces of the foam nickel supported catalysts(150 mm × 25 mm × 2 mm) were stuck on the grounded electrodes. The total length of the reactor was 200 mm, and the effective length was 150 mm. The gap between the high voltage electrode and the grounded electrode was 8 mm, resulting in a reaction volume of 60 cm^3.

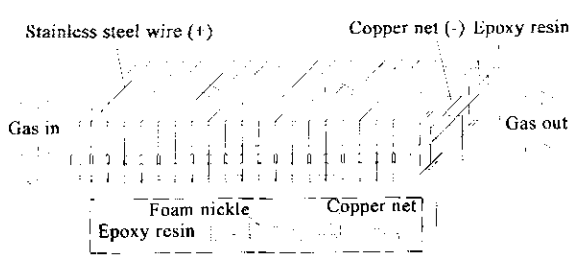

Fig.1 Simplified structure of the wire-plate DBD reactor

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1.2 Catalyst

Co_3O_4/Al_2O_3/foam nickel was used as a catalyst and the mass ratio of Co_3O_4/Al_2O_3/foam nickel was 0.49 : 0.50 : 1.00. An impregnation process was followed for preparing the mixed Co_3O_4/Al_2O_3/foam nickel. The commercial foam nickel support was impregnated with the sol of $Al_2O_3 \cdot nH_2O$, then the aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$. After that, it was dried at 393 K for 2 h, and then calcined at 723 K for 4 h.

1.3 Experimental setup

The experimental setup is shown in Fig. 2. Gas streams of O_2 (>99.99%) and N_2 (>99.99%) from gas cylinders were generated and a set of mass flow controllers were used to regulate the flow rates of feeding gases. Gaseous toluene was regulated by passing part of the nitrogen gas stream through the pure toluene liquid (>99.5%) which was kept in a water bath (T=25 ±1℃). High voltage power was supplied by a booster (0—250 V) cooperated with a high voltage AC transformer (50 Hz, 30 kV) in series. A digital power meter(YF9901, China) was connected to the variable voltage transformer for measuring the power consumption of the whole DBD system.

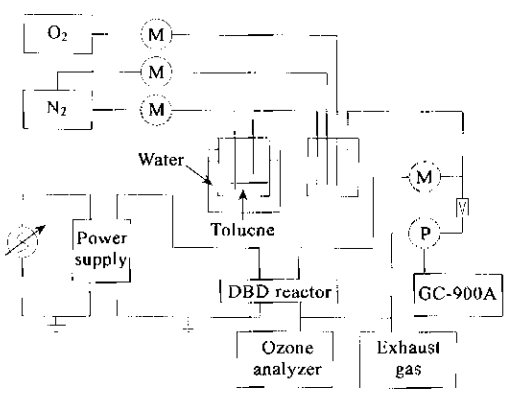


Fig.2 Schematics of the experimental setup

Gas samples were obtained from the effluent by an auto-sampler and were analyzed on-line. Toluene and the reaction products were analyzed by a gas chromatograph (GC-900A, KECHANG, Shanghai, China) equipped with two hydrogen flame ionization detectors(FID). One was for organic compounds(such as methane, benzene and toluene) detection with a 50 m SE-30 capillary column heated at 80℃, and the other equipped with a methanizer was for carbon monoxide and carbon dioxide analysis using a 2 m carbon molecular sieve stainless steel column heated at 65℃. Minor products were measured by a GC-MS (HP 5973N GC-6890) equipped with a 60 m DB-5MS capillary column at 40—220 ℃.The ozone concentration was monitored by an ozone analyzer(DCS-1, LIDA, Shanghai, China). The experiment was carried out at room temperature and atmospheric pressure.

2 Results and discussion

2.1 Effect of oxygen content on toluene decomposition in the DBD system

Since the flue gases emitted from industrial processes always contain some oxygen, a set of tests have been carried out to determine how oxygen content of the gas stream would affect toluene removal efficiency (η_t). Fig.3 shows the experimental results with oxygen content varied from 0 to 20% by volume. The initial concentration of toluene (C_T) was 800 mg/m^3, and the gas flow rate (Q) was 0.03 m^3/h. It was found that toluene removal efficiency increased with the increase of applied voltage, and the highest toluene removal efficiency was observed for the gas stream containing 5% oxygen.

