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Decomposition of dimethyl sulfide in a wire-cylinder pulse corona reactor*

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Abstract: Decomposition of dimethyl sulfide (DMS) in air was investigated experimentally by using a wire-cylinder dielectric barrier discharge (DBD) reactor at room temperature and atmospheric pressure. A new type of high pulse voltage source with a thyratron switch and a Blumlein pulse-forming network (BPFN) was adopted in our experiments. The maximum power output of the pulse voltage source and the maximum peak voltage were 1 kW and 100 kV, respectively. The important parameters affecting odor decomposition, including peak voltage, pulse frequency, gas flow rate, initial concentration, and humidity, which influenced the removal efficiency, were investigated. The results showed that DMS could be treated effectively and almost a 100% removal efficiency was achieved at the conditions with an initial concentration of 832 mg/m^3 and a gas flow rate of 1000 ml/min. Humidity boosts the removal efficiency and improves the energy yield (EY) greatly. The EY of 832 mg/m^3 DMS was 2.87 mg/kJ when the relative humidity was above 30%. In the case of DMS removal, the ozone and nitrogen oxides were observed in the exhaust gas. The carbon and sulfur elements of DMS were mainly converted to carbon dioxide, carbon monoxide and sulfur dioxide. Moreover, sulfur was discovered in the reactor. According to the results, the optimization design for the reactor and the matching of high pulse voltage source can be reckoned.

Key words: Pulse corona discharge, Blumlein pulse-forming network (BPFN), Decomposition, Dimenthyl sulfide (DMS), Specific energy density, Energy yield (EY)

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INTRODUCTION

Odor pollution is an important and challenging issue in the world because of its detrimental influence on human beings and potential pollution to the environment. Many conflicts have been happening between residents and manufactories all over the world due to the odor pollution. Therefore, odor pollution has been becoming an urgent social problem.

Dimethyl sulfide (DMS), primarily from the incomplete coal and oil combustion, petroleum refining, pulp mills, or composting (Tsai *et al.*, 2003), is a typical gaseous odor pollutant. The techniques of washing, oxidation, absorption and adsorption are generally employed to control odors. DMS in stream can be removed by catalytic incineration, chemisorption, and packed tower scrubbing. However, during the process of catalytic incineration, it is difficult to regenerate or dispose the spent carbons, while the catalytic oxidation, which is typically adapted to lower the concentrations of an inlet gas, involves sulfur-poisoning effects. The adsorption amount is small and the adsorbent is costly in chemisorption. The capability of absorbent is limited and it has secondary pollution with packed tower scrubbing.

Due to its relatively low power consumption and high removal efficiency, plasma has great industrial potential. In recent years, non-thermal plasma (NTP) technology has been applied to the odor decomposition (Yoshida *et al.*, 1989; Helfritch, 1993; Zhang *et*

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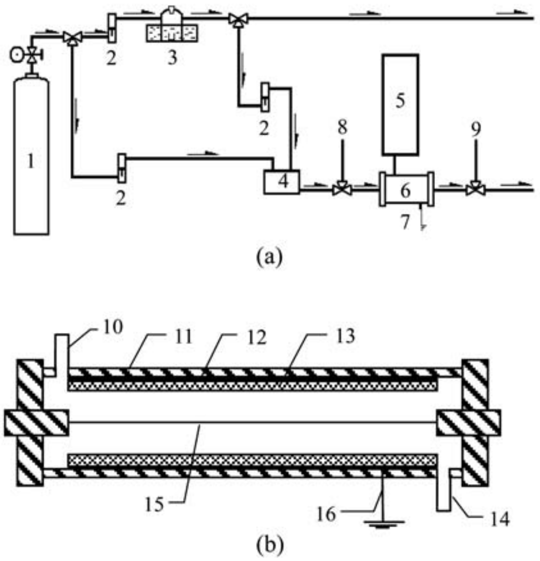
al., 1996; Penetrante *et al.*, 1997; Okubo *et al.*, 2001; Vinogradov *et al.*, 2007). Our previous experiments have shown that the odors can be treated effectively in the wire-plate corona reactor by Blumlein pulse-forming network (BPFN) type of narrow pulse generator (Ruan *et al.*, 2005; Shi *et al.*, 2005).

