

Research Progress of Low Temperature Plasma Technology to Treat Sulfur-containing Malodorous Gas

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Abstract. This paper briefly discusses the source, harm and removal methods of sulfur-containing malodorous gas. At this stage, the main methods for treating sulphur-containing malodorous gases are physical, chemical and biological methods. In contrast, low temperature plasma technology combines the advantages of physical, chemical and biological methods, and can effectively overcome the disadvantages of traditional processes. Through the comparison of various methods, the advantages of low temperature plasma treatment of sulfur-containing malodorous gas are summarized, and the corresponding removal mechanism is proposed. The treatment progress and existing problems of using low-temperature plasma to remove sulfur-containing malodorous gas, especially hydrogen sulfide, carbon disulfide, methyl sulfide, methyl mercaptan and dimethyl disulfide, are comprehensively discussed. A new idea for the simultaneous removal of multi-component sulfur-containing malodorous gas by low temperature plasma is proposed. Compared with traditional methods, low temperature plasma technology has the advantages of simple process, strong applicability, easy operation, and low energy consumption in processing sulfur-containing malodorous gases. The treatment of sulfur-containing malodorous gas by low-temperature plasma technology needs further research.

1 Introduction

The direct emission of malodorous gas will not only endanger human health, but also pose a serious threat to the surrounding environment. It is mainly through the odor group such as sulfur, carbonyl group to stimulate olfactory cells[1-2]. Among many odorous gases, sulfur-containing odorous gases are the most typical ones. According to Chinese regulations, there are 8 kinds of malodorous gases to be restricted, and 5 kinds of sulfur compounds. Sulfur-containing malodorous gases come from a wide range of sources, mainly from the corruption of animals and plants in the natural ecological environment, petroleum processing, various chemical production, storage and transportation processes. Under normal circumstances, the olfactory threshold of human smell for most malodorous substances is below 10^{-9} , which far exceeds the minimum detection concentration of malodorous substances by analytical instruments and the allowable emission concentration of the factory. At this stage, the main methods for treating sulphur-containing malodorous gases are physical, chemical and biological methods, as shown in Table 1. With the rapid development of science and technology, low temperature plasma technology came into being. In contrast, low temperature plasma technology combines the advantages of physical, chemical and biological methods, and can effectively overcome the disadvantages of traditional processes.

Table 1. The comparison of differednt methods to deal with sulfide odors.

	advantages	disadvantages
Physical and chemical methods	High concentration and high efficiency	Incomplete purification, high investment cost, complicated operation, high energy consumption, secondary pollution, etc.
Biological methods	Wide application range, simple equipment, little secondary pollution, low energy consumption, etc.	Slow speed, large area, unstable processing efficiency, etc.

2 The mechanism of action

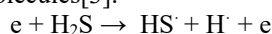
Low temperature plasma can be divided into glow discharge, corona discharge, dielectric barrier discharge, radio frequency discharge and microwave discharge according to different discharge methods. Although the forms of discharge are not the same, the mechanism of low-temperature plasma is similar. It can be expressed as that electrons obtain energy from the electric field. They move at extremely high speed in the electric field and collide with molecules during the movement. In one case, it acts directly with polluting gas, so that polluting gas

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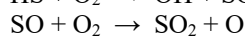
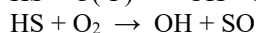
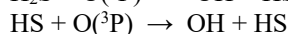
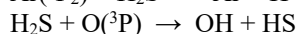
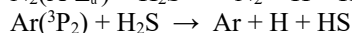
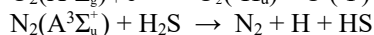
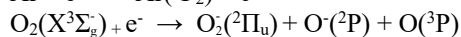
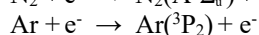
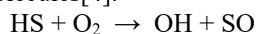
obtains energy and is excited, and is ionized and converted into other substances for removal. In the other case, other gas molecules are ionized to produce active ions. Due to the strong reactivity of the generated active ions, they interact with the polluted gas and convert the polluted gas into other substances.

The mechanism of removing sulphur-containing odorous gas by low temperature plasma is complex. Taking H₂S as an example, based on domestic and foreign research on the degradation of H₂S by low-temperature plasma, it is currently believed that there are two main degradation pathways for H₂S.

- High-energy electrons directly act on H₂S gas molecules[3].



- High-energy electrons act on the intermediate active material. These electron-excited active substances and free radicals act on sulfur-containing odorous gas molecules or on the intermediate products of the decomposition of sulfur-containing odorous gas molecules[4].



The purification mechanism of low-temperature plasma degradation of sulfur-containing waste gas is far from a clear understanding.

