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Advanced Strategies for Hydrogen Sulfide Utilization and Sulfur Recovery: A Comprehensive Study

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Abstract: This paper investigates the treatment and utilization of hydrogen sulfide (H_2S) in natural gas and petrochemical industries. Focusing on low-temperature methanol washing and the Claus process, we analyze their operational principles, benefits, and limitations. Low-temperature methanol washing is recognized for its low energy requirements and wide applicability, but is constrained by methanol's toxicity and difficulties in processing heavy hydrocarbons. The Claus process, conversely, offers an effective sulfur recovery method with a high rate of efficiency, yet it is energy-intensive. Additionally, the study explores the H_2S Methane Reforming (H_2SMR) technology for direct conversion of H_2S into hydrogen and carbon disulfide, highlighting its potential in enhancing resource utilization. The paper emphasizes the role of catalysts in optimizing these processes, suggesting the need for further research in catalyst development and process integration for improved sustainability and efficiency in H_2S treatment.

1. Introduction

The increasing global emphasis on environmental sustainability and green energy has led to a surge in the exploration and development of natural gas. This expansion, however, brings to the fore the challenges associated with the presence of hydrogen sulfide (H_2S) in gas fields, particularly those with high sulfur content. The extraction and processing of such gases not only pose significant safety hazards but also contribute to corrosion issues in pipelines and equipment, necessitating the development of efficient and safe H_2S treatment methods. This paper aims to provide a comprehensive overview of the current state-of-the-art technologies and research advancements in the field of H_2S treatment and utilization. We explore various desulfurization techniques, their mechanisms, and efficiencies, alongside emerging methods for converting H_2S into valuable by-products. The focus is on ensuring safety, minimizing environmental impact, and maximizing the economic viability of these processes, addressing both current applications and potential future developments in this critical area of environmental engineering and energy resource management.

2. Activated Carbon Adsorption Desulfurization

Activated carbon, as a solid hydrogen sulfide treatment agent, performs desulfurization in the presence of oxygen. Hydrogen sulfide is catalytically oxidized to elemental sulfur on the quinone and phenolic groups of the activated carbon surface, disrupting the adsorption equilibrium and significantly enhancing its desulfurization capacity. The reaction process is as follows [1]:

$$\text{Adsorption: } 2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (1)$$

$$\text{Regeneration: } (AMA4)_2S + nS \rightarrow (AMA4)_2Sn+1 \quad (2)$$

Ammonium polysulfide solution is decomposed back into sulfur and hydrogen sulfide through steam heating. However, if activated carbon is impregnated with transition metals, its catalytic activity is significantly enhanced. Additionally, the activated carbon method is very simple to operate, and the recovered sulfur can be very pure. This method does not cause secondary pollution, offering the advantage of zero atmospheric emissions.

3. Wet Desulfurization

Wet desulfurization removes H_2S through the contact of the absorption liquid with the raw gas, suitable for gas streams with large flow rates and high H_2S concentrations. Wet desulfurization mainly includes low-temperature methanol washing, alcohol amine method, liquid phase catalytic oxidation, and alkali solution absorption, etc.

3.1. Low-Temperature Methanol Desulfurization

The low-temperature methanol desulfurization method is a physical desulfurization process developed jointly by Germany's Linde AG and Lurgi GmbH. It leverages the property of methanol's vastly different solubility in hydrogen sulfide (H_2S) at varying temperatures. The absorption of H_2S is conducted at low temperatures and high pressure (-70 to -40 ℃, 3 to 8 MPa), and desorption is achieved at high temperature and low pressure. Low-temperature methanol washing has the advantages of low energy consumption, good stability, and low cost. It is widely used in coal chemical industry, natural gas purification, synthetic ammonia, and other fields, with over 100 sets of low-temperature methanol washing units in operation globally [2]. However, its application is somewhat limited due to issues such as the toxicity of methanol, high investment in refrigeration equipment, and difficulties in separating heavy hydrocarbons in the feed.

3.2. Alkanolamine Desulfurization

The alkanolamine method is the most mature desulfurization technology, widely used in Claus tail gas treatment, removal and enrichment of high-pressure acid gases, etc. [3]. Its principle involves the basic amino groups in organic alkanolamine compounds reacting with H_2S. H_2S is adsorbed at low temperatures and high pressure, and desorbed by heating and reducing the pressure, thereby achieving the adsorption of H_2S and the regeneration of the absorbent. Conventional alkanolamine methods use solvents like monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA). MDEA, due to its stronger selective adsorption and stability for H_2S, has become the mainstream choice for large-scale deep desulfurization and decarbonization.

