Summary of VOCs Treatment Technology in Product Oil Depot

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Abstract: With the continuous development of social industry and economy, environmental problems are increasingly prominent. The problem of VOCs emission treatment needs to be solved. This paper introduces the source and harm of oil vapor produced in oil depot, and expounds the treatment measures of VOCs. The treatment measures of storage tank are introduced. The principle and research progress of four kinds of recovery processes are described. The development mode and research direction of VOCs treatment in oil depots in the future are prospected, the importance of oil vapor recovery is pointed out, and the recovery technology of VOCs should be developed in the direction of intelligence, integration, miniaturization and energy saving.

1. Introduction

China has become a big country of oil consumption, and oil storage tanks are becoming large-scale. Petroleum and its products are mixtures of various hydrocarbons, in which the light components are highly volatile under normal temperature with high vapor pressure. Therefore, in the process of oil storage and transportation, the storage tank will generate a large number of gaseous hydrocarbon VOCs (commonly known as oil vapor) due to temperature and pressure fluctuations. On the one hand, the unorganized discharge of VOCs will bring huge economic losses to the petrochemical industry, at the same time, to a certain extent, it has affected the rational utilization of energy in petrochemical industry, on the other hand, it has caused serious pollution to the atmospheric environment and the natural environment on which people depend [1,2]. Therefore, oil vapor volatilization treatment has become the key content in the application of oil resources.

In 2019, the apparent consumption of refined oil in China was 329.61 million tons, a year-on-year increase of 1.4%. According to the calculation of the oil vapor volatility coefficient in the process of storage and transportation of refined oil in China, the annual loss of oil vapor volatility is about 2.64 million tons. Therefore, oil vapor recovery has great economic value and potential market.

VOCs in the oil depot mainly come from large and small breathing of the tank, emptying of the tank, working loss of the tank farm, leakage of dynamic and static seals and open pipelines, loss under abnormal working conditions, etc. As one of the most important VOCs emission sources in the oil
depot, the tank mainly includes fixed roof tank, internal floating roof tank and external floating roof tank [4].

2. VOCs control measures and technologies for product oil depot

2.1. Source control of storage tank

According to the guide for VOCs Pollution Source Investigation in petroleum industry, the total loss of floating tank can be divided into edge sealing loss, discharge loss, floating plate attachment loss and floating plate joint loss, among which edge sealing loss, floating plate attachment loss and floating plate joint loss belong to static loss and wall hanging loss belongs to work loss [5]. The type selection and edge sealing of the floating plate will significantly affect the VOC emission of the tank. The floating plate is generally divided into pontoon type and pontoon type, which is composed of framework, cover plate, coaming, casing of oil measuring pipe, anti rotation pipe, automatic vent, transition casing, buoyancy unit and sealing device. The edge seal of floating plate is divided into primary seal and secondary seal. Most of the primary seals are sealed with elastic packing. For large floating roof tanks, in order to further reduce oil vapor volatilization, a sealing device will be added to the primary seal, i.e. secondary seal. The secondary seal is mainly sealed by L-shaped elastic plate and nylon rubber film to prevent oil gas volatilization and rainwater from entering the storage tank [6-8]. The VOCs emission of fixed roof storage tank is mainly divided into two parts: the first is evaporation loss in the process of static storage, i.e. small breathing loss; the second is working loss in the process of receiving and delivering materials, i.e. large breathing loss [9]. Emission reduction measures for storage tank mainly include reducing the temperature inside the storage tank, painting the surface of the storage tank with white or aluminum reflective coating, and adopting high-efficiency thermal insulation materials if necessary, Control the feeding temperature to avoid high temperature operation in summer. Adjust the working time to night, install sunshade and spray water cooling system to reduce the impact of sunlight on the oil and gas temperature in the tank; install breathing valve and nitrogen sealing system, and install breathing valve and nitrogen sealing system in the tank, because the supplement and elimination of nitrogen replace part of the oil vapor discharged from the tank; advocate the use of internal floating roof tank It can effectively reduce the evaporation of oil products; improve the structural design of the tank, so as to reduce the steel consumption as much as possible while increasing the pressure of the tank [9-11].

