Discussion on Treatment Technology of Overflowing Waste Gas in Silicone Desulfurization Regeneration Tank

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Abstract. During the process of removing the sulfur-containing gas in the semi-aqueous gas by using the rubber desulfurization process, a large amount of exhaust gas overflows from the top of the rubber desulfurization regeneration tank, which has a heavy odor. After testing, the exhaust gas contains a large amount of carbonyl sulfur (COS), ethanethiol (CH$_3$CH$_2$SH), volatile phenols and other volatile organic gases (VOCs), which has a certain toxicity, volatile and complex chemical composition, causing harm to the surrounding and operators. However, there is no stable, single, and effective exhaust gas treatment for the exhaust gas overflowing from the tannin desulfurization regeneration tank. Characteristics of the exhaust gas generated during the production process of the semi-water gas desulfurization and oxidation regeneration tank is studied in this paper. After process designed, debugged, optimized, and inspected repeatedly, the method of “washing absorption + condensation removal of water + filter + fan + activated carbon adsorption” is proposed. When the exhaust gas outlet concentration is 542mg/m$^3$, the gas outlet concentration is 58.1mg/m$^3$ and the processing system efficiency achieve 89.28% after debugged stably, which has reached the local environmental protection emission limit (120mg/m$^3$).

1. Introduction

In the production process of synthetic ammonia using semi-water gas, the degumming process[1] is used to remove the sulfur-containing inorganic gas in the raw material gas, thereby facilitating the efficient production of the next step. When this process is used to desulfurize the raw material gas, the exhaust gas overflowing from the top of the regeneration tank at a normal pressure of 45°C has a strong pungent odor. After sampling and testing, the exhaust gas contains a large amount of volatile organic gases (VOCs). The main components are toxic gases such as carbonyl sulfur (COS), ethyl mercaptan (CH$_3$CH$_2$SH), volatile phenol, and hydrogen sulfide (H$_2$S). If the exhaust gas is directly discharged into the atmosphere, it will bring great harm to the site operators and the environment. Because of this, it is necessary to adopt a suitable and effective process method to treat the exhaust gas. At present, there are many treatment methods[2] for volatile organic gases, such as washing[3], adsorption[4], UV
photolysis[5], biological treatment[6], etc., but, there is currently no single stable and effective treatment process for the overflowing waste gas of the tannin extractive desulfurization regeneration tank with complex chemical composition. On the basis of continuous analysis, debugging and optimization, this paper proposes a new combined process in order to solve the pollution problem of the overflowing exhaust gas from the rubber desulfurization regeneration tank[7].

2. Probe into the governance process

2.1. Exhaust gas composition analysis

The exhaust gas processed by this system comes from the overflow exhaust gas produced during the production process of the semi-water gas desulfurization and oxidation regeneration tank. The main pollution components are carbonyl sulfide (COS), ethyl mercaptan(CH₃CH₂SH), volatile phenol, hydrogen sulfide(H₂S), etc., the dew point is 45°C under normal pressure; the measured peak flow of exhaust gas is 3684m³/h, the detection value is based on the total non-methane Hydrocarbon (NMHC)[8], with a value of 521 to 586 ppm (average 542 mg/m³). The current concentration of exhaust gas emissions is far below the local environmental protection emission limit[9] (<120mg/m³). Therefore, certain measures must be taken to control the odorous exhaust gas generated at the top of the regeneration tank.

2.2. Initial process

![Figure 1. Preliminary design of waste gas treatment process](image)

The preliminary design of the waste gas treatment process for the tannin desulfurization regeneration tank is shown in the figure above (Figure 1). As shown in Figure 1, after the exhaust gas is adjusted by the inlet regulating valve 2, it enters the exhaust gas filtering device 3. After filtering to remove the dust, it enters the activated carbon adsorption system[10]; through the combined action of the pneumatic regulating valve 4 and the PLC controller, the adsorption is performed. The system is in a "normal operation" state (two adsorption, one standby), and then the cleaned gas after treatment is blown into the exhaust cylinder 7 under the suction of the induced fan.

