Dielectric Barrier Discharge for Hydrogen Sulphide Waste Gas Decomposition

He Xianjun, Feng Fada*, Fu Yunqing, Wang Fushan and Zhang Fengru*

School of Chemistry and Environment, Jiaying University, Meizhou, Guangdong, 514015, China

*Corresponding author’s e-mail: fadafeng@jyu.edu.cn, zhangfengru@126.com

Abstract. Non-thermal plasma is considered to be a suitable treatment technology for H₂S waste gas pollution, but it still need to improve the energy efficiency. This work proposed a cylindrical DBD reactor used for H₂S decomposition. Performance of the reactor is evaluated by O₃ generation and H₂S removal. The results show that the DBD can produce O₃ with high efficiency at high specific input energy or low humidity. With regard to the energy yield of ozone generation, the G-value is about 2.29 molecules (100 eV)-1 at the relative humidity of 18%. The H₂S removal efficiency increases as the specific input energy increases, but a high humidity can reduce the H₂S decomposition. The H₂S with the concentration of 8 mg m⁻³ can be 100% removed at the specific input energy of 4.5 J L⁻¹, but for ozone used only, 65% removal efficiency can be realized at the ozone concentration of 65 mg m⁻³. It is can be concluded that, in addition to the ozone, other active species such as electron, ions and free radicals also play an important role in the degradation of H₂S.

1. Introduction

Plasma is characterized by the existence of electrons, ions, radicals, and excited atoms in mixture with the other neutral molecules of gas system. It can be generated by the input of energy which consists of thermal, electric field, electrons, UV photons, lasers, and radiation[1]. The electric field is the most important method to produce plasma in the application of pollution control. The plasma generated by the dielectric barrier discharge (DBD) and corona discharge has been widely used for waste gas treatment[2]. In the plasma, the energy of electron can be as high as 1-20 eV, so that the reaction processes that require extremely high activation energy can be easily realized[3]. The non-plasma technology is considered to be one of the promising technologies for waste gas pollution control.

Malodorous gas is involved with any gas that produces unpleasant feelings or unendurable odor and damages the environment of human life. It comes from a wide range of sources which include daily life, animal husbandry, and municipal facilities[4]. Malodorous can lead to health damage caused by indirectly affects or direct olfactory stimulation the system of human body[5]. The odor is the most complex of all the environmental pollution problem. Hydrogen sulphide (H₂S) is a common malodorous gas that produced from animals, industrial, and natural sources, especially slaughterhouses, meat processing plants, and waste treatment plants[4]. The odor threshold value of H₂S is about 7.6×10⁻⁴ mg m⁻³, so extremely low concentration of H₂S is enough to generate a strong odor[6]. Traditional treatment methods of H₂S are mainly chemical, physical and biological methods, including absorption, adsorption, and biological filtration[4]. For these methods, there are still some problems such as high energy consumption, secondary pollution and unstable treatment efficiency. For the past decades, plasma for odors treatment has been widely concerned[7]. Plasma and plasma combined with
catalysis or photolysis are used for H$_2$S decomposition[8-10], however, the energy density consumed is still relatively high[11], so it is necessary to improve the energy efficiency of the plasma reactor.

In the present research, characteristics of a cylindrical DBD reactor with quartz dielectric is discussed. The O$_3$ production and H$_2$S decomposition in the reactor is studied by the factors of specific input energy, gas flow and humidity. Compared of O$_3$ oxidation, decomposition of low concentration H$_2$S in the DBD process is evaluated.

2. Experimental section

Figure 1 shows the schematic diagram of experimental setup used in this work, in which the system can be regarded as the simulate H$_2$S generation, DBD reactor, and analysis part with several measurement instruments. The H$_2$S mixed with certain amount of air as simulate waste gas. The humidity was regulated by the air flow into bottle placed water. For H$_2$S removal, the initial concentration of H$_2$S is about 8 mg m$^{-3}$, and the total gas flow rate is 1 to 5 L min$^{-1}$ as the experiment needs. At the end, the sodium hydroxide solution placed in the bottle is used to absorb the H$_2$S. A DBD reactor with a quartz tube of around 22 mm inner diameter and 40 mm length wrapped in a grounded electrode made of stainless-steel mesh, and a stainless-steel high voltage electrode of around 20 mm diameter. And the DBD reactor is powered by a 50 Hz AC high voltage power source. The total discharge volume is about 2.64 cm$^3$.

