Example of VOCs waste gas treatment in a pharmaceutical enterprise

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Abstract. This paper introduces the volatile organic waste gas pollution characteristics and the treatment status of chemical pharmaceutical companies. According to the characteristics of volatile organic waste gas of a pharmaceutical enterprise, after comparing various treatment processes of volatile organic waste gas, the treatment process of alkali washing spray + high efficiency mist eliminator + activated carbon adsorption + nitrogen desorption + condensation was finally adopted. Waste gas treatment scale of 60000m³/h, after stable operation of the equipment. Each emission index reaches the air pollution emission limit stipulated in the "Emission standard of air pollutant for pharmaceutical industry" (GB37823-2019).

1. Introduction

1.1. Classification and pollution of pharmaceutical industry
The pharmaceutical industry is mainly divided into six categories: fermentation pharmaceutical industry, chemical synthesis pharmaceutical industry, traditional Chinese medicine pharmaceutical industry, extraction pharmaceutical industry, biological engineering pharmaceutical industry and mixed packing pharmaceutical industry. Among them, fermentation and chemical synthesis pharmaceutical industry is a major VOCs emissions. China is a big producer of chemical bulk drug, especially the production capacity of fermented pharmaceutical products ranks first in the world. Bulk drug as the upstream products of the whole pharmaceutical industry chain, VOCs pollution is particularly serious[1].

The source of VOCs in the pharmaceutical industry is mainly in the production process, the organic solvent in the raw materials with the production process volatilization and lead to VOCs pollution. For example, in the process of chemical synthesis industrial pharmaceutical production, raw material separation and filtration, fermentation extraction, distillation recovery, purification and drying will emit a large number of solvent evaporative VOCs, and soon spread to the surrounding environment causing harm. At present, the pharmaceutical industry VOCs management level is not high[2].

2. The selection of VOCs waste gas treatment technology for a bulk drug enterprise
This Enterprise is a large-scale chemical bulk drug enterprise in the domestic pharmaceutical industry, with advanced equipment and many varieties. This enterprise produces a large number of VOCs containing waste gas in the process of the production of bulk drug, the components are complex, the types are various, the main waste gas production process equipment is reaction Kettle, vacuum pump, waste liquid pool, etc. If not treated, it will cause serious environmental pollution[3]. In response to the
National Environmental Protection Policy and to reduce the impact on the surrounding environment, the Enterprise has made great efforts to request the professional and technical team to analyze the characteristics of the exhaust gas at each production site and select the best treatment process, in order to improve the environmental air quality around the plant, reduce the emission of air pollutants.

2.1. The pollution of VOCs in this enterprise
The enterprise production exhaust gas emission is normal temperature and pressure (pressure ≤200Pa, temperature ≤40 ℃), the concentration of VOCs in the production workshop exhaust gas is about 80mg/m³ for a long time, the concentration peak when feeding and unloading, up to 1500mg/m³, the average concentration is 250mg/m³. The main components of waste gas are: pyridine, dichloromethane, methanol, hydrogen chloride, ethyl acetate, tetrahydrofuran, n-propanol, N-methylpiperazine, ethanol, n-heptane, acetic acid, isopropyl alcohol, diisopropyl ethylamine, sulfoxide chloride, methyl tert-butyl ether.

2.2. Exhaust gas parameters
Samples were taken and tested at the exhaust gas outlet, and the detection data of VOCs concentration in the exhaust gas were shown in Figure 1.

According to Figure 1, the concentration of exhaust gas produced by this enterprise fluctuates greatly in a day. Every morning from 9:00 to 9:40 and in the afternoon from 16:00 to 16:30 for discharging, the concentration of VOCs in the waste gas will appear peak, with the peak concentration of 1500mg/m³. Usually the concentration is low, the average concentration is about 250mg/m³.

The concentration detection values of the main components in the exhaust gas produced by this enterprise are shown in Table 1.

| No. | Type    | Maximum concentration(mg/m³) | Average concentration(mg/m³) |
|-----|---------|------------------------------|------------------------------|
| 1   | THC     | 900                          | 250                          |
| 2   | NMHC    | 1000                         | 250                          |
| 3   | VOCs    | 2000                         | 300                          |
| 4   | CH₄     | 10                           | 5                            |
| 5   | HCl     | 200                          | 150                          |
| 6   | C₂H₃F₃O₂ | 200                          | 150                          |
In summary, the characteristics of exhaust gas from the bulk drug production line of this enterprise are as follows: exhaust gas composition is complex, emission concentration fluctuates greatly, and contains more chlorinated hydrocarbon substances and acidic substances.

2.3 A description of the VOCs waste gas treatment process of this enterprise

According to the characteristics of the waste gas of the enterprise, the treatment of organic waste gas needs a variety of technology combinations, so as to achieve the effect of both improving the purification rate and economic and practical. This project combines the adsorption method and the condensation method, adopts the multi-tank circulation condensation and reverse purge adsorption to achieve the standard emission of waste gas treatment[4][5].

