Humidity and Oxygen Effects on Dimethyl Sulfide Decomposition Plasma Corona Reactor

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Abstract: The influence of humidity and oxygen on decomposition of dimethyl sulfide (DMS) was investigated experimentally by a wire-cylinder pulse corona reactor at room temperature. The DMS decomposition efficiency was investigated using varying oxygen concentration (0.6%-21.0%), humidity (0%-1.0%) and different balance gas (air, N_2, Ar). DMS conversion in Ar is more efficient than that in N_2 and air at a fixed peak voltage. In addition, it is found that 5% oxygen is the optimum concentration in decomposition of DMS, due to higher conversion of DMS and relatively fewer yields of by products, such as O_3, NO_x and SO_2. The highest DMS removal efficiency was achieved with the gas stream containing 0.3% H_2O in air.

Keywords: Pulse corona discharge, Blumlein pulse forming network, Energy yield, humidity, oxygen concentration

1 INTRODUCTION

Gaseous sulfide compounds are a typical of malodorants that are related to endangering respiratory system and have the potential of further formation of more toxic compounds under certain conditions due to the sulfide contained in the compounds. Therefore, it is necessary to decompose them before exhausting into the air.

The industries involved in olfactory nuisances, i.e., agribusiness, oil refineries, wood, chemical, plastic, and metallurgical industries, pulp mills, sewage and waste treatment plants, attempt to control their emissions. Many refinement processes nowadays are employed to control volatile organic compound (VOC) air pollutants [1-3]. However, most of them are not fitted for decomposition of gaseous sulfide compounds due to their low concentration and low olfactory detection threshold. Therefore, it is necessary to develop state-of-the-art control equipment for gaseous sulfide compounds.

Non-thermal plasma (NTP) techniques have great industrial potential for its relatively low power consumption and high removal efficiency. In recent years, NTP technology has been applied to the decomposition of odor [1, 4-11]. Our previous researches have also shown that the odors can be treated effectively in the wire-plate corona reactor by BPFN type of narrow pulse generator [12-15].

While the work done to date shows promise, many questions remain unanswered. For practical applications, the influence of balance gas mixture on the non-thermal plasma technique should be considered. Some researches on the influence of oxygen concentration and humidity have been reported for various types of VOCs [16-20]. In this study, the influence of various balance gas mixture, including various humidity and oxygen concentration, on the plasma decomposition of DMS in a wire-cylinder DBD reactor was investigated. A high pulse voltage source with a thyratron switch and a Blumlein pulse-forming network (BPFN) was used in our experiments. Detailed experiments were carried out with a focus on DMS decomposition efficiency as well as energy yield using varying humidity and different balance gas (air, N_2, Ar). The influence of oxygen concentration on both DMS decomposition efficiency and products was investigated. In addition, the breakdown voltages of DMS in N_2 and Ar under various gas pressures were studied.

2 EXPERIMENTAL SECTION

A schematic diagram of the experimental setup is shown in Fig. 1. 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 divides into three streams through Teflon tubes. A set of mass flow controls is used to regulate the flow rates of the streams. One stream passes through the DMS generator that is kept in a water bath (T=25±1 □), then is balanced with DMS vapor. Moisture is added to the gas by bubbling the sample gas through a small-volume water bath. Then the two streams are mixed with the large-rate stream in the buffer tank. At last, the mixed stream is introduced to the corona reactor. The arrow shows the gas-flow line. Sampling ports of the simulated gas are located at the inlet and the outlet of the reactor.

A wire-cylinder DBD reactor was adopted for the experiment. The outside part of the reactor was made of epoxy resin. A ceramic tube made of alumina was 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 a film conductor out of aluminum and embedded between the epoxy resin tube and ceramic tube. The corona electrode was of Ni-Cr alloy wire that was 0.5 mm in diameter. The effective volume of the reactor was 143000 mm^3 (45 mm in inner diameter and 90 mm in length).

A BPFN type of narrow pulse generator was used in our experiments [13]. The pulse voltage and current waveforms were measured by using a four channel Tektronix TDS 2014B 350 MHz digital storage oscilloscope capable of sampling 1

GS s^{-1}, a Texas HVP-3020 high voltage passive probe and a CT4 TCP202 current probe.

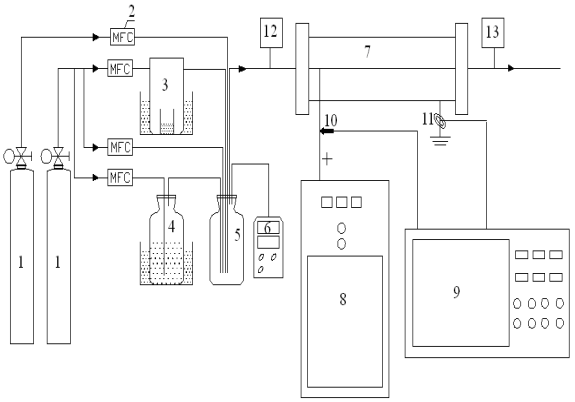

Fig. 1 Schematic diagram of the experimental setup 1.gas cylinder 2.mass flow control 3.DMS generator 4.water vapor generator 5.buffer tank 6.moisture detector 7.wire-cylinder DBD reactor 8.high pulse voltage source 9.digital storage oscilloscope 10.high voltage probe 11.current probe 12.sampling of inlet 13.sampling of outlet.