Chen Hui et al. [12] made an in-depth and comprehensive analysis on the design mode of the liquid level switch of the mechanical floating roof tank, and explored the application effect of the new type of liquid level switch. By analyzing and optimizing the performance of the liquid level switch of oil storage tank, the purpose of safety and environmental protection is realized. Liu Tiechuan et al [13] proposed the application of wireless detection equipment for combustible gas in oil depot, with the detection accuracy of 90% - 95%, which solved the problem of gas monitoring between sealing layers of floating roof storage tank.

2. Development status of oil vapor recovery and treatment technology

In the current oil and gas storage and transportation process, the more common oil vapor recovery technologies mainly include the following basic categories [14-16].

2.2.1. Adsorption method. In oil and gas transportation, adsorption is the most common and general oil vapor recovery technology. The adsorption of adsorbent is used to extract the hydrocarbons in the air, which is used to classify and recycle the hydrocarbons. Adsorption is generally a process of recovery of oil vapor by using substances with similar affinity to the chemical composition of hydrocarbon. Activated carbon is the most commonly used material for adsorption method, without high purchase cost. The data shows that the adsorption capacity of hydrocarbon composition of activated carbon is about 34%, and activated carbon has the advantage of reuse, so low-cost activated carbon is one of the most commonly used adsorbents for adsorption method. Chen Meng [17] of China University of
petroleum modified activated carbon fiber by experiment and analyzed its absorption and desorption performance for oil vapor. After KOH modification, the adsorption performance of activated carbon fiber to oil vapor is improved, and the penetration adsorption capacity is 23.2% higher than the original. After high temperature modification, the penetration adsorption capacity of activated carbon fiber to oil vapor increased by 37.2%. Li Shisheng et al. [18] studied the structure and properties of the commercial activated carbon before and after treatment by activation and hydrogen reduction, N₂ adsorption, IR, element analysis and other characterization methods, and explored the influence of the surface and pore structure characteristics of the activated carbon on its oil vapor adsorption performance. The results show that the pore structure and oxygen-containing groups on the surface of activated carbon change after high temperature steam activation and hydrogen reduction treatment, which has a great influence on the oil-gas adsorption performance of activated carbon and improves the oil-gas adsorption capacity.

2.2.2. Condensation method. It mainly adopts the basic principle of gas condensation and liquefaction. During the transportation and storage of oil and gas, oil and gas can be volatilized into gas. The staff needs to cool down and condense according to the environment they are in, and change the gas oil and gas condensation into liquid, so as to reduce the volatilization of oil and gas and improve the utilization rate of oil and gas. Although the principle of recovery of oil vapor resources by condensation is simple, the operation is difficult. The installation of condensation method has high requirements on the environment, and the recovery of oil vapor is facing many challenges. However, in the storage of oil and gas resources, the recovery of oil vapor resources by condensation method is still unable to promote the smooth progress of the recovery process. The operation of condensation method is not convenient and the recovery effect is not ideal. Huang Weiqiu et al. [19] used Aspen simulation software to study the relationship between the oil vapor recovery rate of condensation method and system energy consumption, and optimized the condensation recovery process. It was found that the three-stage refrigeration process should be adopted with the refrigeration temperature of 2 ℃, -30 ℃ and -120 ℃ respectively. Qin Xiuyu et al. [20] used Aspen Plus simulation software to study the influence of the state equation of water bearing oil vapor and the selection of effective phase state on the simulation sensitivity of condensation, and optimized the existing three-stage condensation process to improve the oil vapor recovery rate of condensation process. Bi Jinbin et al. [21] simulated and optimized the three-stage condensate recovery process by using Aspen Plus process simulation software, providing guidance for the actual production process. Yang Ruihua et al. [22] used Aspen HYSYS, a large-scale chemical process simulation software, to simulate and analyze the condensation characteristics of two kinds of oil vapor, obtained the change rule of non methane total hydrocarbon content in oil vapor at different temperatures, analyzed the influencing factors of oil vapor recovery rate, optimized the condensation temperature of the middle cooling stage, so as to achieve the lowest total energy consumption of the refrigeration unit.

