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Research on Desulfurization Technology of Low Sulfur Marine Fuel Oil

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Abstract: With the implementation of the International Maritime Organization (IMO) marine fuel oil sulfur restriction policy in 2020, the desulfurization technology of marine residual fuel oil has received more attention from the industry. Heavy feedstock is the main component of marine residual fuel oil, and this paper introduces some of the heavy feedstock desulfurization technologies, mainly hydrodesulfurization, oxidation desulfurization, reactive metal desulfurization, adsorption desulfurization, biological desulfurization and extraction desulfurization. The respective advantages, disadvantages and applicability of these heavy feedstock desulfurization technologies are summarized.

Keywords: Marine fuel oil, Sulfur content, Desulfurization technology.

1. Introduction

With the rapid economic development and global integration, as a major shipping and trading country, China's demand for marine fuel oil is huge and will continue to rise in the future. With the frequent international trade, as one of the five major modes of transportation, waterway transportation has the advantages of low cost, long transportation distance and large transportation tonnage, which is incomparable to other modes of transportation, the global demand for marine fuel oil will only increase. The International Maritime Organization (IMO) issued the "Sulfur Restriction Order", requiring the global use of low sulfur marine fuel oil with sulfur content (mass fraction) less than 0.5% in 2020[1], and the specific international marine fuel oil sulfur content limit is shown in Figure 1. Marine fuel oil is mainly made of residual oil, coal tar and clarified catalytic cracking slurry blended with light components. In the past, the research on marine fuel oil mainly focused on the viscosity-temperature and stability of marine fuel oil, but relatively little research was done on the desulfurization technology of marine fuel oil, while the latest regulations on sulfur content make the requirement of heavy desulfurization technology higher and higher.

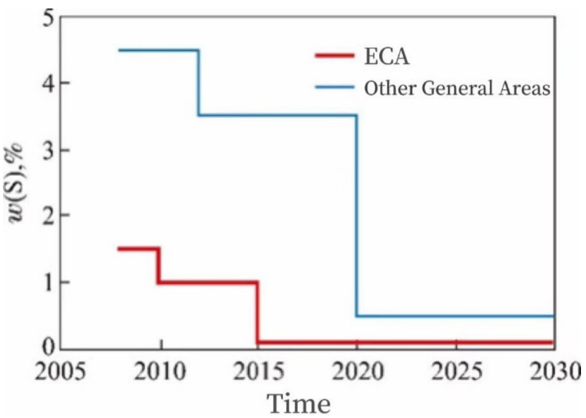

Figure 1. Limit value of sulfur content of marine fuel oil

2. Low Sulfur Marine Fuel Oil Desulfurization Technology

2.1. Hydrodesulfurization

At present, the main residue hydrodesulfurization technologies are fixed-bed and boiling-bed residue hydrotreating, and the desulfurization rate is generally between 81% and 90%, and the sulfur mass fraction of hydrotreating residue can be controlled within 0.5%. However, the residual carbon is generally high and viscous, and a certain percentage of diluted oil (wax oil, catalytic cracking slurry, etc.) needs to be blended as fixed-bed feed, and the installation and operation costs are very high, thus increasing the cost of producing heavy fuel oil, so the direct production of heavy marine fuel oil with sulfur mass fraction below 0.5% by fixed-bed hydrogenation is worth further consideration[2]. The use of boiling bed technology to process reduced pressure residual oil without blending diluted oil and to produce high value-added light oil fraction by-products during the hydrodesulfurization reaction has not been fully implemented in the refineries. However, industrialized equipment has not been fully adopted in various refineries.

2.2. Oxidation Desulfurization

The first step is the oxidation of the organic sulfide; the second step is the removal of the organic sulfide, using the change in polarity of the product to separate it from the oil by extraction. Auterra's FlexUp technology is a heavy oil desulfurization technology that uses air as an oxidizer to effectively treat high-sulfur petroleum hydrocarbons of various viscosities[3]. It is a strong competitive technology for HDS with low investment and operating cost and high desulfurization rate, especially for the direct production of residual marine fuel or its blending components with sulfur fraction below 0.5%.

2.3. Active Metal Desulfurization

Currently, sodium or lithium is used as the active metal in most of the active metal desulfurization, which is more effective and selective than hydrogen for the removal of sulfur active metal. In the case of sodium metal[4], for example, sodium desulfurization must take into account the economics of sodium regeneration, and the sodium desulfurization process requires that a moderate hydrogen partial pressure be maintained in the reaction system to prevent excessive carbon formation. Activated metal desulfurization has high selectivity and high desulfurization rate, and deserves further investigation.

2.4. Adsorption Desulfurization

Various adsorbents, such as activated carbon, molecular sieve, metal oxides, etc., are selected to allow weak chemical interaction between organic sulfur compounds and the transition metal atoms on the surface of the adsorbent[5]. The advantages are simple operation, low investment, suitable for deep desulfurization and no pollution, and the disadvantage is the weak adsorption of alkanes.

2.5. Biodesulfurization

Biodesulfurization technology can remove sulfide from heavy feedstock oil under lower temperature and pressure conditions, relying on genetic recombination technology of bacteria, which provides more efficient and specific strains of substrate. Currently, commonly used strains include Rhodococcus Erythropois, Anthrobacter Paraffineus and Thermophilic Bacterium, which can destroy C-S, allowing sulfur atoms to be oxidized to sulfate[6]. The method requires full contact between sulfur-eating bacteria in the aqueous phase and sulfide in heavy feedstock oil. Biodesulfurization occurs mainly at the oil/water phase interface, where the reaction control steps are the diffusion of sulfide from the main zone of the oil phase to the aqueous phase and the contact with the cell membrane of the bacteria. The efficiency of biodesulfurization is largely related to the particle size of the oil droplets. Its advantages are complete removal of thiophene sulfur, mild operating conditions, and disadvantages are long reaction time and easy emulsification at the oil/water phase interface.

2.6. Extraction Desulfurization

The use of extractants, such as isobutane and acetonitrile, can achieve the effect of desulfurization under specific conditions, depending on the solubility of the extractant for sulfide and fuel oil at a certain temperature and pressure conditions. The advantage is that the reaction conditions are mild, but the disadvantage is that the energy consumption is too large and the oil yield is low.[7]

3. Conclusion

With the recovery of the global economy and the rebound of the shipping market, the global market demand for marine fuel oil is huge, and the production of low-sulfur marine fuel is almost blank in China. The technology of marine fuel blending is limited by the low yield of low sulfur component oil, so there is a limitation for large-scale application. The fixed-bed residue hydrodesulfurization process is a more mature desulfurization technology, but with the current price of fuel oil, optimization research is needed to reduce the cost of producing low sulfur heavy marine fuel. The boiling bed residue hydrodesulfurization technology can produce qualified low sulfur heavy marine fuel, which has good economic feasibility and will become the main force of heavy marine fuel low sulfur and industrialization technology. At present, overseas development of oxidation desulfurization, sodium desulfurization and other emerging residue desulfurization technology is worthy of attention.

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