The concentrations of DMS were measured by the gas chromatograph GC7890II (Tianmei corporation). The products were analyzed by using the FTIR EQ55 (Bruker corporation, Germany). The concentrations of sulfur dioxide, ozone and nitrogen oxides were measured by the gas indicator tubes (Sanhuan corporation), and the minimum detectable limits (MDLs) of which were 0.2 $mg \cdot m^{-3}$, 0.2 ppm and 0.5 $mg \cdot m^{-3}$, respectively.

3 RESULTS AND DISCUSSION

3.1 Influence of Humidity on Decomposition of DMS

Tests are conducted to determine the effect of humidity on DMS removal in air. It is found in Fig. 2 that DMS removal efficiency is promoted as the humidity increases from 0% to 0.3% and decreases when the humidity is greater than 0.3%. It also shows that humidity has more effect on conversion of DMS under a low peak voltage (< 25kV) than that does under a high peak voltage (> 25 kV). The DMS can be decomposed completely at any humidity when the peak voltage is above 35 kV.

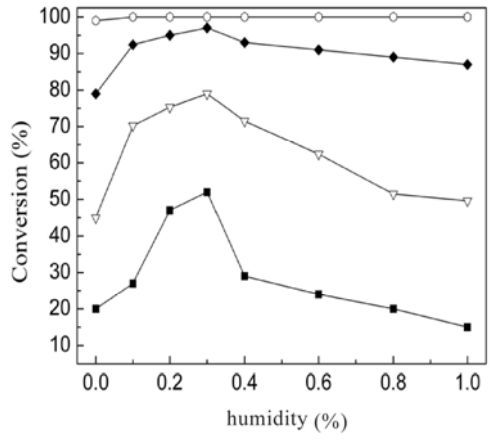

Fig. 2 Effect of humidity on DMS decomposition. Gas flow rate, 1000 ml min^{-1}; Initial concentration, 832 $mg \cdot m^{-3}$ (■ is under the peak voltage of 15 kV, ▽ is under the peak voltage of 25 kV, ◆ is under the peak voltage of 30 kV, ○ is under the peak voltage of 35 kV)

The phenomenon shows that water molecule plays a very important role in the reaction. Water can be decomposed inside the plasma to give ·OH radicals and hydrogen atoms. Energetically, the decomposition of the ·OH radical is also possible due to the weaker strength of its O-H bond (4.4 eV) compared to that of water (5.1 eV). The initiating reactions involving the H_2O excitation are given in reaction 4-5.

$$H_2O + e \rightarrow \cdot H + \cdot OH + e \quad (1)$$

$$\cdot H + O_2 \rightarrow \cdot HO_2 \quad (2)$$

When the humidity is high, part of H_2O molecules collide with high-energy electrons and form ·OH radicals, resulting in higher removal efficiency. However, water also has an adverse effect on DMS removal due to its electronegative characteristics. Increasing the humidity limits the electron density in the system and quenches the activated chemical species. Guo and Ye reported the optimum humidity in toluene decomposition was 0.2% [22]. While the experiments in this research illustrate that the humidity of 0.3% in balance gas by volume promotes DMS decomposition most. It can be explained that 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). The activated chemical species formed from H_2O, such as ·OH, has less contribution to toluene decomposition, but can react with DMS more easily and more effectively. Therefore, the DMS decomposition is still promoted at the humidity of 0.3% at which the conversion of toluene starts to decrease.

3.2 Decomposition of DMS in O_2/N_2

The decomposition of DMS is also carried out under various oxygen concentrations. Oxygen content varies from 0% to 21% by volume. The initial concentration of DMS is 832 $mg \cdot m^{-3}$, and the gas flow rate is 1000 $ml \cdot min^{-1}$. Fig. 3 shows the relationship between the conversion of DMS and the concentration of O_2. The results show that the maximum decompositions of DMS are found at the O_2 concentration of 5% by volume for all tested peak voltages. When the oxygen content is 5 % and the peak voltage reaches 38.5 kV, the DMS removal efficiency of 99.4% is achieved. Snyder found that the optimum O_2 concentration was 3% when using a dielectric barrier corona reactor for decomposition of chlorobenzene in an O_2/N_2 mixture [23]. The similar results for the removal of benzene and toluene were also verified by Ogata [16] and very recently by Ye [20], respectively.

