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Comprehensive Analysis of Nitrogen Oxide Treatment Methods in Nitric Acid Exhaust Gases

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Abstract: This paper provides an in-depth examination of various methods for treating nitrogen oxides (NO_X) in nitric acid exhaust gases, a significant environmental concern in industrial pollution management. The study analyses several techniques, including Selective Catalytic Reduction (SCR), Non-Selective Catalytic Reduction (NSCR), water absorption, dilute nitric acid absorption, alkaline solution absorption, extended absorption method, and adsorption methods (both conventional and pressure swing adsorption). Each method's principle, efficiency, and practical challenges are discussed, highlighting their advantages and limitations. The paper aims to offer insights into the selection of appropriate NO_x treatment technologies based on specific industrial needs, environmental impact, and economic considerations, contributing to the development of more sustainable Industrial practices.

1. Introduction

The main atmospheric pollutants in our country are sulfur dioxide (SO2), followed by nitrogen oxides (NO_X). This is because in the industrial production of dilute nitric acid, ammonia is almost always first oxidized to a NO_X mixture gas, which is then absorbed using water or low-concentration nitric acid. Due to the unique chemical properties of NO_X, the nitric acid absorption tower cannot completely absorb it, and a certain concentration of NO_X is always emitted with the exhaust gas. Although the amount of NO_X emitted from nitric acid production accounts for only a small part of the total NO_X industrially emitted into the atmosphere, its relatively concentrated discharge causes significant local environmental damage and poses serious health risks to humans[1]. Therefore, it is necessary to treat the nitrogen oxide tail gas generated in the production of nitric acid. This article mainly summarizes several methods of nitrogen oxide treatment and analyses their advantages and disadvantages.

2. Catalytic Reduction Method

Catalytic reduction is the earliest widely used method for treating nitric acid exhaust gases in the industry. This method involves adding a reducing agent to reduce the exhaust NO_X to nitrogen gas and water. Depending on whether the added reducing agent selectively reacts with NO_X, catalytic reduction methods are divided into selective catalytic reduction (SCR) and non-selective catalytic reduction (NSCR).

2.1. Selective Catalytic Reduction Method

Selective catalytic reduction uses ammonia as a reducing agent. That is, under the action of a catalyst, ammonia selectively reacts with oxygen in NO_X and not with oxygen in other forms. Ammonia undergoes selective primary reactions with NO_X gas, and at appropriate temperatures, ammonia does not react with oxygen.

$$4NH_3 + 6NO = 5N_2 + 6H_2O \tag{1}$$

$$8NH_3 + 6NO_2 = 7N_2 + 12H_2O \tag{2}$$

$$2NH_3 + NO + NO_2 = 2N_2 + 3H_2O \tag{3}$$

At higher reaction temperatures, due to the presence of about 3% oxygen in the exhaust gas, the following side reactions also occur:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \tag{4}$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O \tag{5}$$

$$2NH_3 = N_2 + 3H_2 \tag{6}$$

Within a certain temperature range, the reaction rate of ammonia with NO_x is much faster than the oxidation rate of ammonia (reactions 4, 5, 6), thus allowing the reaction to be controlled and selective. When the NO/NO_2 (molar ratio) is 1, the process is primarily governed by reaction (3). At this point, the conversion rate of NO_X is the highest. The above reactions occur under the conditions of 200-350 ℃, using transition metal catalysts such as oxides of iron, chromium, vanadium, molybdenum, tungsten, or noble metals like platinum, palladium, rhodium, and ruthenium.

2.2. Selective Catalytic Reduction Method

This method employs hydrogen and natural gas as reducing agents for non-selective catalytic reduction.

$$2NO_2 + 4H_2 = N_2 + 4H_2O \tag{7}$$

$$2NO + 2H_2 = N_2 + 2H_2O \tag{8}$$

$$2H_2 + O_2 = 2H_2O \tag{9}$$

$$CH_4 + 4NO_2 = 4NO + CO_2 + 2H_2O \tag{10}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{11}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{12}$$

The characteristic of the non-selective catalytic reduction process is that during the reaction process[2], the exhaust gas is first directly heated to 400 ℃ by combustion with fuel, and the NO_X in the exhaust gas undergoes catalytic reaction with the fuel, as does the O_2 in the exhaust gas. The exit temperature of the reactor is 670 ℃. The catalysts used in this process are noble metals such as palladium or platinum, loaded on an alumina carrier, with palladium content ranging from 0.1% to 0.5% (wt). The fuel gases used are natural gas (mainly methane), hydrogen, and can also include hydrocarbons, carbon monoxide, etc.