In this study, we investigated the decomposition of DMS in a wire-cylinder dielectric barrier discharge (DBD) reactor to which the odor was fed under NTP induced by positive pulsed corona discharge. A high pulse voltage source with a thyratron switch and a BPFN was used in our experiments. Special attention was paid to some important parameters affecting odor decomposition, including peak voltage, pulse frequency, gas flow rate, and initial concentration. For practical applications, the effect of water vapor on the NTP technique must be considered. In this paper, the effect of humidity on the decomposition of DMS by plasma was investigated. The products and the mechanism of the decomposition of DMS were also studied.



1: air cylinder; 2: flow meter; 3: simulated gas generator; 4: buffer tank; 5: high pulse voltage source; 6: wire-tube reactor; 7: grounding; 8: sampling of inlet; 9: sampling of outlet; 10: gas inlet; 11: shell body; 12: aluminum foil; 13: dielectric barrier; 14: gas outlet; 15: Ni-Cr alloy wire; 16: grounding

Fig.1 Experimental setup (a) and structure (b) of wire-tube reactor

MATERIALS AND METHODS

A schematic diagram of the experimental setup is shown in Fig.1a. The setup mainly consists of an odor feeding system, a dielectric barrier corona reactor, and a high voltage pulse generator. The simulated gas in a standard gas cylinder is divided into three streams through Teflon tubes. A set of flow meters are used to regulate the flow rates of the streams. One stream passes through a DMS generator that is kept in a water bath (T=(25±1) °C), and then is balanced with DMS vapor. Moisture is added to the gas by bubbling the sample gas through a small volume water bath. The other two streams are mixed with the large rate stream in the buffer tank. At last, the mixed stream is introduced into the corona reactor. The arrows in Fig.1a show the gas flow direction. The samples were gathered at the inlet and the outlet of the reactor.

A wire-cylinder DBD reactor is adopted in the experiment. The structure of wire-cylinder DBD reactor is shown in Fig.1b. The outside part of the reactor is made of epoxy resin. A ceramic tube made of alumina is used to form the dielectric barrier wall. The ceramic tube is 8 mm in thickness and 45 mm in inner diameter. The ground electrode is an aluminum film conductor embedded between the epoxy resin tube and ceramic tube. The corona electrode was of Ni-Cr alloy wire with a diameter of 0.5 mm. The effective volume of the reactor was 143 cm^3 (45 mm in inner diameter and 90 mm in length).

A BPFN type of narrow pulse generator is used in our experiments (Ruan *et al.*, 2005). The maximum power output of the pulse voltage source and the maximum peak voltage are 1 kW and 100 kV. The typical waveforms about pulse width and shape were measured as presented in our previous study (Ruan *et al.*, 2005).

The concentrations of DMS were measured by the gas chromatograph GC7890II (Tianmei Corporation, Shanghai). The products of decomposition were analyzed with the FTIR EQ55 (Bruker Corporation, Germany). The concentrations of SO_2, O_3 and NO_x were measured by the gas indicator tubes (Sanhuan Corporation, Beijing), and their minimum detectable limits (MDLs) were 0.2 mg/m^3, 0.2×10^{-6} and 0.5 mg/m^3, respectively.

RESULTS AND DISCUSSION

Peak voltage

The removal efficiencies of DMS increase with an increase in peak voltage at a fixed frequency (Fig.2a). The removal efficiency of DMS can be calculated as

$$\eta = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100\% , \quad (1)$$

where η is removal efficiency of DMS (%), C_{in} is DMS concentration of input (mg/m^3), C_{out} is DMS concentration of output (mg/m^3).

As the voltage increases, the electric field between electrodes enhances. Therefore, electrons are produced and energized more easily by electric field, which accelerate electron avalanche (Nifuku *et al.*, 1997). When the energy of electrons is more than the activation energy of DMS, the bonds of DMS will be broken and it converted into different substances. Meanwhile, more active species, such as O, OH, HO_2, O_3, are produced at higher voltages. The active species play an important role in the decomposition of polluting gases and volatility organic compounds (VOCs) (Yamamoto *et al.*, 1992; Huang *et al.*, 2001). Taking the pulse frequency fixed at 100 pps (pulse per second) as example, the removal efficiency increases from 16% to 100% when the peak voltage rises from 14 kV to 33 kV. Therefore, DMS can be decomposed completely if the peak voltage is high enough. When the peak voltage is close to 44 kV, the spark discharge happens, and the removal efficiency lowers. Energy flows away with the sudden accretion of current at that point.