3.3. Liquid Phase Catalytic Oxidation

The liquid phase catalytic oxidation method transforms H_2S into sulfur through an absorbent under the action of a catalyst, with the catalyst being regenerated after oxidation. Depending on the type of catalyst, this method is mainly divided into arsenic-based, vanadium-based, and iron-based categories. The LO-CAT technology [4] uses an iron ion complex as the catalyst and KOH solution as the absorbent to convert H_2S into sulfur. It has the advantages of strong raw material adaptability, high desulfurization efficiency, few by-products, and low energy consumption. It is gradually replacing the vanadium-based processes dominated by the Stretford method but is mostly applied overseas due to its higher investment costs. Alkali solution absorption, often using Na_2CO_3 solution, reacts with H_2S in countercurrent flow. The absorbent is regenerated by heating. This process is low-cost and simple but has low desulfurization efficiency and difficulty in regenerating the absorbent, thus it is less used in industrial applications.

4. Diversified Utilization of Hydrogen Sulfide

In various desulfurization processes such as dry and wet methods, most of the H_2S can be removed from the raw materials. Containing valuable hydrogen and sulfur resources, extensive research and industrial trials are dedicated to its full resource utilization, producing sulfur, inorganic sulfur, organic sulfur compounds, and high-value-added hydrogen gas. Additionally, the direct utilization of sulfur and carbon-containing natural gas has been a hot research topic in recent years. Reacting H_2S directly with components such as CH_4, CO_2 to produce sulfur products eliminates the need for H_2S removal, simplifying the process flow and reducing substantial equipment investment.

4.1. Claus Process for Elemental Sulfur Recovery

Recovering sulfur from H_2S-containing gas is the main pathway for sulfur resource utilization. Currently, the most mature and widely applied in traditional industry is the Claus process, which partially oxidizes H_2S to remove it and converts it into sulfur, with the product purity reaching 99%. This process has the advantages of simplicity, low cost, operational flexibility, and high sulfur recovery rate, and is widely used in natural gas purification plants, refineries, power plants, coal gasification plants, and other fields. The principle of the Claus technology mainly includes two parts: firstly, 1/3 of the H_2S is oxidized to SO_2, and the remaining 2/3 of H_2S reacts with the SO_2 produced in the reactor in the presence of a catalyst to form sulfur and steam, as shown in the equations:

$$H_2S+3/2O_2 \rightarrow SO_2+H_2O \quad (3)$$

$$2H_2S+SO_2 \rightarrow 3/xS_x+2H_2O \quad (4)$$

$$\text{Overall reaction: } 3\ H_2S+3/2\ O_2 \rightarrow 3/x\ S_x+3\ H_2O \quad (5)$$

In the Claus process, the sulfur in H_2S is converted into sulfur for recovery and can further be used to produce sulfuric acid. However, the hydrogen is wasted as it combines with oxygen to form wastewater. Additionally, the process produces toxic SO_x gases as by-products, causing environmental pollution.

4.2. Decomposition of Hydrogen Sulfide to Produce Elemental Sulfur and Hydrogen

Direct or indirect decomposition of H_2S represents a clean and efficient technological route for resource utilization, yielding sulfur as well as clean energy hydrogen. The reaction process is as

follows:

$$2H_2S \rightarrow S_2 + 2H_2 \quad (6)$$

However, direct thermal decomposition is severely limited by thermodynamics. Studies show [5] that H_2S hardly undergoes thermal decomposition below 850 ℃, and at around 1400 ℃, the conversion rate of H_2S only reaches about 50%, with low conversion efficiency and high energy consumption.

Catalytic thermal decomposition employs metal catalysts to decompose H_2S at high temperatures, reducing the reaction activation energy and increasing the reaction rate. Research focuses on the development of efficient catalysts. Furthermore, efforts are made to promote H_2S decomposition using various methods such as electrocatalysis, photocatalysis, microwaves, and plasma technology. However, due to the immaturity of these technologies, none have yet been industrialized. Researching more efficient catalysts and related equipment development is a primary direction for future studies.

