

Research Progress on VOCs Treatment Technologies in the Petrochemical Industry

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Abstract: As a crucial pillar industry of China's economy, the petrochemical industry emits volatile organic compounds (VOCs) during production every year, which pose numerous potential hazards to the environment and human health. Starting from investigating current domestic and international VOCs treatment technologies, this paper systematically summarizes the shortcomings of existing VOCs treatment technologies, and focuses on introducing the application of new catalytic treatment technologies for VOCs in the petrochemical industry. It is expected to provide important references for the research and improvement of VOCs treatment technologies in the petrochemical industry.

Keywords: Petrochemical Industry; Volatile Organic Compounds; Treatment Technology; Catalysis.

1. Introduction

With the acceleration of China's industrialization process, the emissions of VOCs (volatile organic compounds) have been increasing year by year. In particular, the rapid expansion of small-scale petrochemical enterprises has intensified the difficulty of VOCs control in China. The State Council, in the Action Plan for Sustained Improvement of Air Quality issued in 2023, clearly stated the requirement of "focusing on the coordinated emission reduction of multiple pollutants such as VOCs and nitrogen oxides, and strengthening the comprehensive management of VOCs throughout the entire process and all links".

Similarly, the Work Plan for the Investigation and Rectification of Inefficient and Invalid Air Pollution Control Facilities (Draft for Comments) issued by the Ministry of Ecology and Environment also put forward the new requirement of "carrying out comprehensive investigation and rectification work, and implementing the principle of 'eliminating a batch, rectifying a batch, and upgrading a batch' for treatment technologies". Due to the wide variety of products in the petrochemical industry, in practice, it is necessary to comprehensively consider the entire route of "production raw materials - production processes - final products - end-of-pipe treatment", select appropriate VOCs treatment technologies, and formulate scientific and feasible VOCs control plans, so as to meet the requirements of relevant national, provincial and municipal authorities.

2. Analysis of VOCs in the Petrochemical Industry

2.1. Analysis of VOCs Sources in the Petrochemical Industry

In the petrochemical industry, the emission volume of VOCs varies depending on factors such as products, production processes, production equipment, and storage & transportation facilities. The total VOCs emissions from the chemical industry account for 36% of China's total VOCs

emissions [1], ranking first. First, during the production process, the main sources of VOCs—accounting for the highest proportion—include leaks from dynamic and static seals of equipment, emissions from process operations, emissions from cooling systems, flare emissions, sampling emissions, maintenance emissions, and accident-related emissions.

Second, during the storage and transportation process, the second-largest source of VOCs [2] consists of volatile losses from organic liquid storage and blending, volatile losses from loading and unloading, and losses from wastewater collection, storage, and disposal processes.

Third, there are maintenance emissions and accident-related emissions in the petrochemical industry [3]. Although the above-mentioned sources of VOCs in the petrochemical industry account for different proportions, most of them are unorganized emissions characterized by high concentration and large volume. Therefore, in view of these characteristics of the petrochemical industry, it is necessary to compulsorily strengthen measures to reduce VOCs emissions starting from the emission sources [4].

2.2. Analysis of VOCs Composition in the Petrochemical Industry

In the petrochemical industry, the "refining, storage, and transportation" of gasoline and naphtha are major sources of VOCs. The composition of these VOCs mainly includes alkanes, aromatic hydrocarbons, and oxygenated volatile organic compounds, accounting for 72.80%, 11.19%, and 8.39% respectively. Particularly due to the specific characteristics of the industry, these pollutants are key components of gasoline and diesel. They primarily originate from the volatilization of petroleum components in petrochemical wastewater; the second-largest component is olefins, which are associated with ethylene-industrial product manufactured by petrochemical enterprises. VOCs can be further categorized into subclasses such as oxygenated VOCs, nitrogen-containing VOCs, sulfur-containing VOCs, and halogenated VOCs. This category of VOCs contains large

quantities of substances that easily induce the formation of haze and photochemical smog, and they tend to cause irreversible harm to the human body, such as inducing cancer.

3. VOCs Catalytic Oxidation Method

The catalytic oxidation method refers to a degradation process where volatile organic compounds (VOCs) undergo oxidative decomposition through reactions with oxidants or auxiliary combustion agents at relatively low temperatures (generally below 400°C) under the action of a catalyst. Compared with the thermal oxidation method, catalytic oxidation has a distinct advantage of operating at low temperatures, which significantly reduces the operating cost of VOCs removal. Among all factors, high-efficiency and low-cost catalysts are the key to VOCs removal via the catalytic oxidation method.

The manuscript should include a conclusion. In this section, summarize what was described in your paper. Future directions may also be included in this section. Authors are strongly encouraged not to reference multiple figures or tables in the conclusion; these should be referenced in the body of the paper.