Pulse frequency

Three pulse frequencies (100, 200 and 300 pps) were studied in this experiment. Fig.2a shows that an increase in pulse frequency would increase the removal efficiency. The higher the pulse frequency, the higher the power injected into the reactor, and the more high-energy electrons and active species are produced. When the peak voltage is fixed at 22 kV, the removal efficiencies of DMS at 100, 200 and 300 pps are 32.4%, 61.9% and 78.3%, respectively. However, a high pulse frequency also leads to thermal waste according to our previous study (Ruan *et al.*, 2005). The temperature of the exhaust gas rises with the increase of pulse frequency. Thus, the discharge power is restricted because some ions are being accelerated in the strong electric field, and the discharge power cannot be effectively utilized to decompose DMS. Energy yield (EY) is calculated to evaluate the efficiency of energy utilization at different pulse frequencies.

$$P_{\text{T}}=cV^2f/2, \quad (2)$$

$$SED=P_{\text{T}}/Q, \quad (3)$$

$$EY=\text{C}\eta/SED, \quad (4)$$

where P_{T} is the discharge power (W), c is the storage capacitance of the BPFN (F), V is the charge voltage (V), f is the pulse frequency (pps), SED is the specific energy density (kJ/m^3), Q is the gas flow rate (m^3/h), EY is the energy yield (mg/kJ), C is the DMS initial concentration (mg/m^3), and η is the removal efficiency (%).

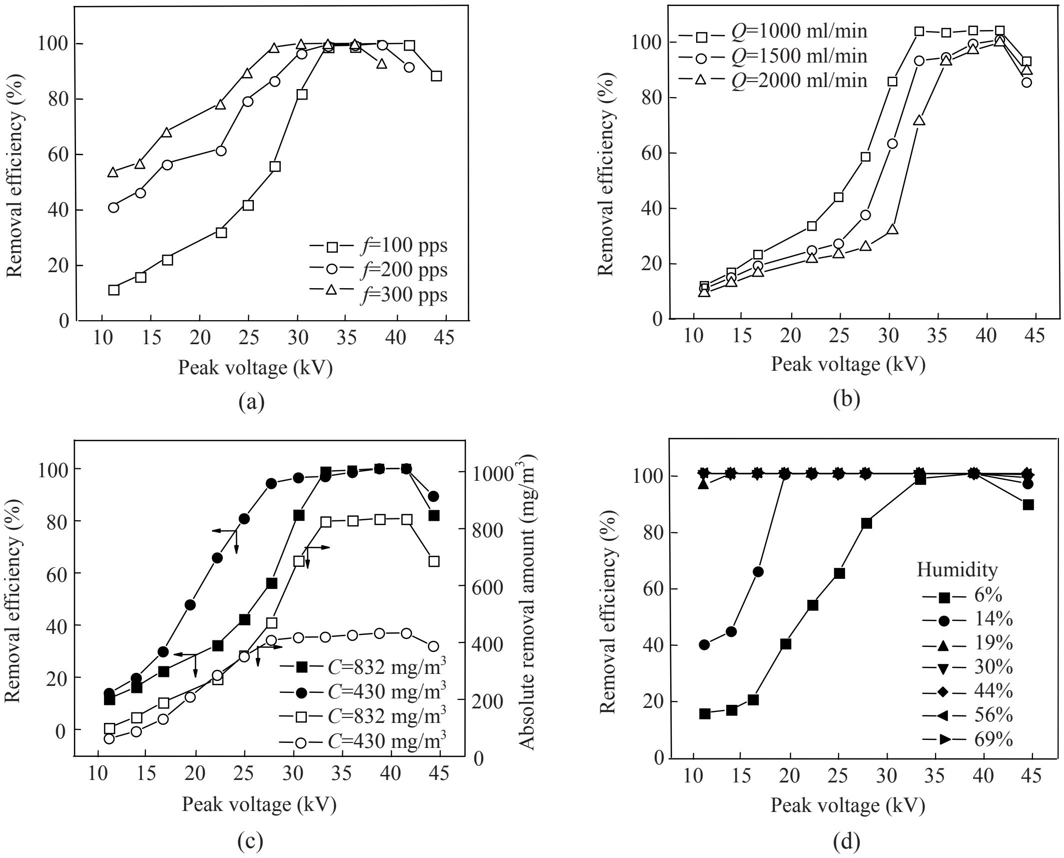
The removal efficiencies of DMS at different pulse frequencies can all reach 100%. However, the EY decreases with the increase of the pulse frequency. It drops from 0.183 to 0.116 mg/kJ when the pulse frequency increases from 100 to 200 pps. And the worst energy utilization occurring at 300 pps is 0.106 mg/kJ. The phenomenon can be attributed to the increase of heat loss at higher pulse frequency. Therefore, lower pulse frequency has advantages in EY as long as the pollutants can be decomposed completely. The pulse frequency is fixed at 100 pps with the rest of the experiments.

