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Review Paper

Review on adsorptive desulfurization of petroleum products by porous carbon adsorbents

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1. ABSTRACT

Today, the drawbacks of the hydrodesulfurization process have led to the development of new methods such as adsorptive desulfurization (ADS), extraction, oxidation, etc. Unlike the hydrodesulfurization method, ADS has the ability to remove resistant sulfur compounds such as DBT and its derivatives without the need for expensive and risky hydrogen and under low operating conditions (temperature and pressure). In this article, in addition to the comparison of modern desulfurization methods, among the solid adsorbents used in the ADS process, the performance of porous carbon adsorbents is investigated due to their unique characteristics such as high surface area and porosity, easy modification of physical-chemical properties and the cost is affordable! Also, for a better understanding of the process, the effective process parameters, kinetics and thermodynamics, and various adsorption mechanisms in the ADS process by carbon materials have been investigated. Finally, various methods of recovery of carbon adsorbents are introduced and the challenges of advancing the ADS process are mentioned.

Keywords: Desulfurization Methods, Adsorptive Desulfurization, Porous Carbon Materials, Petroleum Products, Adsorption Mechanism.

2. INTRODUCTION

Fuels such as gasoline, jet fuel, kerosene and diesel are extracted from crude oil, which is the largest known energy source in the world. But the produced fuels contain sulfur-containing organic and inorganic compounds, which must be desulfurized before consuming petroleum products due to the destructive and adverse effects they have on industries, the environment, and human health. According to the challenges of conventional desulfurization methods, alternative methods have been developed to solve the existing problems. One of these new approaches is the adsorptive desulfurization method, which includes the removal of organic sulfur compounds from petroleum products by physical and chemical adsorption processes, which is a completely affordable and popular method among researchers and industrialists due to the process being carried out at mild temperature and pressure without the need for hydrogens.

3. RESULTS AND DISCUSSION

Hydrodesulfurization (HDS) is the most common method used to reduce sulfur from crude oil in the oil industry; but one of its most important problems is performing the process at high pressure and temperature, which leads to an increase in the cost of the process. Alternative methods proposed for HDS technology are extractive desulfurization (EDS), biological desulfurization (BDS), oxidative desulfurization (ODS), and adsorptive desulfurization (ADS). Among the mentioned methods, there are reports of semi-industrialization for the ADS and ODS desulfurization methods; But other methods are in the (analytical phase maybe a better alternative.

3.1. Adsorptive Desulfurization

This desulfurization method is considered the most economical technology among different desulfurization methods due to its simple operating conditions and renewable capability. The basis of adsorptive desulfurization is the ability of

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adsorbent materials to adsorb sulfur compounds. The advantages of the ADS method compared to the HDS method include performing the process at low pressure and temperature and not using expensive hydrogen. Also, in this method, a high capacity in desulfurization can occur because resistant and strong sulfur compounds are separated; while in the HDS method, it is not possible to separate these compounds. While adsorption is a desirable method for purification and separation that is performed at low cost and with high ease, the efficiency of adsorption technology revolves around the choice of adsorbent.

3.1.1. Non-carbon adsorbents

This category of adsorptive desulfurization is performed using different solid adsorbents such as mineral or inorganic adsorbents (such as zeolites, aluminum silicates, and alumina), metal oxides (such as magnesium oxide, zinc oxide), metallic-organic frameworks (MOFs).

3.1.2. Carbon-based adsorbents

Carbon-based adsorbents include three groups of carbon nano adsorbents, carbon nanotubes and carbon nanofibers. Carbon nano adsorbents also include graphene, graphene oxide, activated carbon, and modified activated carbon. Activated carbon is an adsorbent with a high surface area and pore volume, which is relatively cheap in addition to its high adsorption capacity. Activated carbon is produced from various sources such as coal, plant and polymer waste, sewage sludge, wood, etc., and its use to reduce the amount of sulfur in fuel has attracted the attention of researchers. Modifying the activated carbon adsorbent with acids has a great effect on the final sulfur adsorption results so that the results obtained by modifying the activated carbon with concentrated sulfuric acid or modifying the adsorbent with boric acid increase the desulfurization efficiency.

4. ADSORPTION

Types of adsorption process mechanisms to remove sulfur compounds from petroleum products can be categorized in the following three cases:

1. π complexation: This type of interaction includes the transfer of electrons from the π orbitals of organic sulfur compounds to the empty orbitals of adsorbing atoms or the re-donation of electrons from the d orbitals of adsorbing atoms to the π orbitals of organic sulfur compounds.
2. Acid-base interaction: In this mechanism, the metal sites (Fe, Cr, Al, Cu, Zn, Co, Ag, etc.) of the modified adsorbents act as Lewis acid solutions and bind to the basic sulfur atoms of organic sulfur compounds.
3. Direct interaction of sulfur and metal: It includes the formation of a direct sulfur metal σ bond, through the donation of the lone pair of electrons of the sulfur atoms to the metal atoms of the adsorbents.

In industrial processes, especially the adsorption process, to reduce operating costs, after using the adsorbent during the process, it is recovered and re-entered into the adsorption tower. In desulfurization by adsorptive method, various recovery methods are used, such as thermal recovery, recovery by washing with solvent or a combination of these two methods. Investigations have shown that used adsorbents are regenerated by washing with a number of solvents including methanol, acetonitrile, chloroform, and toluene. However, toluene shows the best results in the regeneration of spent adsorbent.

In table 1, the results of the detailed investigations related to the ADS method can be seen, which include the amount of initial sulfur in the model fuel, the type of adsorbent and the amount of adsorbent used in the process, the recovery methods of adsorbents, which are very important to reduce the cost of the process, and finally, the efficiency of ADS desulfurization is stated Is.

Table 1. Results of desulfurization by porous carbon adsorbents

Fuel	Desulfurization result (percent)	Regeneration method	adsorbent	The initial amount of sulfur (ppm)	sulfur compound	Reference
cyclohexane	98.5	Saturated adsorbent filtering in optimal conditions	AC-HCL	1000	DBT	**[1]**
cyclohexane	99.4	washing with solvent (toluene)	Sn/AC	1000	DBT	**[2]**
i-octane	95	washing with solvent (ethanol) and calcination at 600°C	Al_2O_3/AC	100	DBT	**[3]**
hexane + toluene	96	thermal methods	Ni/AC	59	DBT	**[4]**
n-hexane	97.1	washing with solvent (n-hexane) and thermal method (110°C)	PETAC	200	DBT	**[5]**

5. CONCLUSION

Despite the advantages of the ADS method, this method also has some challenges. One of the challenges of the ADS method is the difficulty of recovering the adsorbents. The adsorption capacity of many adsorbents is low, and often in order to achieve a high desulfurization capacity, more amounts of adsorbents are needed, which increases the total cost of the process due to the high cost of most adsorbents.

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