Discussion on the calculation of waste gas emission in fine chemical industry

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Abstract. The production process of fine chemical industry produces a large number of waste gas, which has complex components, including acidic gases, volatile organic compounds and odor gases. It is difficult to calculate the amount of waste gas in the process because of the sequential batch and discontinuous production. In this paper, the calculation method of waste gas volume of workshop process equipment, storage tank area, sewage treatment station and hazardous waste warehouse is discussed based on the waste gas generation area, point location and exhaust mode of the industry, and the waste gas is classified, which provides reference for the selection of waste gas treatment process and the determination of equipment treatment scale.

Keywords: fine chemical industry; discharge amount; industrial waste gas; rate of discharge.

1 Introduction

The fine chemical industry produces a large amount of acid waste gas and volatile organic waste gas. According to the WTO definition, volatile organic compounds (VOCs) refer to various organic compounds with a boiling point of 50 ° C - 260 ° C at room temperature[1].Studies have found that the volatilization of low-boiling organic solvents used in the production process, such as acetone, methanol, toluene, etc., makes an important contribution to the total VOCs emission[2-4], resulting in environmental pollution problems that seriously affect the health of surrounding residents and restrict the development of regional economy[5]. The foreign literature in this field mainly analyzes the impact of industrial park emissions on the whole city[6-7]. To properly deal with the waste gas generated in the production process, it is necessary to grasp the information of the composition, concentration and emission of the waste gas. At present, the focus of exhaust gas projects in the domestic fine chemical industry is often concentrated on the study of treatment methods. The calculation of VOCs emissions adopts the measured method, material balance algorithm, formula method and emission coefficient method[8], and the calculation of exhaust volume of a single equipment or a certain area is rarely reported in the literature. This paper discusses the calculation of waste gas

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emission in fine chemical industry, and provides a calculation idea for the calculation of waste gas treatment volume in this industry.

2 Calculation of exhaust volume

The waste gas sources of fine chemical industry mainly include industrial waste gas, breathing gas of storage tanks, waste gas from sewage treatment stations and waste gas from hazardous waste warehouses.

2.1 Calculation of process exhaust gas volume in workshop

The industrial waste gas mainly comes from the exhaust port of reaction kettle, metering tank, transfer tank, receiving tank, storage tank, centrifuge, three-in-one, vacuum pump and other equipment. The rate of discharge of VOCs from different equipment is quite different, among which atmospheric distillation, vacuum distillation, centrifugal waste gas and pressure filtration waste gas are high concentration organic waste gas, and the exhaust air volume is also large. The relevant waste gas collection measures and air volume design are shown in Table 1 below.

Table 1. Waste gas collection measures and air volume calculation

Exhaust point	Collection method	Calculation method of air volume	Remark
Reaction kettle, measuring tank, transfer tank, receiving tank, etc	Direct connection	Equipment volume air change volume	Change the air 2-3 times per hour
Centrifuge	Direct connection	Pipeline gas velocity	Pipeline gas speed of 3 ~ 5m/s
Three-in-one	Direct connection	Pipeline gas velocity	Pipeline gas speed of 3 ~ 5m/s
Vacuum pump	Buffer tanks are set at the exit, then direct connection	Maximum pumping rate	Gas volume decline
Equipment involving pressure relief or reaction gas production	Direct connection	a. Calculated according to pressure relief and pressure relief time b. Calculated by rate of discharge and emission time	Such as exhaust gas spots containing hydrogen or carbon dioxide

In the process of chemical production, there are often several exhaust ports in the same set of equipment at different production periods for exhaust. For example, after the reactor reaction is completed, vacuum distillation is required. At this time, the exhaust gas is discharged from the vacuum pump, while the atmospheric exhaust pipeline is closed, and the exhaust gas generated by the reactor listed in Table 1 through the volume of the equipment is not produced. That is to say, the air volume calculation cannot be superimposed, but the maximum exhaust volume under the maximum load should be considered.

Taking a set of atmospheric pressure heating reflux + decompression desolvation section as an example. This set of equipment has 4 stripping reactors, 4 distillate receiving tanks, 4 vacuum pumps, of which the maximum pumping capacity of the vacuum pump is 300m^3/h. Each descaling kettle is equipped with a condenser. The waste gas produced by the descaling reactor is discharged from the tail pipe behind the condenser during the reflux reaction. When decompressing and dissolving, the exhaust gas is discharged from the vacuum pump, and the exhaust port of the condenser supporting the dissolving kettle does not exhaust. Exhaust gas will be discharged from different places at different stages, as shown in Table 2 below.