Gas flow rate (residence time)

Fig.2b shows the removal efficiencies of DMS at different gas flow rates are 1000, 1500 and 2000 ml/min. The residence time of gas flow in the reactor is 8.4, 5.6, and 4.2 s, respectively. At a fixed peak voltage, the removal efficiency decreases with increasing gas flow rate. When the gas flow rate is 1000 ml/min, the removal efficiency reaches 100% at 33 kV.

Initial concentration

The effect of initial concentration of DMS is shown in Fig.2c. The removal efficiency of DMS



(a) (b) (c) (d)

Fig.2 Effect of experimental parameter on the removal efficiency. (a) Pulse frequency and peak voltage (gas flow rate: 1000 ml/min; initial concentration: 906 mg/m^3); (b) Gas flow rate (pulse frequency: 100 Hz; initial concentration: 525 mg/m^3); (c) Initial concentration (pulse frequency: 100 Hz; gas flow rate: 1000 ml/min); (d) Humidity (temperature: 25 °C; pulse frequency: 100 pps; flow gas: 1000 ml/min; initial concentration: 832 mg/m^3)

decreases with the increase of its initial concentration at a fixed peak voltage, but the absolute removal amount increases. The number of DMS molecules increases with increasing initial concentration. However, the input power in the corona reactor did not increase accordingly, which led to the decrease in the removal efficiency. Table 1 indicates that the EY increases with the enhancement of the initial concentration. That is why the absolute removal amount increases.

Table 1 Comparisons of the absolute removal amount and *EY* at different initial concentration

C (mg/m^3)	η (%)	ΔC (mg/m^3)	EY (mg/kJ)
430	96.5	415.0	0.189
832	82.4	685.4	0.312

Note: pulse frequency: 100 pps; gas flow rate: 1000 ml/min; initial concentration: 832 mg/m^3; peak voltage: 30 kV

Humidity

Tests were conducted to determine the effect of humidity on DMS removal in air. It is found that DMS removal efficiency increased with an increase in relative humidity. Fig.2d shows the removal efficiency of DMS reaches 100% at 38.5 kV when the relative humidity is 6%. At 19.25 kV, DMS can be decomposed completely as the humidity is 14%. This phenomenon indicates that water plays a very important role in the reaction. Water is decomposed in the plasma to release OH radicals and hydrogen atoms. Energetically, the decomposition of the OH radical is also possible due to its weaker O-H bond (4.4 eV) compared with that of water (5.1 eV). The initiating reactions involving the H_2O excitation are given in the following reactions Eqs.(5)~(6):

$$H_2O+e \rightarrow H+OH+e, \quad (5)$$

$$H+O_2 \rightarrow HO_2. \quad (6)$$

When the humidity is high, more H_2O molecules collide with high-energy electrons to form OH radicals, resulting in a higher removal efficiency. Some studies believed that low humidity boosted VOC decomposition but high humidity had an adverse effect on VOC decomposition due to its electrone- gative characteristics (Guo *et al.*, 2006). Increasing humidity consumed a quantity of high-energy electrons in system but produced a number of activated chemical species. The activation energy of C-S bonds in DMS (2.9 eV) is smaller than that of C-C bonds in toluene (4.4 eV) according to Guo *et al.*(2006). The activated chemical species that had less contribution to toluene decomposition could react with DMS more easily and effectively. Therefore, the higher the humidity, the higher the removal efficiency of DMS, within the range of experiment condition (relative humidity: 6%~69%). Table 2 shows the EY increases with an increase in relative humidity. When the relative humidity is greater than 30%, the highest EY of 2.87 mg/kJ can be obtained.

