Decomposition characteristics of toluene by a corona radical shower system

WU Zu-liang, GAO Xiang, LUO Zhong-yang, NI Ming-jiang, CEN Ke-fa

(Clean Energy and Environment Engineering Key Lab of Ministry of Education, Zhejiang University, Hangzhou 310027, China. E-mail: wuzuliang@zju.edu.cn)

Abstract: Non-thermal plasma technologies offer an innovative approach to decomposing various volatile organic compounds(VOCs). The decomposition of toluene from simulated flue gas was investigated using a pipe electrode with nozzles for the generation of free radicals. Corona characteristics and decomposition of toluene were investigated experimentally. In addition, the decomposition mechanism of toluene was explored in view of reaction rate. The experimental results showed that the humidity of additional gas has an important effect on corona characteristics and modes and stable streamer corona can be generated through optimizing flow rate and humidity of additional gas. Applied voltage, concentration of toluene, humidity of toluene and resident time are some important factors affecting decomposition efficiency. Under optimizing conditions, the decomposition efficiency of toluene can reach 80%. These results can give a conclusion that the corona radical shower technology is feasible and effective on the removal of toluene in the flue gas.

Keywords: decomposition; corona; radical; toluene

Introduction

Emission of various volatile organic compounds(VOCs) from the semiconductor and paint industries is a typical cause of air pollution. Multifarious technologies have been investigated for decomposing VOCs, including catalytic oxidation, active carbon absorption, thermal decomposition, and condensation and so on. More recently, non-thermal plasma technologies (electrical discharge processing) have offered an effective approach to the problem of decomposing various VOCs. Non-thermal plasma VOCs control technologies include mainly electron beam(Bromberg, 1995; Hsiao, 1995; Penetrante, 1997), nanosecond pulsed corona (Yamamoto, 1992; Chang, 1997), dielectric barrier discharge(Chang, 1995), ferroelectric packed-bed discharge (Nunez, 1993; Futamura, 1998; Yamamoto, 1994; 1996; Zhang, 1994), flow-stabilized direct current discharge process(Kohno, 1994; 1998; Myint, 1997; Otani, 1991), surface discharge (Oda, 1993; 1996) and so on. These means mentioned above have more or less effective on the reduction of VOCs. However, it is necessary for practical application to reduce resident time and improve energy efficiency of VOCs decomposition.

In order to improve the decomposition efficiency, a corona radical shower system is used to decompose VOC in this work. In experimental system, a pipe electrode with some nozzles is used as a discharge electrode placed in the middle of a parallel plate type apparatus. Positive DC high voltage is applied to the discharge electrode. Additional gases with O_2 and H_2O are introduced into the discharging space through the ionization region at the tip of nozzles. Toluene

($C_6H_5CH_3$) is chosen due to typical VOCs existed not only in paint industry but also in house. This paper describes the decomposition characteristics of dilute toluene in dependence of various experimental conditions, e.g., concentration, humidity, resident time and applied voltage. The results will illustrate the feasibility of industrial application to VOCs decomposition through the corona radical shower system.

1 Experimental apparatus and methods

The schematic diagram of experimental apparatus is shown in Fig.1. An ESP power supply(Zhejiang Jinhua ESP Co., China) was used to generate plasma as high-voltage power supply. In order to observe corona easily, the plasma reactor was designed into a vessel(500 mm length, 100 mm width, 100 mm height) made of plexiglass. Two plate electrodes made of stainless steel(450 mm × 80 mm) were adhered to grounded plates of the reactor inner as negative poles. A stainless steel pipe (100 mm length, 6 mm outer diameter, 4 mm inner diameter) with four pairs of nozzles (5 mm length, 1.6 mm outer diameter, 1.0 mm inner diameter) was used as positive electrode. The spacing of nozzles was 20 mm. The pipe electrode was placed in the middle of grounded plates and connected with positive electrode of high-voltage power supply. On the other hand, additional gases $Q3(O_2$ and H_2O) were introduced into the pipe electrode and dissociated at the corona region near the tips of nozzles through electron impacts.