Currently, industrial catalysts for VOCs treatment are mainly noble metal catalysts with high activity. However, due to their high cost, some transition metal oxide catalysts have been developed for treating certain industrial waste gases. Under specific conditions, the catalytic activity of these transition metal oxide catalysts can be comparable to that of noble metal catalysts. For instance, Liang et al. [5] synthesized a transition metal oxide Cr_2O_3 thin-film catalyst using the CVD (Chemical Vapor Deposition) method; the ignition temperature of this catalyst for propylene is approximately 250°C, which is lower than that of the noble metal Pt catalyst. Mountapmbeme Kouotou et al. [6] prepared Co_3O_4 , which can achieve 50% removal of olefin-based VOCs at 300°C-nearly 50°C lower than the 349°C required for 50% VOCs removal by the noble metal catalyst $\text{Au}/\text{Al}_2\text{O}_3$.

In recent years, composite oxide catalysts have also become a research focus, and experiments have confirmed that such catalysts exhibit excellent catalytic performance and broad application prospects. Examples include the CoMnOx bimetallic oxide catalyst developed by Tian et al. [7], as well as the Cu-Co and Cu-Fe-Co ternary metal oxide catalysts prepared by Achraf [8] and Waqas et al. [9], respectively.

4. Multi-technology Coupling

Purely a single method is rarely adopted for VOCs removal. Instead, multiple technologies often need to be coupled to meet the complex operating conditions of VOCs emissions and achieve efficient VOCs abatement. Examples include adsorption coupled with catalytic combustion for treating waste gas in the coating industry[10], adsorption combined with condensation recovery for oil and gas recovery[11], plasma coupled with photocatalysis for toluene removal in the coating industry[12], and the application of adsorption coupled with concentration technology in circulating fluidized beds[13]. Currently, the commonly used technologies in China's market mainly focus on adsorption and combustion, while photocatalytic technology and plasma technology are regarded as future research directions. Compared with China, the mainstream technologies in developed countries abroad also include biological methods in addition to adsorption and combustion. In terms of

adsorption, activated carbon is preferred in China, whereas molecular sieves are favored overseas. For combustion, thermal combustion or regenerative combustion is generally used in China, while developed countries tend to adopt the more costly regenerative thermal oxidation (RTO) technology, with more mature production and application technologies for regenerator materials.

In recent years, multi-technology coupling has emerged as a research hotspot in the field of efficient VOCs abatement, with relevant studies systematically exploring the process optimization, synergistic mechanisms, and industrial applications of different coupling systems. The researcher proposed a novel catalytic strategy combining competitive adsorption with dual-functional sites. By constructing catalytic materials with both acid and oxygen sites, they successfully eliminated dimethyl sulfide, a secondary malodorous pollutant generated during the degradation of sulfur-containing VOCs, providing a new pathway for the treatment of malodorous sulfur-containing VOCs[14]. The MnCoO_x composite oxide catalysts were exhibited excellent catalytic oxidation performance in multi-component VOCs systems, achieving 100% conversion of benzene and toluene as well as 100% CO_2 selectivity at 300°C and 350°C, while clarifying the synergistic degradation mechanism[15]. The modified Co_3O_4 catalysts via a C-N co-doping strategy, revealing the synergistic effect of non-metallic elements in enhancing catalytic redox capacity and water resistance, which provides insights for the development of new catalysts for VOCs treatment under humid conditions[16]. In terms of technical coupling processes, A designed condensation-adsorption coupling process for treating high-concentration VOCs from the dry-cleaning industry, achieving a removal efficiency of 98.5% with long-term operational stability[17]. A non-thermal plasma-wet scrubber coupling system effectively addresses the limitations of single technologies, such as excessive byproducts and low removal efficiency, achieving a maximum removal rate of 99.9% for odorous VOCs[18]. The microwave-assisted adsorption-catalytic combustion dual-bed system enables efficient desorption and catalytic combustion of VOCs under humid conditions, substantially reducing catalyst dosage and treatment costs[19]. The synergistic enhancement effect of plasma-photocatalysis coupling technology on mixed pollutants in an atmospheric-pressure tubular reactor and revealed the in-situ regeneration mechanism of the catalyst[20]. Additionally, the progress of coupling microbial electrochemical systems with photocatalysis, biotrickling filtration, and other technologies, were reviewed, providing theoretical support for the upgrading of biological VOCs treatment technologies[21]. These studies cover key directions such as catalytic material modification, multi-process coupling integration, and adaptation to different operating conditions, laying a solid foundation for the industrial application of multi-technology coupling in VOCs abatement.

5. Conclusion

The petrochemical industry features complex production processes, numerous VOCs emission sources and nodes, and great difficulties in comprehensive control. VOCs emissions can be reduced at the source by selecting low-volatility raw materials, improving processes, and optimizing equipment selection. Additionally, it is necessary to strengthen refined management throughout the entire production process, further

advance LDAR technology, and select appropriate treatment technologies based on the characteristics of VOCs in petrochemical enterprises to meet the requirements of VOCs emission reduction.

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