2.2.3. Absorption method. There are two main methods: normal temperature and atmospheric pressure absorption method and normal pressure and low temperature absorption method. In the recovery process, different types of absorbents should be selected in the absorption tower, and the volatile oil vapor resources can also be sprayed with the absorber on the top of the tower to fully dissolve the oil and gas resources and strengthen the oil and gas recovery effect. Xiehongyan [15] measured the phase equilibrium data of the binary system of organic soluble absfov97 isopentane (the most abundant component in oil and gas) with a small vapor-liquid double circulation equilibrium kettle, and used the regression calculation function of ProII software to fit the parameters of PR model. Finally, the optimization design of the process is carried out from the theoretical plate number, desorption temperature, liquid gas feed mass ratio of absorption tower and absorbent. Dong Junbo et al. [23] used Pro II large-scale process simulation software to simulate and optimize the oil vapor recovery system, and analyzed the influence of the liquid inlet volume of the absorption tower, the inlet pressure of the vacuum pump and the theoretical plate number of the absorption tower on the oil vapor recovery rate
and tail gas concentration, all of which increased the oil vapor recovery rate from 95.1% to 98.7% and greatly reduced the cost. Koujie et al [24] designed the oil vapor recovery technology scheme based on low-temperature absorption and thermal storage oxidation, which has better oil vapor absorption capacity and treatment effect, and solved the problem of single oil vapor recovery technology in emission standard.

2.2.4. Membrane separation. When recovering oil vapor, the volatile oil and gas resources should be attracted to the inner part of the gas holder first. The gas holder is equipped with multi-layer film materials with various apertures. The molecular diameter of the oil vapor components is greatly different. During the process of passing through the gas holder, the molecules will be separated under the action of the film. With the above method, the water vapor and oil gas of oil vapor resources can be separated automatically, and then can be discharged into the atmosphere smoothly without affecting the ecological environment, which provides many conveniences for the treatment and recovery of oil vapor resources. Membrane separation technology is a kind of oil vapor recovery technology, which has been widely used in the process of oil and gas storage and transportation. Chen Chuan et al [25] prepared a hollow fiber composite membrane, which improved the gas extraction efficiency. Yang Chengcheng [26] participated in the development of perfluroinated (AF) glass composite membrane for small treatment capacity, low concentration (the inlet oil vapor volume concentration is only 10% - 30%) of the mixed gas treatment effect can meet the requirements of gas station emission index.

At present, the integration of several single recycling methods and the joint use of multiple recycling methods are the trend of future technology development. The process of condensation + adsorption [27, 28] is used, i.e. the oil vapor enter the oil vapor recovery unit through the gas phase pipeline for condensation and liquefaction recovery, and then through the high-efficiency adsorption and separation of activated carbon, the condensed oil liquid is delivered to the storage tank through the return pump. This method can eliminate the hidden danger of temperature rise in adsorbent bed of single adsorption method, has strong system independence, large operation flexibility, low energy consumption and investment compared with single condensation method, good economic benefit, convenient skid mounting, convenient transportation and installation, small floor area, suitable for the treatment of high concentration and large amount of volatile oil vapor. Changling Petrochemical Co., Ltd. [29] combined with the characteristics of highway truck loading oil, adopted the combined process of "condensation + membrane separation + adsorption" oil vapor recovery, and solved the problem of oil vapor leakage after refitting and operation. Hu Jiacheng [30] simulated several oil vapor processes by Aspen Plus, and put forward the oil vapor recovery combined process of absorption + membrane separation + adsorption, which has good economic benefits while meeting the national standards and enterprise requirements. Jinghaibo et al. [31] integrated with catalytic combustion and ammonia absorption refrigeration, the oil gas condensation adsorption recovery system can reduce energy consumption by about 30% when the recovery rate is only reduced by about 2%, realizing a significant reduction in energy consumption.

3. Research focus and development trend
To sum up, for the oil and gas storage and transportation process, the existing oil and gas volatilization problem is the core content that needs to be checked, which not only needs to control the source to reduce the volatilization emission of oil and gas as much as possible, but also needs to focus on the effective treatment around the oil and gas recovery technology, improve the oil vapor recovery level to solve the problem of energy waste and environmental pollution in the process of oil and gas storage and transportation.

In the future research, we should increase the research and development of adsorbent, absorbent, refrigerant and other materials. We should actively study high-precision recovery devices and design automatic and intelligent recovery devices. We should adopt scientific methods according to the unique characteristics of gas to optimize the recovery process facilities with high precision and high
integration and meet the related requirements of high recovery rate, low cost and low energy consumption. We will continue to improve recycling technology and optimize process design.

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