Concerning the reason for the influence of O_2 in plasma system, it has been reported that long-lived active oxygen species and ozone play an important role in the decomposition of benzene in a pulse corona reactor [23]. In order to

investigate the role of ozone in our case, DMS with ozone was injected downstream of the corona reactor without discharge. Ozone was produced by an ICAN CFY-3 ozone generator. When the initial concentration of DMS was 832 $mg \cdot m^{-3}$ with 1200 $mg \cdot m^{-3}$ of ozone, the conversation of DMS reached to 70%. Thus, the experimental results indicate that the DMS can react with ozone easily.

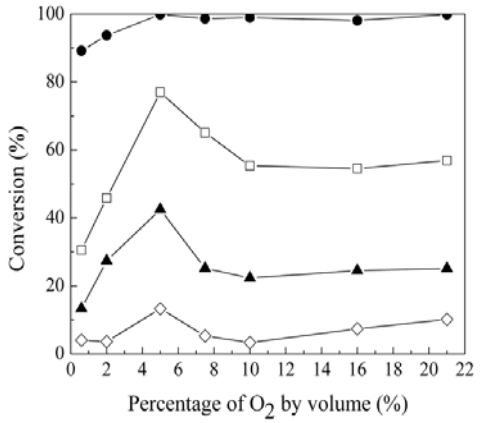

Fig. 3 Decomposition of DMS in O_2/N_2. Gas flow rate: 1000 $ml \cdot min^{-1}$; initial concentration: 832 $mg \cdot m^{-3}$. (□: 11 kV; ▲: 22 kV; □: 33 kV; ●: 38 kV)

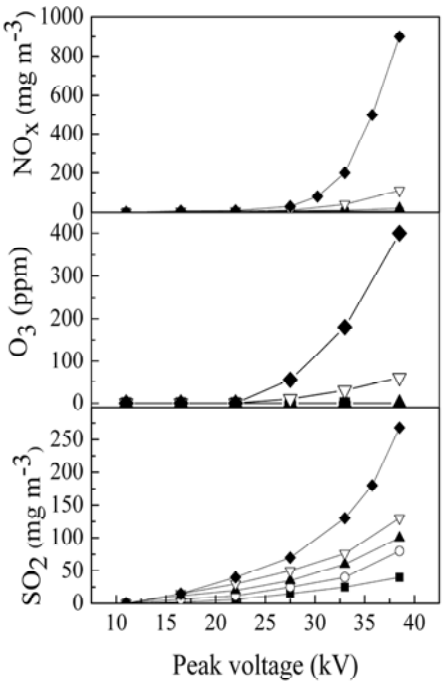

Fig. 4 Effect of O_2 concentration on the yield of O_3, NO_x and SO_2. Gas flow rate, 1000 $ml \cdot min^{-1}$; initial concentration, 832 $mg \cdot m^{-3}$. (◆: 21 □; ▽: 10 □; ▲: 5%; ○: 2%; ■: 0.6%)

What interesting is that when the concentration of O_2 is higher then 5 %, the conversion efficiency of DMS decreases slightly. It is due to oxygen's electron negative characteristics. A large number of high energy electrons will impact the increasing oxygen molecules. Therefore, increasing oxygen content will limit electron density in the system and reduce the power deposited into the plasmas. As a result, appropriate oxygen content is essential for DMS destruction. However, the real reason should be studied further in the next research.

3.3 Influence of Oxygen Concentration on Product

In our cases of DMS removal, nitrogen oxides, ozone, sulfur dioxide, carbon dioxide and carbon monoxide were all observed by FTIR. Although the amounts of ozone, nitrogen oxides and sulfur dioxide are little, they are hazardous to humans and ambient atmosphere. Therefore, quantifying the products during decomposition of DMS is one of the most important issues for the plasma chemical processes.

The yield of O_3, NO_x and SO_2 are shown in Fig. 4 when the concentration of O_2 varies from 0% to 21% by volume. When the peak voltage is 38.5 kV and the concentration of O_2 varies from 0% to 21%, both the concentration of O_3 and NO_x increase dramatically. Meanwhile, the yield of SO_2 increases with the increase of the concentration of O_2 in influents. The conclusion drawn from Fig. 6 suggests that 5% O_2 induced relatively higher conversion of DMS. Concurrently, the yield of O_3, NO_x and SO_2 are relatively low, 0 ppm, 20 $mg \cdot m^{-3}$ and 100 $mg \cdot m^{-3}$, respectively, under the peak voltage of 38.5 kV when O_2 concentration was 5%. Therefore, 5% oxygen is the optimum concentration in this study of decomposition of DMS.

4 CONCLUSIONS

On the basis of the present experimental results, it can be summarized that balance gas mixture has various influence on decomposition of dimethyl sulfide in a wire-cylinder pulse corona reactor. Breakdown voltage of DMS in Ar is lower than that of DMS in N_2, both of which are proportional to the gas pressures. The maximum decomposition of DMS is found in Ar comparing with in N_2 and air at a fixed peak voltage. 5% oxygen is the optimum concentration in decomposition of DMS, due to relatively higher conversion of DMS and fewer yields of O_3, NO_x and SO_2. The highest DMS removal efficiency is achieved with the gas stream containing 0.3% H_2O in air.

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