Table 2. Exhaust emissions from atmospheric pressure heating reflux + decompression desolvation section

Device name	Desoldering kettle	Receiving tank
Equipment specification /L	3000	2000
Equipment quantity/set	4	4
Maximum number of devices used at the same time /set	4	4
Exhaust gas production of a single equipment under normal pressure /m^3	6	4
Maximum load exhaust gas production under normal pressure / m^3	24	16
Exhaust gas production of a single equipment under negative pressure / m^3	300	/
Maximum load exhaust gas production under negative pressure / m^3	400	/
Maximum exhaust gas production / m^3	400	

Note: The use of 4 vacuum pumps is considered as 1 just started, 2 stable operation, 1 not started. The exhaVust gas volume of the vacuum pump is gradually reduced. At the beginning, it is the maximum exhaust volume. After the vacuum degree comes up, the exhaust volume decreases, and can be calculated according to the corresponding vacuum degree. The pumping volume of a single vacuum pump is estimated at 50m^3/h during normal operation.

Under normal pressure condition, that is, when the vacuum pump is not running, the maximum exhaust gas is composed of the exhaust of the condenser and the exhaust of the condensate receiving tank, that is, 24+16=40m^3/h;

Under negative pressure conditions, that is, when the vacuum pump is running, the exhaust port of the condenser and the condensate receiving tank are closed, and only the vacuum pump exhauts 400m^3/h.

2.2 Calculation of exhaust gas volume in storage tank area

Liquid materials in the fine chemical industry are stored in tanks. Waste gas will be generated during storage and production. The storage of material storage tank mainly results in respiratory loss (small breath) and work loss (large breath). Respiratory loss is due to changes in temperature and atmospheric pressure, it causes the expansion and contraction of the steam generated by the vapor discharge, it appears in the tank without any liquid level change, also known as small breathing. The loss caused by the combination of loading and unloading is called the work loss, also known as the big breath. By setting nitrogen seal, it can effectively reduce the occurrence of small breath waste gas; When loading and unloading materials, the balancing pipe can effectively reduce the production of large breathing exhaust gas. The exhaust gas volume of the storage tank is designed according to *Design specification for tank farms of storage and transportation system in petrochemical industry*.

Calculation method of large breath waste gas of storage tank: The amount of liquid gas exhaled in the tank caused by liquid entering the fixed roof storage tank, when the liquid flash point (closed) is higher than 45°C, should be considered as 1.07 times the maximum liquid intake; When the liquid flash point (closed) is lower than or equal to 45°C, 2.14 times the maximum liquid intake should be considered[9].

Storage tank small breathing exhaust gas calculation method: The amount of air inhaled by the tank due to the contraction of the gas in the tank caused by the maximum temperature drop of the atmosphere and the amount of gas exhaled due to the expansion of the gas in the tank due to the maximum temperature rise of the atmosphere should be determined according to Table 5.1.6. Only the exhaled volume is taken into account when performing the exhaust volume statistics[9].

2.3 Calculation of waste gas volume of sewage treatment station and hazardous waste warehouse

Different from industrial waste gas, waste gas from sewage treatment stations and hazardous waste warehouses is space ventilation in closed Spaces (or workshops). The amount of waste gas from sewage station pools is calculated according to the odor treatment technical regulations of urban sewage treatment plants, based on gas production per unit water surface + space ventilation[10], and the amount of waste gas from sludge dewatering rooms and hazardous waste warehouses is calculated according to space volume × ventilation times. As shown in Table 3 below.

Table 3. Calculation of waste gas volume in sewage treatment station and hazardous waste warehouse

Name	Air volume calculation basis
High concentration wastewater area	Gas production per water surface area 3 ~ $10m^3/(m^2 \cdot h)$ +1 ~ 2 space ventilation
Low concentration wastewater area	Gas production per water surface area 3 ~ $10m^3/(m^2 \cdot h)$ +1 ~ 2 space ventilation
Sludge dewatering room	Space volume ×8 ~ 12 times /h
Hazardous waste warehouse	Space volume ×3 ~ 6 times /h

3 Classification of waste gas

Because the pollution sources of exhaust gas are different, the physical properties of process exhaust gas are very different, therefore, the exhaust gas emitted in the production process should be set up in different gas collection methods according to different emission sources, and be treated. The following purposes can be achieved through classification:

(1) Collection purpose: pipes of different materials are used to collect pollutants of different nature to avoid pipeline corrosion. Substances that react with each other are collected separately to achieve the purpose of safe transportation.