3. Water Absorption Method

Water can react with NO_2 to produce nitric acid and NO, but NO does not react with water and has a very low solubility in water, therefore, the efficiency of water absorption method under normal pressure is not high. In water, NOx (mainly NO_2) reacts with water to form nitric acid (HNO_3) and nitrous acid (HNO_2):

$$2NO_2 + H_2O = HNO_3 + HNO_2 \quad (13)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad (14)$$

In actual industrial processes, the gas is usually directed through one or more absorption towers, which are filled with water or dilute nitric acid. The gas contacts the descending liquid during its ascent, thereby increasing the gas-liquid contact area and improving the absorption efficiency of NOx. This method is relatively simple, but it is almost ineffective for the absorption of NO.

4. Dilute Nitric Acid Absorption Method

The solubility of NO in nitric acid with a concentration above 12% is 100 times greater than in water, making it effective for the removal of NO from gas sources with high NO content. Therefore, the dilute nitric acid absorption method can be used for the treatment of nitric acid exhaust gases. In the process, the removal efficiency of NO_X can be enhanced by increasing the absorption pressure, lowering the absorption temperature, employing oxygen-rich oxidation, and controlling the residual oxygen concentration. Dilute nitric acid is used as the absorption medium in this method. Compared to water, dilute nitric acid can more effectively absorb and convert nitrogen oxides, as it provides additional nitrate ions (NO_3^-) which aid in the chemical conversion of NO_X. Gaseous NO and NO_2, when contacting dilute nitric acid, undergo chemical reactions to form more nitric acid. The main chemical reactions are:

$$2NO_2 + H_2O = HNO_3 + HNO_2 \quad (15)$$

$$3NO_2 + H_2O = 2HNO_3 + NO \quad (16)$$

$$NO + NO_2 + H_2O = 2HNO_2 \quad (17)$$

$$2HNO_2 + O_2 = 2HNO_3 \quad (18)$$

In actual operation, the exhaust gas first passes through one or more absorption towers. These towers are filled with dilute nitric acid, ensuring that the gas fully contacts the descending dilute nitric acid during its ascent, thus improving the absorption efficiency of NO_X. The efficiency of the absorption process is affected by temperature. Generally, a lower temperature is conducive to improving the absorption efficiency of NO_X, so the temperature of the absorption tower is usually controlled. The nitric acid obtained through the dilute nitric acid absorption method can be further concentrated and purified to prepare higher concentration nitric acid, thereby effectively utilizing resources. The nitric acid obtained through the dilute nitric acid absorption method can be further concentrated and purified to prepare higher concentration nitric acid, thereby effectively utilizing resources.

5. Alkaline Solution Absorption Method

The alkaline solution absorption method typically employs alkaline solutions such as sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), or potassium hydroxide (KOH). These alkaline solutions can effectively react chemically with nitrogen oxides[3].

$$NO + NO_2 + Na_2CO_3 = 2NaNO_2 + CO_2 \quad (19)$$

$$2NO_2 + Na_2CO_3 = NaNO_2 + NaNO_3 + CO_2 \quad (20)$$

$$2NO + O_2 = 2NO_2 \quad (21)$$

$$2NO_2 + 2NaOH = NaNO_2 + NaNO_3 + H_2O \quad (22)$$

$$NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O \quad (23)$$

The salts obtained through the alkaline solution absorption method (such as sodium nitrate, sodium nitrite, etc.) can be further processed and utilized, or treated as waste. The alkaline solution absorption method is simple and effective, but it may produce solid waste that requires further processing, and the cost of the alkaline solution also needs to be considered.