As simulated flue gas, air containing toluene was introduced into reactor. Air supplied from gas cylinder was divided into two flows after silicon gel dryers. The rate of each flow was controlled with a flow meter. One flow($Q1$)
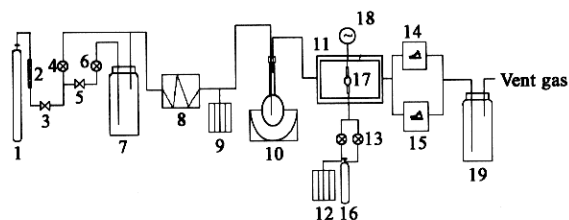
Fig.1   Schematic diagram of experimental apparatus
1. air cylinder; 2. dryer; 3, 5. valve; 4, 6, 13. flow meter; 7. bubbler; 8. mixing box; 9, 12. water vapor generator; 10. thermostat; 11. reactor; 14. GC; 15. GC-MS; 16. oxygen cylinder; 17. nozzle electrode; 18. high-voltage power supply; 19. absorption bottle

was introduced into the bubbler that contained toluene. The air with almost saturated toluene vapor was mixed evenly with the other flow($Q2$) in a mixing box. Under the condition of keeping the total flux($Q = Q1 + Q2 = 1 \text{ m}^3/\text{h}$) unchanged, the prescribed toluene concentrations were obtained by adjusting the two fluxes with flow meters. After gas out of the mixing box and a certain quantitative water vapor were mixed again, they got into a thermostat to be heated. At last, the mixed gases entered reactor to be treated. On the other hand, after adding humidity, oxygen entered the pipe electrode. Through controlling water vapor flux and oxygen flux by flow meters, different humidity additional gas could be gained. The humidity of simulated flue gas and additional gas was measured with humidity meters(Taishi Co.). Samples of the treated gas were analyzed qualitatively and quantitatively by gas chromatography (GC9790, FID, DB-624 capillary column, Wenlin Fuli Co., China) and HRGC-LRMS(trace 2000, finngan voyager, USA) at the outlet of the reactor. The effluent gas was collected after passing the gas stream through a gas bubbler containing a small portion of ethanol. The experiment was gone along under atmospheric pressure and at 50 ℃ .

Stable streamer corona can be observed during the experiment through adjusting flow rate and humidity of additional gas. Fig. 2 is a typical photograph of streamer corona when applied voltage 26.5 kV, additional gas flux 1000 ml/min and relative humidity of additional gas 26%. This photograph shows that fan-shape stable coronas cover the discharging space uniformly between two grounded plates. This kind of streamer corona is favorable to giving rise to free radicals.

Because water molecule can absorb electrons in streamer corona and produce negative ion that move slowly, corona could be produced more difficultly and discharge current can be lower. Fig. 3 is the curve diagram about discharge current in dependence of discharge voltage when different humidity oxygen enter the pipe electrode. It can be seen from Fig. 3 that the increase of oxygen humidity heightens onset voltage and sparking voltage. However, discharge current decreases with the increase of oxygen humidity. And we found from the experiment that bigger the
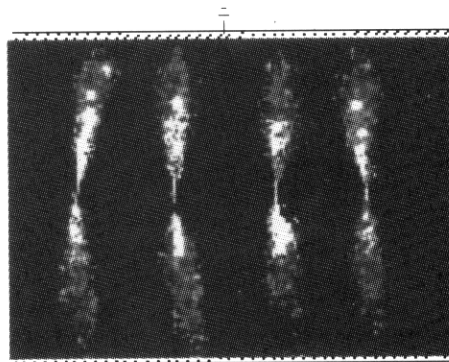

Fig.2   Streamer corona photo
Simulated flue gas: $Q = 1 \text{ m}^3/\text{h}$, $t = 50 ℃$, $RH = 13\%$; $V = 26.5$ kV; additional gas: $Q3 = 1000$ ml/min, $RH = 26\%$

humidity of oxygen was, smaller the corona region was. When the relative humidity of oxygen reached 77%, corona only glistened at the tip of nozzles. Hence the relative humidity of oxygen should not be in excess of 60%.
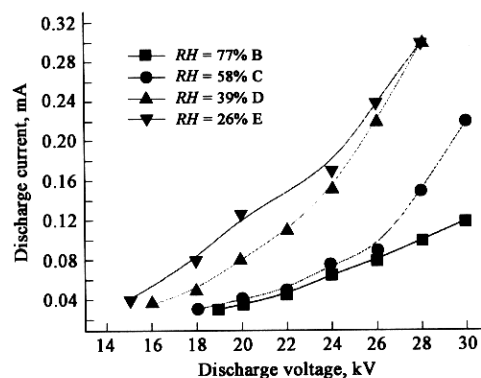