(2) Treatment purpose: Design targeted waste gas pretreatment process after classifying pollutants of different nature, reduce the total cost and ensure the normal operation of the end treatment equipment to prevent equipment corrosion.

(3) Standard purpose: Classify and pre-treat pollutants containing N, S or halogens to avoid excessive emission values caused by a large number of by-products after end-combustion treatment.

3.1 Industrial waste gas classification

(1) High-concentration organic waste gas

① High concentration general organic waste gas in workshop: This kind of waste gas is mainly produced in the workshop synthesis, concentration, centrifugation, distillation, rectification and other production processes, the main pollutants are acetone, ethyl acetate, isopropyl alcohol, ethanol, toluene, methanol, n-hexane, n-heptane and so on. This kind of organic waste gas can be directly incinerated for final disposal by simple pretreatment.

② High concentration and low boiling organic waste gas: This kind of waste gas is mainly produced in the workshop synthesis, concentration, centrifugation, distillation, rectification and other production processes, typical pollutants such as ether. These gases are volatile because of their high vapor pressure or low boiling point, resulting in particularly high exhaust gas concentrations. As a solvent, ether is widely used in the salt formation reaction in the fluorine chemical industry. It has low boiling point, low lower explosive limit and high safety risk, so it should be collected separately and pre-treated to reduce concentration.

③ Halogen-containing organic waste gas: This kind of waste gas is mainly produced in the workshop synthesis, concentration, centrifugation, distillation, rectification and other production processes, the main pollutants are dichloromethane, dichloroethane, chloroform and so on. Halogenated waste gas into the incineration system will produce hydrogen chloride, corrosion equipment, in the presence of benzene series of the system may produce dioxins, need to do a good concentration control, minimize the proportion of the total waste gas.

④ Nitrogen-containing organic waste gas: This kind of waste gas is mainly produced in the workshop synthesis, concentration, centrifugation, distillation, rectification and other production processes, the main pollutants are acetonitrile, triethylamine, DMF and so on. Because the industrial waste gas often has a variety of components, it is difficult to remove all through a process, often using a combined treatment process, and the final treatment process is mostly incineration. Nitrogen containing waste gas into the incineration system to consider the content of nitrogen oxides in the final exhaust, like chlorine containing waste gas, before entering the incineration system to strictly control the proportion of nitrogen containing waste gas.

(2) Low-concentration organic waste gas

Low-concentration organic waste gas mainly comes from the feeding room and the discharge port of the steam/rectification foot in each workshop. The main pollutant is the main solvent in the workshop. The amount of waste gas produced is small and the concentration is low.

(3) Waste gas containing hydrogen chloride and hydrogen fluoride

Hydrochloric acid is one of the important raw materials in chemical industry, widely used in chemical raw materials, dyes, medicine, food, printing and dyeing, leather, sugar, metallurgy and other industries. Hydrochloric acid is highly volatile and will produce a large amount of hydrogen chloride gas during use. Fluorine chemical enterprises use hydrofluoric acid as raw material to synthesize products, and produce a large amount of hydrogen fluoride gas in the process of fluorination. These two kinds of acid gases are highly corrosive and water-soluble, and have high requirements for the material of the pipeline and treatment equipment, and can be centrally collected and unified for nearby treatment.

(4) Hydrogen-containing waste gas

Some pharmaceutical industry hydrolysis, hydrogenation process will produce hydrogen containing waste gas, hydrogen itself is non-toxic, but belongs to flammable and explosive gas, explosion limit range is wide, there are safety risks, workshop collection after alkali seal directly discharged or sent to the waste gas treatment system for proper treatment.

3.2 Waste gas from sewage treatment station

The waste gas of sewage station includes high concentration waste gas of sewage station and foul odor gas of sewage station. High concentration waste gas mainly comes from anaerobic tanks, hydrolytic acidification tanks, high concentration collection tanks, etc., containing relatively high concentrations of VOCs, and the components depend on the solvents and production materials used in the production workshop.

The odor generating unit mainly includes the regulating tank, biochemical tank, sludge tank and sludge dewatering room, etc. The main pollutants are H2S, NH3 and a small amount of VOCs, which are covered and sealed for collection, and air pipes are set up to collect the waste gas into the waste gas centralized treatment device.