3 Treatment of single-component sulfur-containing malodorous gas

3.1 H₂S

As the most common component in malodorous gas, H₂S has always been the focus of research on the removal of malodorous gas by low-temperature plasma. Techniques for H₂S degradation by various discharge modes have been developed, as well as plasma and other combined removal techniques.

The decomposition of H₂S to produce hydrogen is one of the main methods for treating hydrogen sulfide by plasma. Reddy et al.[5] use dielectric barrier discharge to decompose H₂S for hydrogen production. They investigated the effects of ground electrode material, discharge gap, dwell time, and H₂S concentration on decomposition efficiency and hydrogen production energy consumption, and explored the kinetic process of H₂S decomposition by dielectric barrier discharge. It was found that the material of the grounding electrode had little effect on the decomposition efficiency, but the other factors had great influence on the decomposition efficiency. And the longer the residence time, the lower the H₂S concentration, and the higher the efficiency of H₂S conversion to H₂ and S. When the discharge gap is

3.5 mm, the residence time is 6.8 s, and the gas flow rate is 150mL/min, the energy consumption for hydrogen production can be reduced to 1.6eV/molecule at the lowest, but the conversion rate of H₂S is only 18% at this time. Although low energy consumption for hydrogen generation was achieved in this study, hydrogen production was relatively low, only 18%, and the whereabouts of sulfur elements and by-products of reaction were not paid attention to. Nunnaly et al.[6] used gliding arc plasma to degrade H₂S. By increasing O₂ content in the mixture, the energy consumption of hydrogen production can be reduced and the decomposition rate of H₂S can be improved without reducing H₂ production. When the flow rate of H₂S is 14L/min and the flow rate of O₂ is 2.8L/min, the minimum required SER for hydrogen production is 1.0 eV/molecule. The minimum SER required for H₂S decomposition is 0.43 eV/molecule, which is very close to the optimal value in the study of low-voltage micro-discharge.

In the study of H₂S removal from exhaust gas (especially low concentration H₂S), plasma technology or combined plasma technology is used to convert H₂S into a form that is less toxic, non-toxic or easier to be purified by other ways. Huang et al.[7] used the combined technology of dielectric barrier plasma and ultraviolet-vacuum ultraviolet rays to treat H₂S and convert H₂S into H₂O and SO₄²⁻. Studies have shown that factors such as Kr gas pressure, applied voltage, gas residence time, and H₂S inlet concentration significantly affect the removal efficiency of H₂S. When applied voltage is 7.5kV, retention time is 0.4s, inlet concentration is 27.1mg/m³, and Kr pressure is 47kPa, the removal efficiency of H₂S can reach 93%, and the main reaction products are H₂O and SO₄²⁻. The study only considered ultraviolet rays generated by the combination of Kr and Br₂, and did not further study the comparison of the combination of other rare gases and halogens, and failed to effectively use the H and S elements in the recovery of H₂S. Dang et al.[8] added metal oxide catalyst to dielectric barrier discharge plasma reactor, which can increase O₃ content in the reactor and improve H₂S treatment efficiency. Finally, H₂S is oxidized to S, H₂SO₃, and H₂SO₄. This study lacks catalyst selection conditions, preparation methods, and recycling plans, and does not pay attention to the whereabouts of H elements.

At present, the research direction of hydrogen sulfide removal by low temperature plasma technology is mainly focused on the decomposition of H₂S to produce hydrogen and the combination of plasma and other technologies, but most of the research is still in the experimental stage. The main research direction in the future is to further reduce the energy consumption required for decomposition and reduce the generation of secondary pollutants while improving the conversion rate of H₂S.

3.2 CS₂

CS₂ is an organic sulfur compound, which can be converted into H₂S and other substances under certain conditions. Because CS₂ may be accompanied by the generation of a variety of by-products in the different concentrations, it is more complex than H₂S removal. At present, some achievements have been made in the removal of CS₂, but there are still many problems to be further explored.

Yan et al.[9] used DC corona discharge plasma to treat CS₂. With the increase of input energy, the removal effect of CS₂ is obvious. When the input energy reaches 230J/L, the removal efficiency of CS₂ reaches 90%. It was found in the experiments that the short-term presence of active substances (free radicals) was more important than the long-term presence of active substances in the conversion process of CS₂.

Tsai et al.[10] used RF discharge plasma to decompose CS₂ into solid sulfur in the low-oxygen environment. There was no elemental sulfur formation in the absence of oxygen and in the oxygen-rich condition ($V(O_2)/V(CS_2) = 3$). When $V(O_2)/V(CS_2)=0.6$ and input power was 90W, 76.9% of CS₂ was converted into elemental sulfur.