Fig.3   Discharge voltage-current characteristics at different relative humidity of additional gas
Simulated flue gas: $Q = 1 \text{ m}^3/\text{h}$; additional gas: $Q3 = 1000$ ml/min

2   Experimental results and analysis

2.1   The effect of applied voltage and toluene concentration

Toluene decomposition efficiency as a function of its concentration at different applied voltage is shown in Fig. 4. It can be seen from Fig. 4 that toluene decomposition efficiency increases with the increasing applied voltage before discharge is not broken down. When the change of applied voltage in a range of 22—25 kV, the decomposition efficiency changes larger. As far as the reason is concerned, it might be explained that the corona discharge transforms from glow discharge to streamer discharge after the applied voltage exceeds 23 kV. Consequently, the discharge current elevates more, which brings more free radicals correspondingly. And more radicals lead to greater probability of oxidation of toluene, i.e., higher destruction efficiency.
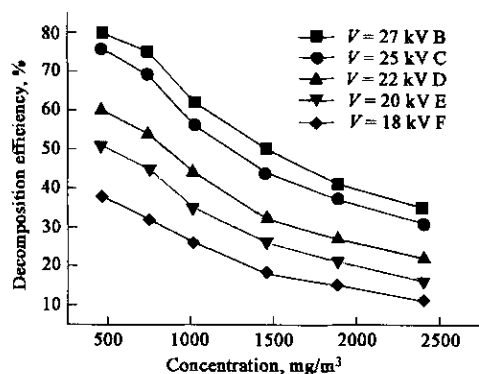
Fig.4   Decomposition efficiency of toluene as a function of concentration

Additional gas: $Q3 = 1000$ ml/min, $RH = 26\%$; simulated flue gas: $Q = 1$ m³/h, $t = 50$℃, $RH = 51\%$

From decomposition efficiency of different concentration toluene, it can be shown that the de-toluene efficiency drops with increasing concentration. However, when the concentration increases further, the decreasing trend of de-toluene efficiency slows down. According to experimental results, we can see that a good decomposition effect can be achieved at low concentration through the radical shower system. The maximum decomposition efficiency of toluene can reach 80%. However, high-concentration toluene is decomposed more difficultly. Under the condition of toluene concentration beyond 800 mg/m³, the decomposition efficiency is less than 50% commonly. However, in the view of absolute decomposing amount, it enhances with the increasing concentration, namely, energy utilization ratio of the high concentration toluene is a little higher than that of the low.

2.2   The effect of simulated flue gas humidity

Water molecules are dissociated into strong-oxidative free radicals (such as OH˙ and O˙) through the impact of high-energetic electrons. These radicals change the element of active species in the corona region, which has great effect on chemistry reaction, e.g., radical reaction. Otherwise, water vapor can absorb electron energy and decrease electron activity, which is disadvantage to decomposition of toluene. Therefore it is necessary to study how simulated flue gas humidity affects decomposition efficiency.

Decomposition efficiency of toluene as a function of relative humidity of simulated flue gas at different applied voltage is shown in Fig.5. It can be seen obviously from Fig. 5 that the increasing humidity of simulated flue gas is beneficial to toluene decomposition at first. When the relative humidity reaches 50%—56%, decomposition efficiency is maximum. Subsequently, it showed a descending trend. Our explanation is: more water in the simulated flue gas makes water molecule and high-energetic electron impact more frequently and more free radicals are generated at first, which can promote decomposing reaction. However, when the humidity of simulated flue gas reaches a certain value, the

energy of electron is consumed excessively on the impact with water molecule, which will be harm for the destruction of toluene. Therefore it is very important to control the humidity of simulated flue gas. Under common conditions, the relative humidity had better be controlled at about 50%.
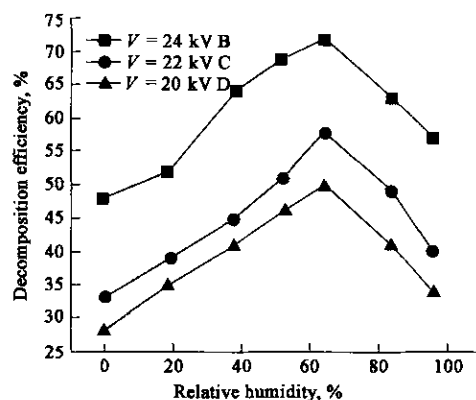