3. Test results and analysis

After the system platform is set up, debug the effect of the system's exhaust gas treatment. Opening the ventilator, adjust the inlet disc valve of the exhaust gas treatment system appropriately to stabilize the exhaust gas flow at 3680m³/h. Through the PLC control system, the corresponding pneumatic butterfly valve (4, 6 in Figure 1) is adjusted to keep the system in normal operation.

Sampling and testing, it was found that the exhaust gas concentration value of the exhaust cylinder was 285ppm (the value of non-methane total hydrocarbons was 276 mg/m³), which failed to reach the local environmental protection emission limit. At this time, the following attempts were made to improve the exhaust gas treatment system: ① The standby adsorber was incorporated into the system at
the same time, and the measured value of the exhaust gas emission concentration was 232ppm. Compared with the previous 285ppm, the value decreased, but it has not reached the local level Environmental protection emission limit; ②When an adsorber was operated separately, it was found that the value of exhaust gas emission concentration rose to 305ppm, and obviously the system processing efficiency decreased.

Observing the layout of the initial process (Figure 1), it was found that the activated carbon adsorber is in a negative pressure state under the current operating state. In fact, the adsorption performance of activated carbon increases with increasing pressure; when the pressure is lower than atmospheric pressure, the activated carbon is in a desorbed state[11]. Then, for the layout of the initial process, the actual working process of the activated carbon adsorber in a negative pressure state is desorption, which is very unfavorable to the adsorption of activated carbon. Efforts should be made to change the adsorption state of the activated carbon to make it in a positive pressure state in order to better perform the adsorption operation.

Normally running system for a period of time, stop and check the system equipment. It was found that the surface of the dry filter was completely wet, and there was effusion at the bottom of the dry filter box; the surface of the activated carbon was wet, and a heavy odor was emitted around the activated carbon.

According to the above experiments, it can be found that the exhaust gas treatment efficiency of the system under normal operating conditions is not high, only 49%. Changing the number of adsorbers used and comparing the exhaust emission concentration values, it was found that when the amount of activated carbon is increased (ie, the number of adsorbers used is 3), the exhaust emission concentration values have been significantly reduced, and the amount of activated carbon that may be used by the system under normal conditions not enough. The negative pressure operation state of the adsorption system can make the activated carbon adsorption system in a positive pressure adsorption state by changing the position of the fan arrangement. The actual situation of the exhaust gas at the inlet was studied, and it was found that the water vapor content in the exhaust gas overflowing from the top of the tannin desulfurization regeneration tank was saturated at the working temperature (45°C). Attachables are easy to condense and accumulate into small droplets. The droplets will soak the micropores on the surface of the filter and the activated carbon, and even accumulate to a certain extent and will fall to the bottom of the box.

In addition, the exhaust gas inlet concentration is too high, and the current exhaust gas treatment system may not be able to handle it.

Based on the detailed analysis of the above several aspects, the main reasons that cause the exhaust emission concentration to fail to reach the local environmental protection emission limit may be: (1) the system does not use enough adsorbent; (2) the adsorption system is in a negative pressure state which is not conducive to adsorption; (3) The water content of the exhaust gas is too large; (4) The concentration of the exhaust gas inlet is too high.

For these possible reasons, optimize based on the original process system, and debug, verify and analyze again.

4. Optimized process flow

4.1. Optimization of system adsorbent dosage

Adjust the amount of activated carbon in each adsorber from the original 1.5m$^3$ to 2.5m$^3$. Under normal operating conditions of the detection system is 158ppm (the total value of non-methane hydrocarbons is 142mg/m$^3$), obviously the adsorbent increasing the amount has positive influence, but the value of the exhaust gas emission concentration still does not reach the ideal environmental emission limit, and further optimization of the system is needed.
4.2. Optimization of fan position
Adjust the position of the fan in the exhaust gas treatment system. Tune-up the fan to the front of the adsorber. The adsorption system will be in a positive pressure adsorption state. The outlet value is 232ppm (the total non-methane hydrocarbon value is 226mg/ m$^3$), which is lower than the original 285ppm exhaust gas emission concentration value. Explicitly it has played a positive role, but the value of the exhaust gas emission concentration still does not reach the ideal environmental protection emission limit, and the system needs to be further optimized.