4.3. Reaction of Hydrogen Sulfide with Methane to Produce Carbon Disulfide and Hydrogen

With the international sulfur market becoming increasingly saturated and the economic benefits of sulfur declining, exploring new pathways for the utilization of hydrogen sulfide to achieve safe and efficient use is a significant challenge. Hydrogen Sulfide Methane Reforming (H_2SMR) technology uses H_2S and CH_4 as raw materials, with H_2 and CS_2 as the main products, representing a new approach to direct conversion and hydrogen production from sulfur-containing natural gas. The reaction process is as follows:

$$2H_2S + CH_4 \rightarrow 4H_2 + CS_2 \quad (7)$$

The advantages of this technology include: no need for separation and removal of H2S from natural gas, saving equipment and costs; full utilization of C, H, and S resources in the raw materials, with high hydrogen production efficiency as a clean hydrogen production route; no greenhouse gas emissions, making it clean and environmentally friendly; the main products are H_2 and CS_2, which are gaseous and liquid at room temperature respectively, facilitating separation; the product CS_2 has higher added value and can be used as an organic solvent or in the production of viscose fibers, rubber accelerators, pesticide intermediates, and other chemicals, as well as in producing gasoline hydrocarbon liquid fuels. Currently, research on H_2SMR is limited and is still in the laboratory research and simulation study phase. Early thermodynamic studies mainly discuss the impact of process conditions such as temperature, pressure, and feed composition on the conversion rate of raw materials and the yield of H_2 and CS_2 during the reforming process.

The design and development of catalysts are crucial for H_2SMR. A research team [6] compared the reaction data without a catalyst and with a MoS2 catalyst, finding that the catalytic reaction rate was significantly higher than the thermal reaction rate. The design principles for H_2SMR catalysts are to be resistant to high temperatures and H2S corrosion, and to meet the requirements of reaction activity, stability, and product selectivity under moderate operating conditions. Mart ńez-Salazar [7] and others used La_2O_3-ZrO_2 as the carrier to obtain the Mo/La_2O_3-ZrO_2 catalyst, which reduced the reaction activation energy, achieving a hydrogen selectivity of 40%. Later, SBA-15 molecular sieves were introduced into ZrO_2 carriers for structural modification, producing Mo(Cr)/ZrO_2-SBA15 and Mo(Cr)/ZrO_2-La_2O_3 catalysts [8]. Experiments showed that the structure of SBA-15 molecular sieves was destroyed at high temperatures, forming a $ZrSiO_4$ mixed phase with poor stability. However, Mo(Cr)/ZrO_2-La_2O_3 showed higher activity for CH_4 and H_2S reforming reactions, producing higher yields of H_2 at 800~900 ℃, up to 64%. The study suggests that Cr/Mo sulfides as bifunctional catalysts can effectively dissociate H_2S and are sufficiently stable, while the

addition of La_2O_3 can enhance the specific surface area and thermal stability of the catalyst. F éix [9] and others synthesized nano γ-Al_2O_3 carriers by the sol-gel method and impregnated them with different concentrations of iron nitrate solution to obtain Fe_2O_3/γ-Al_2O_3. It was found that the selectivity of the product CS_2 is related to the Fe^{3}+ ions in the octahedral coordination sites of hematite (α-Fe_2O_3), and the tetrahedral coordination Fe formed by the catalyst is conducive to hydrogen production. Operating for 14 hours at H_2S/CH_4=12 and 950 ℃, the conversion rates of CH_4 and H_2S reached 100% and 65%, respectively.

5. Conclusion

In conclusion, this study provides a comprehensive analysis of key methodologies for hydrogen sulfide (H_2S) treatment and utilization, primarily focusing on low-temperature methanol washing, the Claus process, and H_2S Methane Reforming (H_2SMR). Each method presents unique advantages and challenges. Low-temperature methanol washing stands out for its low energy consumption and effectiveness in purifying natural gas but is limited by the toxicity of methanol and challenges in handling heavy hydrocarbons. The Claus process, a prevalent method for sulfur recovery, is favored for its high sulfur recovery rate and operational simplicity, though it demands significant energy input.

The emerging H_2SMR technology shows promise in directly converting H_2S into valuable products like hydrogen and carbon disulfide, proposing a novel approach for utilizing sulfur-containing natural gas. However, it faces hurdles in terms of industrial scalability and economic viability. The critical role of catalysts in these processes is evident, with ongoing research required to develop more efficient and environmentally friendly catalysts. Future work should focus on improving the sustainability and efficiency of these methods, considering the integration of various technologies for more effective H_2S management in the energy sector.

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