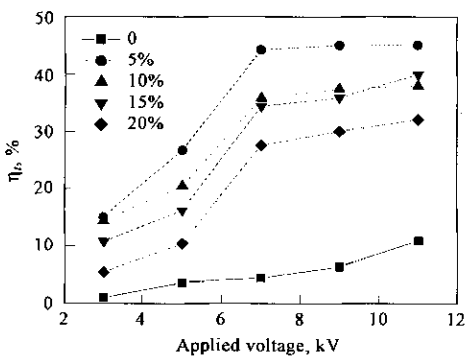


Fig.3 Dependence of toluene removal efficiency on oxygen content (Q=0.03 m^3/h; C_T=800 mg/m^3)

The decomposition mechanism of toluene was explored in view of reaction rate (Wu *et al.*, 2004). When the applied voltage is higher, the produced electric field is stronger and the resumed power is higher. More electrons react with toluene and break the bond between the toluene molecules, thus the removal efficiency of toluene increases. Oxygen plays a very important role in the reaction. A low-temperature electrical discharge in an oxygen-containing gas mixture produces mainly oxygen radicals as active species. Rate constants for major initiating radical reactions involving the excitation and dissociation of O_2 and N_2 were given as follows(Herron, 2001).

$$e+O_2 \longrightarrow O_2(^1\Delta g)+e \quad K=7.3e\text{-}10\ cm^3/(molecule \cdot s) \quad (1)$$

$$e+O_2 \longrightarrow O+O+e \quad K=8.9e\text{-}10\ cm^3/(molecule \cdot s) \quad (2)$$

$$e+O_2(^1\Delta g) \longrightarrow O+O+e \quad K=8.9e\text{-}10\ cm^3/(molecule \cdot s) \quad (3)$$

$$e+O_2 \longrightarrow O+O(^1D)+e \quad K=2.7e\text{-}09\ cm^3/(molecule \cdot s) \quad (4)$$

$$e+O_2(^1\Delta g) \longrightarrow O+O(^1D)+e \quad K=2.7e\text{-}09\ cm^3/(molecule \cdot s) \quad (5)$$

$$O+O_2+M \longrightarrow O_3+M$$

K=1.4e-14 cm^3/(molecule·s) (6)

$O+O_3 \longrightarrow O_2+O_2$

K=8.0e-15 cm^3/(molecule·s) (7)

$e+N_2 \longrightarrow e+N_2(A)$

K=1.4e-09 cm^3/(molecule·s) (8)

$e+N_2 \longrightarrow N^*+N+e$

K=9.4e-11 cm^3/(molecule·s) (9)

(N^* is electronically excited nitrogen species)

A higher O_2 content in the gas streams leads to the generation of more highly reactive O radicals in the DBD reactor, resulting in a higher removal efficiency. However, O_2 has an adverse effect on toluene removal due to its electronegativity. The electronegative property of oxygen tends to trigger the electron attachment reactions and changes the associated electron energy distribution. Increasing oxygen content would limit electron density in the system, and reduce the power deposited into the plasmas (Lee and Chang, 2003). As a result, appropriate oxygen content is essential for toluene destruction. In the experiment, when oxygen content was 5%, the removal efficiency was the highest.

2.2 Effect of gas flow rate on toluene decomposition in the DBD system

Dependence of toluene removal efficiency on applied voltage with the gas flow rate ranging from 0.018 to 0.042 m^3/h in the DBD system is shown in Fig.4. The initial concentration of toluene was 5300 mg/m^3, and the oxygen content was 5%. It was clear that flow rate had a significant effect on the destruction efficiency. The toluene removal efficiency increased with the decreasing of gas flow rate. Although the toluene removal efficiency was relatively low at the high initial concentration of toluene (5300 mg/m^3). Decreasing the gas flow rate, namely increasing the retention time in the reactor, would increase the energy obtained by toluene molecules from the system and improve the probability of collision between toluene molecules and electrons, which resulted in a higher toluene removal efficiency.

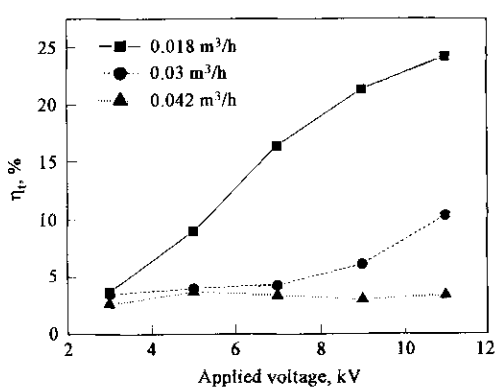


Fig.4 Dependence of toluene removal efficiency on gas flow rates [O_2]=5%; C_t=5300 mg/m^3

2.3 Effect of initial concentration on toluene decomposition in the DBD system

Fig.5 shows the dependence of toluene removal efficiency on gas concentration. The oxygen content was controlled at 5% and the gas flow rate was 0.03 m^3/h. Experimental results indicated that η_t decreases with increasing inlet concentration of toluene for the gas streams with oxygen. The highest η_t of 80.8% was achieved when the toluene concentration was 80 mg/m^3. Fig.6 shows the dependences of ozone concentration on gas concentration. Ozone concentration increased with the decrease of the toluene concentration.