Fig.5   Decomposition efficiency of toluene as a function of relative humidity of flue gas

Additional gas: $Q3 = 1000$ ml/min, $RH = 26\%$; simulated flue gas: $Q = 1$ m³/h, [toluene] $= 750$ mg/m³

2.3   The effect of gas resident time

Under dry conditions, when the flux of simulated flue gas is 100 L/min, 50 L/min, 33.3 L/min, 20 L/min, 15 L/min, 11 L/min, 9 L/min respectively (the corresponding resident time is 3 s, 6 s, 9 s, 15 s, 21 s, 27 s, and 33 s respectively), the effect of resident time on decomposition efficiency is studied. Fig.6 is the curve diagram showing the decomposition efficiency as a function of resident time at the different concentration of toluene. It showed that the prolonging resident time can improve obviously the decomposition efficiency. When the resident time is about 20 s, the decomposition efficiency reaches higher level. Further does the resident time increase, further does the increasing rate of decomposition efficiency drop. The reason could be that short-lived free radicals limit the diffusion in the reactor and the process of reactions. Considering economy, longer resident time is not better effective. The resident time should
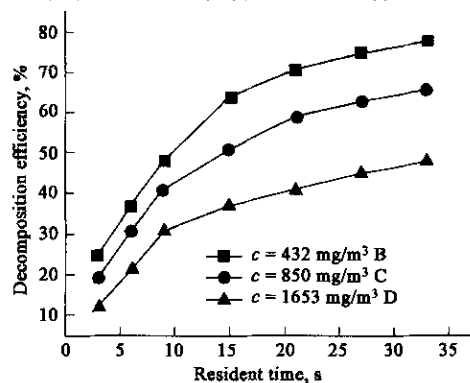

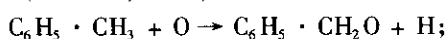Fig.6   Decomposition efficiency of toluene as a function of resident time

Additional gas: $Q3 = 1000$ ml/min, $RH = 26\%$; simulated flue gas: $t = 50$℃, $RH = 51\%$, $V = 25$ kV
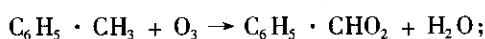
be controlled at about 20 s.

3 Toluene decomposing theory discussions

The principle processes of VOCs decomposition induced by high-energetic electrons in plasma are electron and radical impact dissociation of molecules(Chang, 1989). Concretely, the destruction processes include mainly three means: (1) High-energetic electrons generated by DC corona discharge impact reactant molecules, which leads low-energy chemical bonds of reactant to cleave. Then original molecule structure of reactant is destroyed and reactant molecule is dissociated into various free radicals. Subsequently, a serial of radical reactions and oxidization reactions are preceded and VOCs are decomposed finally. (2) High-energetic and strong-oxidative active species(such as OH˙, O˙, O_3) react directly with reactant. These radicals combine with reactant molecules, which destroy the stability of original molecules and dissociate chemistry bonds into new intermediates that are easy to be oxidized further. Through a serial of complex reactions again, VOCs are decomposed at last. (3) VOCs ions are produced through charge transfer reactions of VOCs with ions that are generated by gas discharge. And then they are recombined with electrons into various hydrocarbon free radicals. Subsequently, radical reactions and oxidation reactions are on continuously until reactant is decomposed.
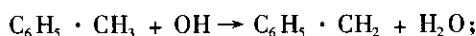
At present, we think usually that VOCs are decomposed through the above there means. However, which is more important will be confirmed according to specific reactant. For toluene, the direct reactions of toluene with radicals are insignificant except for OH radicals, analyzed from the reaction rate coefficient. The reaction rates of these radicals are below(Miziolek, 1994):
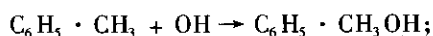
$$C_6H_5 \cdot CH_3 + O \rightarrow C_6H_5 \cdot CH_2O + H;$$
$$k = 8.4 \times 10^{-14} \text{ cm}^3/\text{s},$$
$$C_6H_5 \cdot CH_3 + O_3 \rightarrow C_6H_5 \cdot CHO_2 + H_2O;$$
$$k = 1.5 \times 10^{-22} \text{ cm}^3/\text{s},$$
$$C_6H_5 \cdot CH_3 + OH \rightarrow C_6H_5 \cdot CH_2 + H_2O;$$
$$k = 7 \times 10^{-13} \text{ cm}^3/\text{s},$$
$$C_6H_5 \cdot CH_3 + OH \rightarrow C_6H_5 \cdot CH_3OH;$$
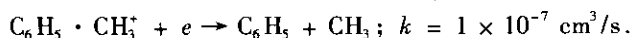$$k = 5.2 \times 10^{-12} \text{ cm}^3/\text{s}.$$

