Analysis on treatment measures of tank exhausting waste gas in oil-refining enterprises

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Abstract. In recent years, the problem of atmospheric pollution has become more and more serious. Emissions came from oil-refining enterprises cannot be underestimated. And the pollution of tank exhausting waste gas is the main source in oil-refining enterprises. This paper analyzes the causes of oil tank exhausting waste gas. Several methods for decreasing emission were reviewed. There are many ways to treat exhausting waste gas from oil tank. This paper focuses on adsorption method, absorption method, condensation method, biodegradation method and catalytic oxidation method, and the future research focus is put forward.

1. Introduction
The rapid development of Chinese oil-refining enterprises has brought great economic benefits as well as harm to the environment and ecology. The contradiction is becoming sharper and sharper between industrial pollution and environmental protection. In China, the production scale of oil refining enterprises has been expanding, and the processing quantity of inferior crude oil has been greatly increasing, which has caused the waste gas pollution to become increasingly prominent. In recent years, people has paid more attention to the pollution caused by oil-refining industry, meanwhile the state has urged all of enterprises to make more efforts to eliminate air pollution source. Therefore, whether the refinery can survive or not has great relevance to near-zero emissions in the long run.

There are many sources of pollution in oil refinery, among which oil storage tanks are the most important origin of odor pollution. The odor pollution includes not only hydrogen sulphide, mercaptan, etc, and volatile sulfide, but also high concentrations of hydrocarbons and benzene series. A large number of organic gas emissions not only seriously pollute the environment, but also caused the loss of oil gas. In order to curb emissions and protect the environment, local and state have implemented a series of relevant regulations and policies and set stricter emission standards.

2. Causes of waste gas pollution in the tank area
The exhaust emission in tank farm is mainly affected by oil properties, storage conditions, operating conditions, external environment, etc. Breathing loss and working loss are the most important factors of exhaust emissions in tank farm. When the tank oil is loaded or unloaded, the oil is blended, or the ambient temperature changes, the gas pressure above the fluid levels will change. To prevent occurrence of accidents, the tank top breathing valve will balance the pressure inside the tank by discharging oil gas or inhaling external fresh air.

2.1. Working loss
When the tank oil volume increases along with the liquid level gradually rises, the oil-gas space is compressed, which results in the gas phase pressure increases. Once the gas pressure exceeds the
safety control pressure of the tank, the top breathing valve will be opened automatically for safety and then the oil steam is discharged from the breathing valve. Conversely, when the tank oil volume decreases along with the liquid level gradually declines, the gas phase pressure reduces since the oil gas space is enlarged. In the case, the evaporation rate of the oil is accelerated in the tank, sometimes the outside air is sucked into the tank until the oil gas is saturated. The vaporized oil-gas will be discharged into the atmosphere when the pressure of the next tank rises, resulting in environmental pollution.

2.2. Breathing loss
When the oil liquid level is motionless, the oil gas pressure inside the tank also will change with the ambient temperature. At night, the temperature of oil-gas decreases with the lower ambient temperature, thereby the oil-gas is condensed and the tank pressure is reduced. Once the pressure is reduced to the set value of the negative pressure of the breathing valve, external air will be inhaled to supplement the tank pressure for re-balance. Instead, the gas pressure increases as the higher temperature rises by day, when the pressure exceeds the set point of the breather valve, the oil-gas is discharged into the atmosphere. That means the oil gas emission from frequent tank breathing caused by the temperature difference between day and night lead to the environmental pollution.

3. Methods of tank farm waste gas emission reduction
There are many factors that affect the evaporation of oil-gas in storage tanks, such as oil properties, operating conditions, external environment, etc. In order to reduce the environmental pollution caused by oil-gas evaporation, the following measures have been adopted.

3.1. Choose the suitable tank structure
According to the volatility and storage capacity of oil products, storage tanks with different structures are used for oil storage. In oil-refining enterprises, the commonly used oil storage tanks include external floating-roof tank, vault tank, inner floating roof tank, etc. For light oil, due to its more volatility the inner floating roof tank is often recommend to use. The inner floating roof tank is added with a floating tray on the basis of the vault tank. The floating tray clings to the liquid level and floats with the liquid level. This way greatly reduce the oil-gas space above the liquid level, thereby consequently reducing the volatilization of the oil-gas.

3.2. Control operation process
In order to reduce exhaust emissions during operation process, it is necessary to regularly check the sealing conditions of tanks, especially mechanical breather valves and hydraulic safety valves. When a bug is found, fix it in time. For stationary tanks, try to use high-level storage. When receiving oils, large flow is used to control the large evaporation of oil-gas. When sending oils, small flow is used to avoid rapid inhalation the air and cause the back-and-forth exhalation.

3.3. Control oil temperature change
The breathing loss of the oil tank is caused by the change of the ambient temperature. In order to reduce the wavy degrees of oil tank temperature, white or silver paint can be sprayed on the tank to reflect the heat radiation of the sun, so as to restrain the change of oil temperature in the tank. In addition, spray systems can also be installed on the outside of the tank. When the temperature is high, the cooling water can be sprayed to reduce the temperature of the tank and reduce oil-gas pollution.