In addition to corona and radio frequency discharge, plasma combined technology is also used in the treatment of CS₂. Zhu et al.[11] used the combined technology of dielectric barrier discharge low temperature plasma and MnO₂ catalyst to treat CS₂. The results showed that, under the combined action of DBD and MnO₂ catalyst, CS₂ is 10% more efficient than DBD alone. However, there is no difference between CS₂ products produced by the two methods, which both contain CO, CO₂, COS and SO₂. Fang et al.[28] designed a combined DBD plasma-photolysis technology to remove CS₂. This is 20% more efficient than DBD plasma alone. The main reason is that 207nm ultraviolet light produced by KrBr* excited by the discharge in the DBD reactor is absorbed and decomposed by SC₂.

3.3 Dimethyl sulfide

Dimethyl sulfide is a common organic sulfur odor pollutant. The decomposition products are mostly complex sulfides. Chen et al.[12] used micro-plasma to treat dimethyl sulfide with Ar gas as a carrier gas. The effects of residence time and electrode number on the degradation of dimethyl sulfide were investigated, and the main products were analyzed. The treatment efficiency of dimethyl sulfide with two pairs of electrodes is higher than that of a single pair of electrodes. Although a good purification effect has been achieved in the experiment, the energy consumption is too high and the by-products are too complex.

Chen et al.[13] used wire-barrel pulsed discharge plasma to treat dimethyl sulfide. The effects of different equilibrium gases, humidity, and oxygen content on the degradation of dimethyl sulfide were investigated. Experiments showed that the breakdown voltage of dimethyl sulfide in Ar atmosphere was lower than in N₂.

Moreover, the removal efficiency of methyl sulfide in Ar atmosphere was much higher than that of N₂ carrier gas.

Wei et al.[14] used biological drip filtration and plasma collective combination technology to treat methyl sulfide. In this method, methyl sulfide is oxidized to simple compounds such as methanol and COS, and the intermediate and methyl sulfide are oxidized to sulfate, water and CO₂ in the biological process without any other by-products. Chen et al.[15] degraded methyl sulfide by activated carbon adsorption and dielectric barrier discharge. It was found that in addition to adsorption, activated carbon also had a significant synergistic purification effect with plasma.

3.4 Methyl mercaptan

Methane mercaptan is a common organic sulfur malodorous gas in petroleum processing enterprises. However, there are few studies on the treatment of methyl mercaptan by low temperature plasma technology, and the progress is relatively slow. Li[16] treated methyl mercaptan in a plasma reactor with non-thermally strong medium. It was found that voltage relative to residence time and initial concentration had the greatest effect on the decomposition efficiency of methyl mercaptan.

Tsai et al.[17] mainly investigated the effect of O₂ content on the degradation of methyl mercaptan, as well as the degradation products and reaction pathways using RF plasma. In the presence of oxygen, the degradation products of methyl mercaptan included SO₂, CS₂, OCS, CO, CO₂, CH₄, C₂H₄C₂H₂, H₂, H₂O, HCOH, and CH₃OH. Czernichowski[18] used gliding arc discharge plasma to treat methyl mercaptan. When the voltage reached 5kV and flow rate was 70m³/h, methyl mercaptan removal efficiency was close to 100%.

3.5 Dimethyl Disulfide

As a widely used catalyst in petroleum industry, dimethyl disulfide is one of the eight key odor monitoring substances. There are few reports about the treatment of dimethyl disulfide exhaust gas by low temperature plasma. Hatakeyama et al.[19] used RF plasma to photolyze dimethyl disulfide in the air. The main products were found to be CH₃S and CH₃SOH. Xia et al.[20] used dielectric barrier discharge plasma to degrade dynamic dimethyl disulfide exhaust gas. The conversion rate of dimethyl disulfide under different residence time, inlet gas concentration and applied voltage was studied. Due to its own characteristics, synergistic effects tend to occur. While different component gases are removed at the same time, the production of by-products is also reduced.

4 Treatment of multi-component sulfur-containing malodorous gas

The composition of industrial waste gas is more complicated, and there are often multi-component sulfur-containing malodorous gases. It is imperative for low

temperature plasma to simultaneously remove multi-component sulfur-containing odorous gases. Generally, the sulfur element in organic sulfur and hydrogen sulfide has strong reducibility.

Tsai et al.[21] studied the synergistic purification of CS₂ and SO₂ using RF discharge plasma. They found that when V(CS₂)/V(SO₂)=2, the conversion rate of both reached the maximum over 95%. At this time, most of S element formed elemental sulfur.