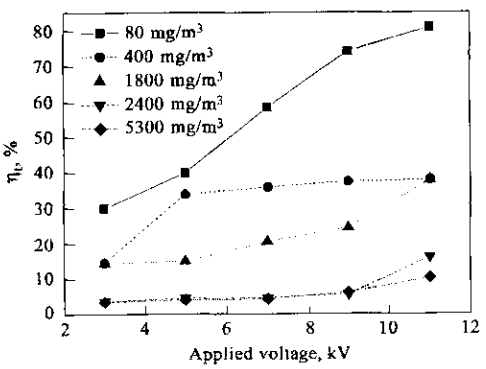


Fig.5 Dependence of toluene removal efficiency on gas concentration [O_2]=5%, Q=0.03 m^3/h

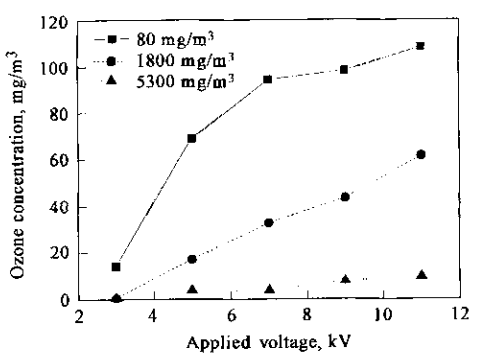


Fig.6 Dependence of ozone concentration on gas concentration [O_2]=5%, Q=0.03 m^3/h

When the initial concentration is low, the amount of toluene molecule is few, but at the same time the input power is a fixed value, therefore the probability of collisions between toluene molecules and electrons is larger and toluene removal efficiency is higher. On the other hand, when the initial concentration is low, few toluene molecule collides with the electron, and more energy could be deposited to oxygen molecule, thus the ozone concentration is high.

2.4 Effect of catalyst on toluene decomposition in the DBD system

Experimental tests were conducted to determine the dependence of toluene removal efficiency on

energy density with/without catalyst (Fig.7). The reaction condition of 5% O_2 and 0.03 m^3/h gas flow rate was applied to the system. The initial concentration of toluene was 800 mg/m^3. It suggested that toluene removal efficiency increased significantly when Co_3O_4/Al_2O_3/foam nickel catalyst was introduced into the discharge area. For example, when toluene was decomposed at 11 kV, toluene removal efficiency was 37% with DBD system compared to 62% in the DBD treatment with the catalyst *in situ*. The influence of the catalyst on ozone formation is presented in Fig. 8. It shows that ozone concentration increased with the increase of applied voltage, and the catalyst could suppress the ozone formation to a great extent.

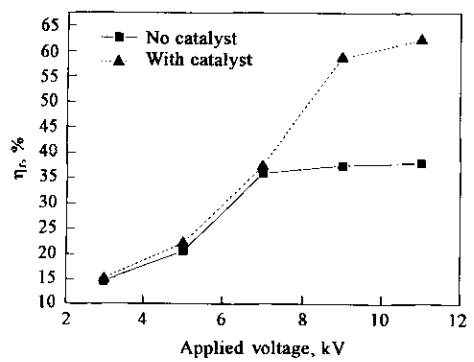


Fig.7 Removal efficiency of toluene by the plasma process with/without the catalyst
Q=0.03 m^3/h; $[O_2]$=5%; C_T=800 mg/m^3

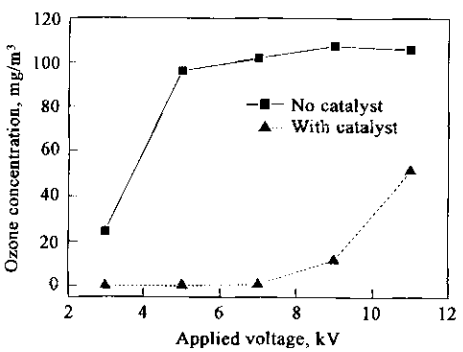


Fig.8 Ozone concentration with/without the catalyst
Q=0.03 m^3/h; $[O_2]$=5%; C_T=800 mg/m^3