3.3 Waste gas from hazardous waste warehouse

There will be a small amount of organic pollutants and odor during the temporary storage of hazardous waste. First of all, each hazardous waste must be stored in a closed container indoors with a gas collection device and connected to the waste gas treatment system for treatment.

4 Exhaust gas treatment system and design air volume

The waste gas of fine chemical industry is characterized by multi-component emission in the form of mixture, often containing acid gas, common organic matter and odor gas[11]. In space, the point is wide; The time is mostly intermittent discharge; The emission of pollutants is unstable, and different pollutants will be discharged from the same equipment in the production process. The composition of pollutants is complex, and the types and concentrations of pollutants vary greatly[12]. According to the composition of the waste gas and emissions, concentration, temperature and other physical and chemical properties, choose different treatment methods, commonly used treatment processes are condensation method, absorption method, adsorption method, incineration method, biological method, plasma method. The components with high concentration of organic matter and recovery value in waste gas can be combined with adsorption and condensation. Large gas volume, low concentration of organic waste gas can be treated by the combination of absorption, adsorption and incineration, among which the absorption method is mostly used as a pretreatment means to remove soluble and acidic gas, to ensure a good origin environment for subsequent treatment equipment; The adsorption method aims at the treatment of waste gas containing chlorine and nitrogen, creating conditions for subsequent entry into the incineration system. Odor waste gas is mostly treated by biological method or multistage absorption method.

When low concentration waste gas is treated by absorption method and biological method, the equipment selection can be carried out according to the calculated amount of waste gas. When it comes to the treatment of flammable and explosive components and incineration and other treatment processes, it is also necessary to check whether the aforementioned amount of exhaust gas is reasonable according to the rate of discharge of pollutants. For the exhaust gas containing mixed organic compounds, its import control concentration should be less than 25% of the most explosive components or the lower limit of the explosion limit of the mixed gas, according to the exhaust gas volume calculated by the front speed method, through the rate of discharge of each pollutant, the concentration can basically meet the intake requirements. Incineration method, typical such as RTO, the intake concentration is lower than the lower explosive limit of 25%, which is the basic safety requirements, especially the RTO furnace explosion prevention and control, does not mean that the RTO furnace can be stable operation, it must calculate the calorific value of each component of the imported exhaust gas, and check whether the concentration of the exhaust gas collection at the maximum rate of discharge meets the normal operation of RTO. Taking the waste gas containing toluene as an example, when the lower explosive limit is 25%, the concentration is 10.9g/m3, and the caloric value of toluene combustion is 3905kJ/mol, then the caloric value of the waste gas is 463kJ/m^3. When the temperature difference between import and export is 60°C, the heat loss of RTO during normal operation is 72.22kJ/m^3, so the RTO furnace is still overtemperature and cannot operate normally. It is necessary to continue to dilute to 1701mg/m^3 before normal operation, and the RTO furnace design must adopt the diluted air volume.

In the design air volume review, an important data is involved, that is, the rate of discharge of organic matter. Existing studies mostly use emission coefficient method or reverse estimation method to calculate VOCs production, such methods can not trace VOCs production to each process, and some components are easily subject to the constraints of instrument detection limits and detection time. Ye Han-yun et al.[13] proposed a forward calculation of VOCs generation based on process parameters and material properties based on the analysis of the characteristics of fine chemical production process and VOCs generation mechanism. The results show that the mechanism of VOCs generation in fine chemical production is because the inert gas in the equipment carries organic vapor into the atmosphere. The main processes of VOCs generation include: feeding, heating, chemical reaction gas taking out, cleaning and purging, vacuum pumping, pressure relief and evaporation. The chemical process simulation software Aspen and the recommended formula in literature [14] were used to estimate the production volume of VOCs generation link in the main process, and the VOCs emissions of each process link were obtained, which is an important working condition data in the design of waste gas treatment system.

5 Conclusion

This paper discusses the calculation method of waste gas volume of workshop process equipment, storage tank area, sewage treatment station and hazardous waste warehouse in combination with the waste gas generation area, point location and exhaust mode of fine chemical industry, and proposes to check whether pollutant concentration meets the needs of stable operation of treatment equipment through pollutant discharge rate, and finally obtain the appropriate design and treatment scale. Improve the authenticity and accuracy of the whole plant exhaust emissions accounting.

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