Lu et al.[22] used gliding arc plasma to treat the mixed gas of NH₃ and H₂S in the waste gas of municipal sewage sludge drying. They found that applied voltage and air velocity can significantly affect treatment effect. When applied voltage was above 11kV and gas flow rate was 4.72m/s, treatment effect is close to 100%. The energy consumption of simultaneous degradation of NH₃ and H₂S was 38% lower than that of degradation alone. The presence of NH₃ can significantly inhibit the production of SO₂. The presence of H₂S also reduces the production of NO and HCN.

Yan et al.[23] used pulsed corona plasma to treat sulfur-containing exhaust gas. When discharge power is 5.6W, the removal efficiencies of H₂S, methyl mercaptan, and methyl sulfide are 90%, 69%, and 52%, respectively. When activated carbon fiber was added to the back end of the reactor, pollutant removal efficiency reaches 98%.

5 Conclusion

Compared with traditional methods, low temperature plasma technology has the advantages of simple process, strong applicability, easy operation, and low energy consumption in processing sulfur-containing malodorous gases. At present, a lot of work has been done on the treatment of sulfur-containing odorous gas by low temperature plasma technology at home and abroad, and some achievements have been made. However, the current research mainly focuses on the removal of single-component inorganic sulfur malodorous gas, and there is less research on the synergistic purification of organic sulfur malodorous gas and multi-component sulfur-containing malodorous gas. At present, low temperature plasma treatment of sulfur-containing malodorous gases (especially organic sulfur malodorous gases) has serious secondary pollution by-products. Therefore, future research is mainly carried out from the following aspects.

- The research on the mechanism of low-temperature plasma treatment of sulfur-containing malodorous gas should continue to be further studied. Finally, the high added value of elemental sulfur can be recovered and utilized while degrading sulfur-containing odorous gases.

- The combined treatment technology of plasma and catalyst or biological process should be developed vigorously. The control of organic sulfur odor gas reaction byproducts should be paid more attention.

- Research on the simultaneous removal of multi-component sulfur-containing malodorous gas by low-temperature plasma should be strengthened. By strengthening the synergy between different gases, it can achieve the collaborative purification of multi-

component sulfur-containing malodorous gases with different concentrations.

- The existing production process should be improved. By improving resource utilization efficiency, the emission of pollutants can be reduced at the source.

References

1. Z. Fu, P.J. He, G.J. Li, Environmental Sanitation Engineering, **12**, 3(1997)
2. G.J. Zhang, K. Li, Q. Li, Materials Review, **29**,137 (2015)
3. G.B. Zhao, S. John, J.J. Zhao, Chem. Eng. Sci., **62**, 2216 (2007)
4. Y. Itikawa, J. Phys. Chem. Reference Data, **38**, 1 (2009)
5. E.L. Reddy, J. Karuppiah, J. Energy chem., **22**, 382 (2013)
6. T. Nunnally, K. Gutsol, A. Rabbitovic, Int. J. Hydrogen Energy, **39**, 12480 (2014)
7. L. Huang, L.Y. Xia, X.X. Ge, Chemosphere, **88**, 229 (2012)
8. X.Q. Dang, J.Y. Huang, L. Kang, Energy Procedia, **16**, 856 (2012)
9. X. Yan, Y.F. Sun, J. Hazard Mater., **261**, 669 (2013)
10. C.H. Tsai, W.J. Lee, C.Y. Chen, Ind. Eng. Chem. Res., **41**, 1412 (2002)
11. C.Z. Zhu, J. Lu, X.H. Wang, Plasma Chem. Plasma Process, **33**, 569 (2013)
12. H.H. Chen, C.C. Wen, J.D. Liao, J. Hazard Mater., **185**, 201 (2012)
13. J. Chen, Q.F. Su, H. Pan, Chemosphere, **75**, 261 (2009)
14. Z.S. Wei, H.Q. Li, Bioresource Technol., **146**, 451 (2013)
15. J. Chen, Y. Weng, Journal of Chemical Engineering of Chinese Universities, **25**, 495 (2011)
16. X.J. Li, Environmental Protection of Chemical Industry, **22**, 125 (2002)
17. C.H. Tsai, W.J. Lee, C.Y. Chen, Ind. Eng. Chem. Res., **40**, 2384 (2001)
18. A. Czernichowski, Oil Gas Sci. Technol., **54**, 337 (1999)
19. S. Hatakeyama, H. Akimoto, J. Phys. Chem., **87**, 2387 (2001)
20. L.Y. Xia, H.J. Fang, Acta Scientiae Circumstantiae, **27**, 1000 (2007)
21. C.H. Tsai, Y.F. Wang, Energy Fuels, **18**(2), 465 (2004)
22. S.Y. Lu, L. Chen, Chemosphere, **117**, 781 (2014)
23. N.Q. Yan, Z. Qu, Ind. Eng. Chem. Res., **45**, 6420 (2006)