Some researchers reported that real synergy effects between non-thermal plasma and catalysis could be available by introducing the catalyst into the discharge zone. When catalysts were placed *in situ*, the input energy could be depressed and the pollutant conversion could be strengthened(Roland *et al.*, 2002; Ogata *et al.*, 1997; Francke *et al.*, 2000; Oda *et al.*, 2002). Ozone as a main long-living oxidant was transported to the catalyst and could take part in heterogeneous oxidation reactions on its surface. Thus the catalyst could dissociate ozone and improve the carbon dioxide selectivity. But for many cases, the non-thermal plasma reactor could not combine catalyst effectively. Some researchers applied packed-bed discharge to combine plasma and catalyst (Ogata *et al.*, 2003; Holzer *et al.*, 2002; Li *et al.*, 2002; Muhannad and Jiang, 2000; Kim *et al.*, 2005; Kang *et al.*, 2002). Although it has been found that packed-bed dielectric barrier discharge reactor is effective in terms of energy efficiency, carbon balance, and nanometer-sized aerosol formation, the treatment of high flow of gas as required in industrial processes needs to minimize the pressure drop in the reactor due to the presence of the pellets. In this paper the wire-plate DBD reactor with a new type of Co_3O_4/Al_2O_3/foam nickel catalyst *in situ* was designed. Foam nickel was a special support, which was thin and porous. It could be stuck on the electrodes therefore the pressure drop could be reduced greatly. In addition, the catalyst was easy to be removed. Such a reactor would be hopeful to be used in industry.

2.5 Products analysis

Methane, benzene, ozone, carbon monoxide and carbon dioxide were detected after DBD reaction when the oxygen was enough(>5%) in the gas stream. CO and CO_2 were the main products. The relationship between COx concentration with applied voltage is shown in Fig.9. It was found that the concentrations of CO and CO_2 increased with the increase of applied voltage, but CO_2 increased more than CO when the applied voltage was larger than 7 kV. In the reaction, CO was produced earlier than CO_2. For example, when the applied voltage was lower than 5 kV, few CO was produced, and no CO_2 existed in the products. This is due to that the electron energy is not high enough for the oxygen to be ionized in the reaction when the electric field strength is low. Only a part of toluene is oxidized to CO, and it is difficult to be oxidized to CO_2. Whereas when the applied voltage is high, CO is oxidized to CO_2, thus the amount of CO_2 increased more than CO.

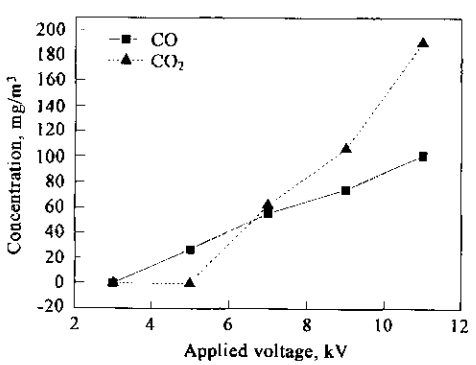
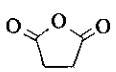
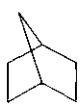
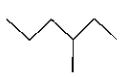
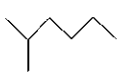


Fig.9 Dependence of concentrations of CO and CO_2 on applied voltages
Q=0.03 m^3/h; $[O_2]$=5%; C_T=800 mg/m^3

When the oxygen content was low (< 5%), CO and CO_2 were little in the reaction. And some byproducts, such as C_3H_6O, C_7H_{16} , C_7H_{12} and $C_4H_4O_3$ were produced via GC-MS analysis. The molecular structure of these byproducts is shown in Table 1. In addition, certain yellow product that was observed in the DBD reactor, but the composition was unclear. Maybe it was aromatic polymer.

Table 1 The molecular structure of some byproducts

Molecular formula	Molecular structure	Molecular formula	Molecular structure
C_3H_6O		$C_4H_4O_3$	
C_7H_{12}		C_7H_{16}	
C_7H_{16}			

3 Conclusions

An experimental investigation was conducted to remove toluene from flue gas by an atmospheric-pressure DBD process. Experimental results suggest that DBD technology could effectively destroy toluene molecules. An optimal toluene removal is achieved at around 5% of oxygen content. The superimposed wire-plate dielectric barrier discharge reactor with Co_3O_4/Al_2O_3/foam nickel catalyst *in situ* is effective in toluene destruction and ozone dissociation. Products analysis indicates that the main products were CO and CO_2 when oxygen is more than 5%.

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