6. Extended Absorption Method

Hebei Cangzhou Dahua Group uses a combination of the extended absorption method and the non-selective reduction method for exhaust gas treatment. This method is designed based on the process characteristics of Shuangfeng Company[4], mainly utilizing the waste liquid in the synthesis of ammonia—carbonization mother liquor—to absorb exhaust gas. The product can be sold as fertilizer, and the process is simple, economical, and easy to operate. The main reaction equations are:

$$(NH_4)_2CO_3 + 2NO = NH_4NO_3 + NH_4NO_2 + CO_2 \quad (24)$$

$$(NH_4)_2CO_3 + NO_2 + NO = 2NH_4NO_2 + NO_2 \quad (25)$$

7. Adsorption Method [5]

7.1. Conventional Adsorption Method

The conventional adsorption method, as opposed to pressure swing adsorption, utilizes porous adsorbents to absorb NO_X from nitric acid tail gas for purification purposes. Common adsorbents include activated carbon, molecular sieves, and silica gel. Activated carbon has a strong adsorption capacity for NO_X. The desorbed NOx can be returned to the front end of the nitric acid production system. Using special activated carbon, NO_X can also be reduced to N_2. However, the low ignition point of activated carbon poses significant challenges for its regeneration, limiting its use. Molecular sieves have strong selective adsorption capabilities for NO_2 and water. The two adsorb onto the internal surface of the molecular sieves, forming nitric acid and releasing NO, which, along with the NO and O_2 in the exhaust gas, is catalytically oxidized to NO_2 on the molecular sieve and then adsorbed.

7.2. Pressure Swing Adsorption Method

Pressure swing adsorption utilizes the characteristic of solid adsorbents to selectively adsorb different gases under certain pressures, achieving gas separation. The separation of NOx is based on the differential adsorption capacity of NO_X on specialized adsorbents compared to other components in the exhaust gas. At room temperature, the NO_X in the exhaust gas is adsorbed by the adsorbent. The purified exhaust gas (N_2 and O_2) is released directly; the adsorbed NO_X is desorbed from the adsorbent through temperature elevation for regeneration and returned to the absorption tower to increase nitric acid production.

8. Conclusion

This paper has comprehensively explored various methods for treating nitrogen oxides (NO_X) in nitric acid exhaust gases, a significant concern in industrial pollution. We discussed the principles, advantages, and limitations of several techniques, including catalytic reduction (both selective and non-selective), water absorption, dilute nitric acid absorption, alkaline solution absorption, extended absorption, and adsorption methods (both conventional and pressure swing).

Selective Catalytic Reduction (SCR) and Non-Selective Catalytic Reduction (NSCR) methods utilize reducing agents like ammonia, hydrogen, and natural gas to convert NO_X into harmless nitrogen and water. SCR, in particular, shows high efficiency and selectivity under controlled conditions. However, challenges such as temperature sensitivity and catalyst selection are notable.

Water and dilute nitric acid absorption methods capitalize on the chemical reactions between NO_X and the absorbing medium to remove NO_X from exhaust gases. While effective, these methods have limitations regarding the absorption efficiency, especially for water absorption at normal pressure.

The alkaline solution absorption method, using substances like NaOH and Ca $(OH)_2$, presents a simple yet effective approach, though it generates solid waste that requires further treatment. The extended absorption method, employed by Hebei Cangzhou Dahua Group, integrates synthetic ammonia waste liquid for exhaust gas absorption, proving to be an economical and straightforward solution.

Lastly, adsorption methods, both conventional and pressure swing, offer an alternative approach. They use adsorbents like activated carbon and molecular sieves for NO_X removal. However, issues related to the regeneration of adsorbents, particularly for activated carbon, pose significant challenges.

In conclusion, while each method has its merits and demerits, the choice of a suitable NO_X treatment method depends on specific industrial requirements, environmental regulations, and economic considerations. Future research and development in this field could focus on enhancing the efficiency, reducing the costs, and minimizing the environmental impact of these methods to provide more sustainable solutions for NO_X emission control in nitric acid production.

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