Compared reactive rate with radical reaction, the transfer reactions of toluene with ions and recombination of toluene ions and electrons are more important (Miziolek, 1994).

$$C_6H_5 \cdot CH_3 + O^+, O_2^+, N^+, N_2^+ \rightarrow$$
$$C_6H_5 \cdot CH_3^+ + O, O_3, N, N_2;$$
$$k = 1 \times 10^{-10} \text{ cm}^3/\text{s},$$
$$C_6H_5 \cdot CH_3^+ + e \rightarrow C_6H_5 + CH_3; \quad k = 1 \times 10^{-7} \text{ cm}^3/\text{s}.$$

However, the ion densities are much lower by 4—5 orders of magnitude, compared with radical densities. Therefore the above two means are not most important in the destruction of toluene and the high-energetic electron impact

dissociations may provide additional probable reaction channels. As far as the impact reaction of reactant and electron is concerned, the relation between electron energy and bond energy of various chemistry bonds of reactant plays a very important role on the reaction carrying out well. Researches have shown that the electron energy produced by corona discharge is in the range of 2—20 eV. Moreover, the most distribution of electron energy is in the range of 5—12 eV(Dors, 1998). However, chemistry bonds' energies of toluene are lower(Table 1; Toshiaki, 1997). Therefore the energy of electron is able to break down the chemistry bonds of toluene, which promotes the impact reaction favorably.

Table 1 Dissociation energy

Chemistry bond	Dissociation energy, eV
C-H in CH_3	3.5
C-C between CH_3 and phenyl	3.8
C-H in phenyl	4.6
C = C in phenyl	5.5

Besides, the electron density is as high as 10^{12} cm^{-3} in the discharge channel, where the reaction rate is the order of 10^{-6} cm^3/s(Urashima, 1995). Significant amounts of COOH · H, COOH · CH_3, $COOHC_6H_5$, N_2HCH_3 and OHC_6H_4 molecule observed in aerosol particles(Nunez, 1993), and C_xH_y observed in a gas phase (Zhang, 1994), support existence of the above electron impact dissociated byproducts formation channels. These dissociated byproducts also react further with strong-oxidative free radicals(such as OH˙, O˙, HO_2^-) produced by plasma processes dissociating additional gas. They are decomposed into CO_2 and CO finally which are examined from the effluent in the experiment. So in the course of decomposition of toluene, the electron impact reaction plays the most significant role.

4 Conclusions

The decomposition of toluene under different operating conditions using a corona radical shower system was investigated and the following conclusions were draw: (1) Water vapor of additional gas can restrain discharge. High voltage and low concentration help to improve decomposition efficiency of toluene. When applied voltage is 27 kV and toluene concentration is 460 mg/m^3, decomposition efficiency reached above 80%. (2) Moderate humidity of simulated flue gas makes for enhancing decomposition efficiency. When the relative humidity of simulated flue gas gets to 50%—56%, the destruction efficiency reaches maximum. (3) Extending resident time can improve the destruction efficiency. However, the increasing rate of efficiency will slower after a certain time. Considering economy and decomposition efficiency, we had better control the resident time at about 20 s; (4) According to the analysis of reaction rate and experiment results, the toluene decomposition mainly depends on electron impact dissociation.

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