Table 2 Comparison of the *EY* at different relative humidity

Relative humidity (%)	Peak voltage (kV)	*EY* (mg/kJ)
6	38.5	0.04
14	22	0.29
19	13.5	1.76
30	11	2.87
44	11	2.87
56	11	2.87
69	11	2.87

Note: removal efficiency: 100%; pulse frequency: 100 pps; gas flow rate: 1000 ml/min; initial concentration: 832 mg/m^3

Product analysis

Identifying the by-products during decomposition of DMS in air is one of the most important issues for the plasma chemical processes. In the cases of DMS removal, nitrogen oxides, ozone, sulfur dioxide, carbon dioxide, and carbon monoxide were all observed by Fourier Transform Infrared (FTIR). Moreover, some sulfur was also discovered adhering to the corona wires.

Fig.3 shows the effect of DMS decomposition on the concentration of ozone. The concentration of ozone decreased with the existence of DMS. Thus, the experimental results indicate that the DMS can react with ozone.

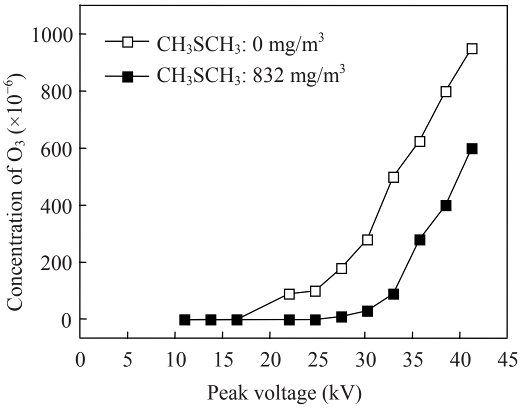


Fig.3 DMS decomposition on the concentration of ozone

Many studies consider that the chemical reaction in the pulse corona reactor starts with dissociation of oxygen, nitrogen and water vapor by high-energy electrons impact to air molecules. The possible reactions of ozone and nitrogen oxides generation in a corona discharge are as follows (Kim *et al.*, 2001; Kogoma *et al.*, 2001; Ruan *et al.*, 2005):

$$O_2+e \rightarrow 2O+e, \quad (7)$$

$$N_2+e \rightarrow 2N+e\ , \quad (8)$$

$$H_2O+e \rightarrow OH+H+e, \quad (9)$$

$$O+O_2+M \rightarrow O_3+M\ (M=O_2 \text{ or } N_2), \quad (10)$$

$$N+O_2 \rightarrow NO+O, \quad (11)$$

$$N+OH \rightarrow NO+H, \quad (12)$$

$$NO+nO \rightarrow NO_x, \quad (13)$$

$$N+NO_2 \rightarrow N_2O+O. \quad (14)$$

Research on the decomposition mechanisms of DMS is scarce. Based on the analysis of the products and some papers (Tsai *et al.*, 2003), the possible reactions of DMS decomposition are as follows:

$$CH_3SCH_3+O+e+M \rightarrow H_3S+CH_3SO+CH_3+e+M\ (M=O_2 \text{ or } N_2), \quad (15)$$

$$CH_3+O\ (O_2 \text{ or } O_3) \rightarrow CO+CO_2+H_2O, \quad (16)$$

$$CH_3S+O\ (O_2 \text{ or } O_3) \rightarrow CO+CO_2+H_2O+SO_2+S, \quad (17)$$

$$CH_3SO+O\ (O_2 \text{ or } O_3) \rightarrow CO+CO_2+H_2O+SO_2. \quad (18)$$

The byproducts can be harmful for human and pollute the air when the ozone, nitrogen oxides and sulfur dioxide are produced in the reactor and exhausted to the atmosphere. Some literature has reported that activated carbon fiber and catalyst are effective in the removal of these pollutants (Yoshida *et al*., 1989; Mochida *et al*., 2000; Futamura *et al*., 2002). Therefore, these products can be removed.

CONCLUSION

The experiments show that odor gas DMS can be removed effectively by pulse corona discharge. Almost 100% removal efficiency was obtained for the air containing 832 mg/m^3 DMS with the gas flow rate of 1000 ml/min. The optimum pulse frequency is 100 pps.

Humidity boosts removal efficiency and improves EY greatly. The EY of 832 mg/m^3 DMS was 2.87 mg/kJ when the relative humidity was above 30%.

In the case of DMS removal, ozone and nitrogen oxides were observed in the exhaust gas. The carbon and sulfur elements of DMS were mainly converted to carbon dioxide, carbon monoxide and sulfur dioxide. Moreover, sulfur was discovered in the reactor.

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