The whole waste gas treatment process is divided into three steps:

2.3.1. The adsorption process:

2.3.2. The regeneration process:

2.3.3. The cooling process:

The exhaust gas at each discharge point of the workshop, under the suction action of the blower, the exhaust gas first enters the alkali washing tower for washing treatment, and the acid gas and water-soluble substances in the exhaust gas are removed. After further defogging, the exhaust gas enters the adsorption bed, and the porous structure of activated carbon is used to adsorb VOCs compounds. After saturated, the activated carbon was regenerated with hot nitrogen. The high concentration organic gas after desorption entered the condenser to get condensation, and the condensate was recovered by stratification. After desorption and regeneration, the adsorption bed was cooled and waited for the next adsorption process.

Nitrogen is used as the desorption gas to regenerate the activated carbon in the adsorption device, which improves the desorption efficiency and the safety of the desorption system, and less waste water is produced by desorption and condensation with steam. The interlocking automation of desorption process is realized by setting multiple temperature sensors, pressure sensors, oxygen content sensors and other high-precision monitoring instruments to ensure the desorption and condensation effect.
3. Engineering parameters

3.1. Technical parameters of main equipment

3.1.1. Technical parameters of preprocessing system
Quantity: 30000 m³/h; Unit: 2 sets; Process size: Φ3.0m×H7.5m; Tower material: FRP; Thickness of glass fiber reinforced plastic tower: ≥12mm; Corrosion resistance requirements: acid and alkali corrosion, hydrofluoric acid corrosion resistance; Packing form: Φ38mm pall ring; Nozzle type: PTFE spiral nozzle; Jetting Angle: 120 degrees; Number of spray layers: two layers; Spray flow per layer: 40m³/h(0.3MPa); Number of packing layers: two layers; Thickness of packing layer: 1m/layer; Demister form: double PP baffle.

3.1.2. Technical parameters of activated carbon adsorption and condensation recovery system:
Quantity: 60000 m³/h; Main material: SUS304; Thermal insulation material: rock wool + color steel plate; Operation mode: 3 groups (2 groups run and 1 group regenerate) 24 hours continuous automatic operation; Automatic control mode: PLC+ touch screen; Steam consumption per hour: ≤1.0t/h (steam pressure 0.6Mpa); 1.5 h/d or less; Normal temperature cooling water demand: ≤250t/h (inlet water temperature below 40°C, temperature difference between inlet and outlet 5°C); Low temperature cooling water demand: 40t/h (inlet water temperature is lower than -7°C, temperature difference between inlet and outlet is 7°C); Nitrogen consumption: ≤160m³/h, ≤1h/d; Power of supporting circulating fan: ≤15KW, ≤20h/d; Supporting electric heating power: ≤45KW, ≤6h/d;

Unit: 1 set
Accessory equipment:
(a) Special adsorption purifiers
Treatment air volume: 30000m³/h; Dimensions: Φ2600×L8000mm; Main material: SUS304 (thickness 8mm); Insulation: 100mm thick rock wool +0.5mm aluminum leather; Adsorbent: special VOCs particulate carbon, brand: Datong Yunguang.; Properties of adsorbent: carbon tetrachloride adsorption value >90%; Ash content < 5%; Water < 5%; The intensity of > 90%; Iodine value > 1000 mg/g; Bulk density: 430 ~ 470g/L;; Chemical waste gas special adsorbent weight: 7 tons/set; Quantity: 3 sets (2 with 1 spare; This is three sets of adsorbers attached to the treatment system.)

(b) Nitrogen regeneration systems
Treatment air volume: 12000m³/h; Main material:SUS 304; Insulation: 100mm thick rock wool +0.5mm aluminum leather; Gas heating and heating speed: >100 °C / hour; 12000m³/h Gas heating and cooling speed: >100 °C / hour; Nitrogen desorption temperature: >110 °C; Electric heating power: 45KW; Steam consumption per hour: <1.0t/h (steam pressure 0.6MPa); Normal temperature cooling water demand: <250t/h (inlet water temperature is below 40°C, inlet and outlet temperature difference is 5°C); Low temperature cooling water demand: <40t/h (inlet water temperature is lower than -7°C, temperature difference between inlet and outlet is 7°C); Nitrogen consumption: <160m³/h; Daily use time ≤1h; Condensate separation storage capacity: >3.5m³; Unit: 1 set.

(c) Automatic control systems
Model No. : Non-standard; Explosion-proof requirements: placed in a non-explosion-proof area; Automatic control requirements: Siemens PLC+10 inch touch screen; Electrical components: Schneider; Box material: SUS304; Unit: 1 set.

3.2 Economic and technical index
The total investment of the project is 5 million yuan, and the operating cost is 1 million yuan/year. After the treatment, each emission index have reached the limits of air pollution emission stipulated in the "standards for air pollutants emission in pharmaceutical industry" (GB37823-2019).
4. Conclusion
The VOCs waste gas of bulk drug enterprise containing complex pollutants containing more chlorine hydrocarbons and hydrogen chloride acid. The above exhaust gas should not be treated by combustion method. Compared with the traditional treatment process, the "alkali washing spray + efficient mist eliminator + activated carbon adsorption + nitrogen desorption + condensation recovery process" adopted in this case has the characteristics of high efficiency, energy saving and high degree of automation. After being treated by this system, the exhaust gas can be discharged up to the standard. It improves the pollution control level and corporate image of enterprises, plays a demonstration role in energy conservation and emission reduction of enterprises in the pharmaceutical industry, plays a guiding role in environmental governance of the entire pharmaceutical industry, and can promote the renewal and development of environmental protection standards in relevant industries.

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