3.4. Adopt nitrogen sealing technology
The most effective way to inhibit the evaporation of light oil is inert gas protected. Inert gas is introduced into the tank to increase the pressure of oil-gas, thereby inhibiting the volatilization of low boiling point oils and reducing the emission of harmful gases. The nitrogen system in the refinery provides support for nitrogen protection of storage tanks. Through the nitrogen pipeline, the tank can
be connected to other tanks, when the tank pressure is low, it can reduce the evaporation of oil by supplementing nitrogen.

4. Waste gas treatment technology
The control tank temperature, inert gas seal and other measures can reduce the volatilization of harmful gas to some extent, but inevitably some oil-gas will also be discharged into atmosphere. In order to prevent evaporation of oil-gas from polluting the atmosphere, it is necessary to dispose the exhaust gas from the oil tank. The main processing technologies include absorption, adsorption, condensation, biodegradation and catalytic oxidation and so on.

4.1. Absorption
Absorption is based on those substances forming similar intermolecular attraction, which can be dissolved by each other to transfer harmful substances from oil-gas phase to liquid phase. The choice of absorbent is the key to absorption technology. Surfactants can be added to the absorbent to improve the solubility of the absorbent to contaminants. At present, absorption methods mainly include alkali absorption, organic amine absorption, low temperature distillate oil absorption and so on.

Alkali absorption is effective for sulfides such as hydrogen sulfide and mercaptan, which are absorbed in the alkali absorber. The common alkali is sodium hydroxide solution. Alkali absorption can remove most of the sulfides in low-concentration exhaust gas, but almost no purification effect on hydrocarbons. The absorption process for treating refinery exhaust gas is simple and easy to operate. However, with the continuous absorption of waste gas, the absorption efficiency decreases slowly. Besides, the desulfurized liquid that can not be regenerated becomes a new waste pollutant, resulting in second pollution.

The low-temperature distillate absorption method is to absorb the exhaust gas emitted from the storage tank in a low temperature absorption tower. The absorbents can be diesel or other distillates. The low-temperature distillate absorption technology not only absorbs sulfides in the exhaust gas but also has high absorption efficiency for hydrocarbons. This technology has achieved the dual function of odor control and oil recovery, and has a high removal rate of non-methane hydrocarbons in the exhaust gas.

4.2. Adsorption
Adsorption technology is widely used in refinery waste gas treatment. By this technology, adsorbents are used to adsorb molecules of VOCs and malodorous substances to achieve purification of exhaust gas. The adsorption technology is relatively simple, with emphasis on the selection of adsorbent materials. The adsorbent should have a dense pore structure, a large inner surface area, and a stable chemical property. Appropriate material can effectively improve the adsorption efficiency. Commonly used adsorbents include carbon-based adsorbents, oxygen-containing adsorbents, etc.

The adsorption technology for treating oil-refinery waste has variable temperature adsorption and pressure swing adsorption. This technology is suitable for less treating amount, low concentration and low pressure.

4.3. Condensation
Gaseous pollutants have different saturation vapor pressures at different temperatures and pressures. Because of this property, organic pollutants from oil tank can be extracted by reducing temperature or increasing system pressure, so that exhaust gas can be purified. In general, Application of the condensation technology requires the very low temperature and ultra high pressure, which will greatly increase the cost and difficulty of processing. Condensation technology is mainly used hence to treat organic waste gas with high concentration and recovery value. In order to achieve the balance between exhaust gas treatment efficiency and operational cost, condensation technology is often used in combination with adsorption, combustion or other purification techniques.
4.4. Biodegradation
Biodegradable refinery waste is the microbial degradation of pollutants into small organic molecules, non-hazardous inorganics. It is necessary to select different microbial strains and suitable treatment conditions for dealing with different pollutants. According to the different purification equipment, biodegradation can be divided into: biofilter, biotrickling filter and bio-scrubber. Biodegradation of refinery exhaust gas has attracted more and more attention due to its advantages of simple operation, low operating cost, and low secondary pollution. It's important to point out that for multi-component and complex malodorous gases, the biodegradation capabilities of microbial is low, and the recovery period is longer after the death of microbial bacteria.

4.5. Catalytic oxidation
The principle of catalytic oxidation is organic waste gas was oxidized by oxygen in the presence of catalyst, harmless substances such as water and carbon dioxide are produced. The key of catalytic oxidation technology is the choice of catalyst. In practice, appropriate cocatalysts can be added to increase the catalytic performance. It has that advantage of mild reaction condition, multiple harmful gases and no secondary pollution. However, the catalyst is difficult to fix and has catalyst deactivate issue. In the treatment of the refinery gas, catalytic oxidation technique has utilized of its mild reaction conditions, no secondary pollution, and high removal efficiency and so on to deal with a variety of harmful gas.

5. Conclusion
With the progress of science and technology, newest application of waste oil gas pollution control isinnovated constantly. Because of polluting emissions constantly changing everywhere, which includes composition, concentration and flow and so on, Utilizing of single technology is difficult to effectively treat refinery waste gas. In recent years, some combination technologies have developed rapidly, such as low-temperature diesel-alkali absorption, adsorption-membrane separation, absorption- incineration, low-temperature diesel absorption- alkali washing- catalytic oxidation. At present, the important research on waste gas treatment focuses on how to turn refinery waste gas into valuable substances, and how to economically achieve simultaneous processing and recycling.

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