The applied voltage on the DBD reactor is monitored by a digital oscilloscope (DS1102E, Rigol, China) with a voltage probe (P5104, Tektronix, USA). The discharge power of the DBD reactor is monitored by V-Q Lissajous method, and the measurement circuit is detailed described in our previous works[12]. The concentration of O$_3$ and H$_2$S in the gas are measured by an ozone monitor (UV-100, Eco, USA) and a multi-gas monitor (MultiRAE, RAE, USA), respectively. The temperature and humidity are measured by a hygrothermograph (RS232, Center, China).

![Figure 1. Schematic diagram of experimental setup.](image)

The SIE, H$_2$S removal efficiency ($\eta$), and energy yield (EY) of by the following equations.

$$\text{SIE (J L}^{-1}) = \frac{\text{discharge power (W)\times 60}}{\text{gas flow rate (L min}^{-1})}$$  \hspace{1cm} (1)

$$\eta = \frac{[\text{H}_2\text{S}]_{\text{in}}-[\text{H}_2\text{S}]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}} \times 100\%$$  \hspace{1cm} (2)

$$\text{EY (g kWh}^{-1}) = \frac{3.6 \times ([\text{H}_2\text{S}]_{\text{in}}-[\text{H}_2\text{S}]_{\text{out}})}{\text{SIE}}$$  \hspace{1cm} (3)

Where, $[\text{H}_2\text{S}]_{\text{in}}$ and $[\text{H}_2\text{S}]_{\text{out}}$ are the H$_2$S concentration in the inlet and outlet (mg m$^{-3}$), respectively.

3. Results and discussion

3.1. Characteristics of DBD reactor

Figure 2 shows a typical Lissajous Q–V figure of the DBD reactor. Based on the Lissajous figure, the dielectric capacitance ($C_d$), the capacitance (C) of the DBD reactor, the discharge voltage across air...
gap ($U_{\text{dis}}$), and the minimal external voltage required to maintain the discharge ($U_{\text{min}}$) is 68 pF, 12 pF, 5.8 kV, and 6.8 kV, respectively. The discharge power of DBD reactor can be calculated with surface area of the V-Q parallelogram. Figure 3 shows the effects of applied voltage ($V_{p-p}$) on the discharge power of the DBD reactor. The discharge power is linear with the applied voltage. At the applied voltage of about 13 kV and 25 kV, the discharge power of the DBD reactor is 0.0156 W and 0.457 W, respectively. Actually, the microdischarges can be observed clearly between the gas gap of dielectric and high voltage electrode at the applied voltage of 18 kV.

Figure 2. Typical Lissajous Q-V figure of the DBD reactor.

Figure 3. Effects of applied voltage on the discharge power of the DBD reactor.

3.2. DBD induced O$_3$ generation

Figure 4 shows the effects of SIE on ozone generation with different gas flow. The ozone concentration increases as the SIE increases. That is, for the same gas flow, the more the energy input, the more the amount of O$_3$ generated. Obviously, for ozone generation in the DBD reactor, the SIE plays a vital role. However, the gas flow has no significant direct effect on the ozone generation. In the DBD plasma process, O$_2$ in air can be decomposed by high energy electron, and the oxygen radical is produced simultaneously. And then the combination of O$_2$ molecules and oxygen radical produces O$_3$. The fundamental reactions can be expressed by the following equations[13]:

\[
\text{O radical production: } O_2 + e \rightarrow O + O + e \quad (4)
\]
\[
\text{O}_3 \text{ generation: } O_2 + O + M \rightarrow O_3 + M \quad (5)
\]

Where M refers to oxygen and nitrogen in air.

According to the energy yield or so-called G-value, G(O$_3$) can be approximately expressed by the following equations[13]:

\[
[O_3]_p = 2.5G(O_3)^{\varepsilon} \quad (6)
\]

Where, G(O$_3$) is the G-values for ozone generation. Regarding to the ozone production, figure 5 re-plots the experimental data shown in figure 4 with the gas flow of 1 L min$^{-1}$. Based on the figure 5, the G(O$_3$) can be calculated about 2.29 molecules (100 eV)$^{-1}$.