4.3. Optimization of exhaust water content
Add a condenser at the front of the dry filter device, and use low-temperature water (15°C) as a cooling medium to cool and remove the exhaust gas. Under normal operating conditions, the exhaust emission concentration value is 128ppm (the value of non-methane total hydrocarbons is 119mg/m$^3$). The exhaust emission concentration value is lower than the local environmental protection limit, but it is too close to the environmental protection limit, so further optimization is needed.

4.4. Optimization of exhaust gas inlet concentration
In order to further ensure that the system meets the long-term emission standards and ensure that the activated carbon has a long enough use time, an exhaust gas absorption tower is added at the entrance of the exhaust gas into the treatment system (Figure 2). As shown in Figure 2, by adding an alkaline solution absorption tower to the exhaust gas inlet, the inlet concentration of the activated carbon adsorption system is reduced. After the absorption tower is added, the exhaust gas concentration measured after absorption and absorption in the absorption tower is 230ppm (the value of total non-methane hydrocarbons is 221.3mg/m$^3$). Under normal operating conditions of the system, the exhaust gas emitted to the exhaust pipe is divided into multiple periods. The concentration was measured, and the average value was 68 ppm (the value of non-methane total hydrocarbons was 58.1 mg/m$^3$). Obviously, the optimized exhaust gas treatment system at this time achieved good treatment results and achieved stable local environmental protection emissions limit.

5. Discussion and analysis of optimization results
After the system was optimized and adjusted, a good exhaust gas treatment effect was achieved. Through the optimization of the fan position, it can be found that the exhaust gas treatment efficiency has increased by 9.23%, indicating that activated carbon is more suitable for adsorption under positive pressure, and the molecules of harmful substances in the exhaust gas are more easily captured and collected by the micropores of the activated carbon; subsequently, the amount of adsorbent was
increased. This step increased the treatment efficiency of the exhaust gas treatment system by 15.50%, indicating that the activated carbon adsorbent can not only effectively adsorb harmful components in the exhaust gas, but also increase the amount of adsorbent can significantly improve the efficiency of the exhaust gas treatment. The optimization of this step improves the treatment efficiency of the exhaust gas treatment system by 4.24%. The reduction of the moisture in the exhaust gas ensures that the activated carbon has more micropores for adsorbing harmful components in the exhaust gas instead of adsorbing water molecules in the exhaust gas; Finally, the optimization of the exhaust gas inlet concentration was carried out. This step improved the treatment efficiency of the exhaust gas treatment system by 11.24%. The optimization of the exhaust gas inlet concentration prevented the activated carbon from adsorbing and saturating too quickly. Exhaust gas outlets meet long-term emissions.

The processing efficiency of the system before optimization is 49.08%, and the processing efficiency after optimization is 89.28%. The processing efficiency of the system is significantly improved after optimization, indicating that the optimization has played a good role.

6. Conclusion

By comparing treatment technology and effect, it is found that the optimized treatment system has a stable treatment effect on the overflow gas from the rubber desulfurization regeneration tank, and the exhaust gas treatment efficiency can reach 89.28%. Therefore, for the overflowing exhaust gas of the tannin desulfurization regeneration tank (the exhaust gas concentration is 542mg/m³), the treatment process of this optimized system "washing absorption + condensation removal of water + filter + fan + activated carbon adsorption" can achieve good exhaust gas treatment effect. The exhaust gas concentration at the system discharge port can reach the standard limit of the local environmental protection bureau below 120mg/m³.

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