Figure 6 shows the effects of relative humidity on O$_3$ generation. The humidity has a negative effect to the O$_3$ generation, for example, at the applied voltage of 24 kV, 396 mg m$^{-3}$ and 138 mg m$^{-3}$ O$_3$ generated at the relative humidity of 18% and 80%, respectively. As showed in the equations (7) and (8)[14], H$_2$O can be decomposed by high energy electron in the plasma process, and the H$_2$O can consume O generated in the equation (4) as well, so that the energy used for O$_3$ generation decreased.

\[
\text{H}_2\text{O} + e \rightarrow \text{H}^+ + \text{HO}^\cdot \quad (7)
\]
3.3. DBD induced H$_2$S decomposition

Figure 7 shows the effects of SIE on H$_2$S removal efficiency with different gas flow. The H$_2$S removal efficiency increases as the SIE increases with different gas flow. However, there is no significant difference of H$_2$S removal efficiency between gas flow of 1 L min$^{-1}$ and 3 L min$^{-1}$ which is agree well with the ozone generation mentioned before. For the gas flow of 5 L min$^{-1}$, the H$_2$S removal efficiency is relatively low because of the short residence time in DBD reactor. For the gas flow of 1 L min$^{-1}$, the energy yield of H$_2$S removal is about 6.4 g kWh$^{-1}$ at the SIE of 4.5 J L$^{-1}$.

Figure 8 shows the effects of SIE on H$_2$S removal efficiency with different relative humidity. The H$_2$S removal efficiency increases as the SIE increases. For the same SIE, the H$_2$S removal efficiency decreases as the humidity increases. For example, at the SIE of about 4.5 J L$^{-1}$, the H$_2$S can be removed completely at the humidity of 18%, which is much higher than that of relative humidity of 50% with removal efficiency of 32%. Moreover, for the humidity of 80%, little H$_2$S is removed when the SIE is less than 7.8 J L$^{-1}$. It is obviously that H$_2$O can reduce the H$_2$S decomposition in the plasma process. At the high humidity, most of the electrons generated in discharge can be captured by H$_2$O molecules. Besides, the H$_2$O can consume the energy which generates O$_3$. The mechanism for the H$_2$S decomposition by O$_3$ can be described as equations (9) and (10)[9]. The overall plasma chemical reaction of H$_2$S with high energy electron and active species is likely to be as equations (11)[15].

$$\text{H}_2\text{O} + \text{O} \rightarrow \text{HO} + \text{HO}^- \quad (8)$$

$$y = 5.732x \quad R^2 = 0.9976$$

$$\text{Humidity} \\ 18\% \quad 30\% \quad 50\% \quad 80\%$$

$$\text{O}_3 \text{ produced (mg m}^{-3}\text{)}$$

Applied voltage (kV)
H$_2$S + O$_3$ → SO$_2$ + H$_2$O \quad (9)

SO$_2$ + O$_3$ + H$_2$O → H$_2$SO$_4$ + O$_2$ \quad (10)

H$_2$S + e/O$_3$/HO$^•$/O$^•$ → ... → Final products \quad (11)

Figure 7. Effects of SIE on H$_2$S removal efficiency with different gas flow.

Figure 8. Effects of SIE on H$_2$S removal efficiency with different relative humidity.

Figure 9 shows the relationship between H$_2$S removal and O$_3$ concentration in the reactor with and without plasma process. For O$_3$ oxidation process, the O$_3$ is produced by an upstream ozonizer. The H$_2$S removal efficiency increases as the O$_3$ concentration in the reactor increases. For the plasma process, H$_2$S removal efficiency is almost 100% when the O$_3$ concentration is about 65 mg m$^{-3}$ at the SIE of 4.5 J L$^{-1}$, compared to the removal efficiency is about 65% with only O$_3$ oxidation. In this point of view, the ozone produced in DBD plays a critical role for H$_2$S decomposition. However, the high concentration of ozone is not enough to complete remove the H$_2$S, so the active species such as ions and free radicals produced in DBD process can play an important role for H$_2$S decomposition.

Figure 9. The relationship between H$_2$S removal and O$_3$ concentration with and without plasma.

4. Conclusions

The result shows that the plasma can be generated conveniently by the cylindrical DBD reactor with quartz dielectric. The DBD reactor has higher O$_3$ production efficiency at the condition of higher SIE or lower humidity. The DBD reactor has a high energy efficiency, and the G-value is about 2.29 molecules (100 eV)$^{-1}$ at the relative humidity of 18%. The H$_2$S removal efficiency increases as the SIE increases, and a higher humidity will lead to reduction of H$_2$S decomposition. For plasma process, the H$_2$S with the concentration of 8 mg m$^{-3}$ can be removed completely at the SIE of 4.5 J L$^{-1}$ with 65 mg
m⁻³ ozone concentration, but for the same concentration of ozone used alone to treat H₂S, only 65% removal efficiency can be realized. In addition to the ozone, other active species such as electron, ions and free radicals also play an important role in the degradation of H₂S.

Acknowledgments
This work is supported by the Natural Science Foundation of China (No. 21507043), Guangdong Natural Science Foundation (No. 2016A030307009, 2018A0303130089), Guangdong Undergraduate Innovation and Entrepreneurship Training Program (No. 201810582032S), Special Funds for the Cultivation of Guangdong College Students’ Scientific and Technological Innovation (“Climbing Program” Special Funds) (No. pdjh2018b0471), and Yangjiang Polytechnic Applied Technology Collaborative Innovation Center Project.

References
[1] Meichsner, J.U.R., Schmidt, M., Schneider, R., Wagner, H. (2012) Nonthermal plasma chemistry and physics. CRC Press, Boca Raton.
[2] Li, S., Huang, Y., Wang, F., Liu, J., Feng, F., Shen, X., Zheng, Q., Liu, Z., Wang, L., Yan, K. (2014) Fundamentals and Environmental Applications of Non-thermal Plasmas: Multi-pollutants Emission Control from Coal-Fired Flue Gas, Plasma Chem. Plasma Process., 34: 579-603.
[3] Winands, H., Yan, K., Nair, S.A., Pemen, G., van Heesch, B. (2005) Evaluation of corona plasma techniques for industrial applications: HPFF and DC/AC systems, Plasma Process. Polym., 2: 232-237.
[4] Feilberg, A., Sommer, S.G. (2013) Ammonia and Malodorous Gases: Sources and Abatement Technologies. In: Sommer, S.G., Christensen, M.L., Schmidt, T., Jensen, L.S. (Eds.), Animal Manure Recycling: Treatment and Management. Blackwell Science Publishing, Oxford. pp. 153-175.
[5] Dorman, D.C., Moulin, F., McManus, B.E., Mahle, K.C., James, R.A., Struve, M.F. (2002) Cytochrome oxidase inhibition induced by acute hydrogen sulfide inhalation: Correlation with tissue sulfide concentrations in the rat brain, liver, lung, and nasal epithelium, Toxicol. Sci., 65: 18-25.
[6] Xia, L., Gu, D., Tan, J., Dong, W., Hou, H. (2008) Photolysis of low concentration H₂S under UV/VUV irradiation emitted from microwave discharge electrodeless lamps, Chemosphere, 71: 1774-1780.
[7] Huang, L., Xia, L., Ge, X., Jing, H., Dong, W., Hou, H. (2012) Removal of H₂S from gas stream using combined plasma photolysis technique at atmospheric pressure, Chemosphere, 88: 229-234.
[8] Czernichowski, A. (1999) Plasmas for destruction of H₂S and mercaptans, Oil Gas Sci. Technol., 54: 337-355.
[9] Wang, X., Xu, K., Ma, Y., Ning, P., Cheng, C., Wang, L., Cheng, J. (2016) Simultaneous Removal of H₂S and Dust in the Tail Gas by DC Corona Plasma, Plasma Chem. Plasma P., 36: 1545-1558.
[10] Xuan, K., Zhu, X., Cai, Y., Tu, X. (2018) Plasma Oxidation of H₂S over Non-stoichiometric LaxMnO₃ Perovskite Catalysts in a Dielectric Barrier Discharge Reactor, Catalysts, 8: 317.
[11] Zhu, T., Wang, R., Bian, W., Chen, Y., Jing, W. (2018) Advanced oxidation technology for H₂S odor gas using non-thermal plasma, Plasma Sci. Technol., 20: 054007.
[12] Feng, F., Zheng, Y., Shen, X., Zheng, Q., Dai, S., Zhang, X., Huang, Y., Liu, Z., Yan, K. (2015) Characteristics of Back Corona Discharge in a Honeycomb Catalyst and Its Application for Treatment of Volatile Organic Compounds, Environ. Sci. Technol., 49: 6831-6837.
[13] Ye, L., Feng, F., Liu, J., Tang, X., Huang, Y., Liu, Z., Yan, K. (2014) Toluene Decomposition by a Two-stage Hybrid Plasma Catalyst System in Dry Air, IEEE T. Plasma Sci., 42: 3529-3538.
[14] Ma, H, Chen, P., Ruan, R. (2001) H₂S and NH₃ removal by silent discharge plasma and ozone combo-system, Plasma Chem. Plasma P., 21: 611-624.
[15] Zhang, H., Ji, T., Zhang, R., Hou, H. (2012) Destruction of H₂S Gas with a Combined Plasma Photolysis (CPP) Reactor, Plasma Sci. Technol., 14: 134-139.