Use of an absorber for the regeneration of hydrotreating catalysts using a steam-air mixture

Alisher Jumaboev[1*] and *Shoxrux* Jumaboyev[1]

[1]Fergana Polytechnical Institute, Fergana, Uzbekistan

Abstract. This article explores the processing of high-sulfur petroleum products into low-sulfur fuels without harming the environment. Specifically, it discusses the implementation of EURO-3 standards at the Bukhara Oil Refinery in Uzbekistan since 2022. The study examines the hydrodesulfurization process used to treat high-sulfur heavy fractions of oil. The primary aim of the research is to improve the method of oxidative regeneration of hydrotreating catalysts. Modern techniques are proposed for restoring the activity of used catalysts, one of which involves regeneration with a steam-air mixture. This new method offers numerous advantages over traditional approaches, including significant savings in energy and materials, reduced process duration, and decreased emissions of harmful gases into the environment. Consequently, this method not only enhances production efficiency but also plays a crucial role in protecting both the environment and human health.

1 Introduction

With the decrease in crude oil resources and their availability, two trends have emerged in world practice - an increase in the depth of oil refining and the processing of high-sulfur petroleum products to meet needs. In this regard, requirements for environmental protection have become more stringent, that is, reducing emissions into the atmosphere. Following Western countries, the CIS countries began to produce low-sulfur fuel for the domestic and foreign markets [1,2]. In particular, at the Bukhara oil refinery in Uzbekistan, the EURO-3 standard began to operate in 2022. The production of such ultra-low-sulfur fuel is only possible using the latest generation of hydrotreating catalysts with an aluminum oxide carrier impregnated with salts of the active components.

To process high-sulfur heavy fractions of oil (boiling range 540–580°C) and residual oil distillation products (fuel oil, tar, distillates), hydrodesulfurization is used (the so-called, although it includes, in addition to removing sulfur, the removal of other impurities); this process has a great depth of transformation. The goal is to prepare raw materials for catalytic cracking and hydrocracking, for the production of low-sulfur electrode coke. Operating mode: operating pressure 10–20 MPa, hydrogen-containing gas: raw material ratio 600–

* Corresponding author: mavlonbek5488@gmail.com

1000:1, hydrogen content in hydrogen-containing gas – up to 90%. Hydrogen consumption is 0.1–1% by weight of the raw material. The catalysts are aluminum-cobalt-molybdenum or aluminum-nickel-molybdenum, the yield of liquid products is 92–94% [10-14].

2 Relevance and objectives of the study

Hydrotreating catalysts lose their activity over time during operation due to clogging or poisoning of the active components. In some cases, the decrease in activity is reversible. And for a number of catalysts, activity can be restored to 95% of the original. Then the activity of the activated catalyst is always lower than the activity of the new catalyst, so returning the activity of the spent catalyst to an equilibrium level will extend the life of the catalyst.

The purpose of this research is to develop a method for the oxidative regeneration of a hydrotreating catalyst used for the hydrotreating of straight-run gasoline, with a fewer number of technological stages and at the same time allowing to maintain high, maximum activity of the catalyst [1-3].

3 Materials and research methods

Since hydrotreating catalysts are very expensive, instead of replacing the used catalyst with a new one, the used catalysts are regenerated. There are two ways to use catalysts with reduced activity. The first option involves regeneration and further use for less intensive hydrogenation processes. The second option involves the regeneration of catalysts with reactivation so that they can be reused in oil refining by hydrogenation without losing the quality of the resulting product. In any of these cases, oxidative regeneration of the hydrotreating catalyst is necessary. Oxidative regeneration of hydrotreating catalysts allows their activity to be restored to approximately 85-95%. Conducting oxidative regeneration under optimal conditions helps to maximize recovery of original activity and reduce the overall cost of achieving full activity compared to a new catalyst [1-3]. In addition, there are currently no industrially developed technologies for the complete regeneration of modern supported hydrotreating catalysts[12-15].

There is a known method for regenerating a hydrotreating catalyst, when the coked catalyst is regenerated directly in hydrotreating reactors in a flow of oxygen-containing gas(fig.1). The disadvantages of the proposed method are the need to stop the reactor for a long time during the regeneration process, the low rate of recovery of catalyst activity, the presence of additional stages of removing the catalyst from the reactor, and the absence of such disadvantages as screening the catalyst from dust after regeneration, as well asleading to corrosion of technological equipment operating in a caustic environment - NaOH-alkali [6-9].

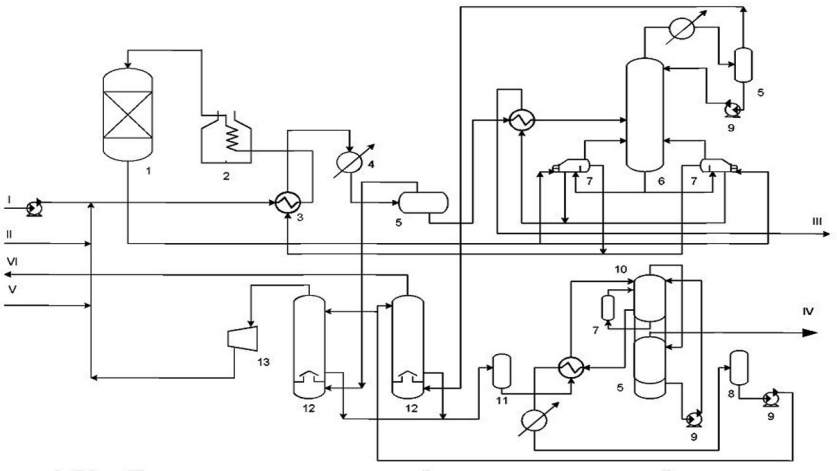

Fig. 1. - Technological scheme for the regeneration of a hydrotreating catalyst using the classical method: 1 – reactor; 2 – furnace compartment; 3- heat exchanger; 4- refrigerator; 5 – separator; 6 – stabilization column; 7 – reboiler; 8 – separator for separating the MEA solution; 9 – pump; 10 – distillation column; 11 – degasser; 12 – phase separator; 13 – compressor; I- raw materials (straight-run gasoline). Not used for regeneration!); II - Supply line for inert gas nitrogen; III – hydrotreated gasoline; IV – hydrogen sulfide; V – hydrogen gas to the plant network; VI – hydrocarbon gas.

To regenerate the catalyst in stationary reactors, the catalyst layer is cleaned of residual oil products by blowing with an inert gas, most often nitrogen N_2 with an oxygen content of no more than 0.2%, to prevent combustion of residual oil products. The coke combustion circuit can be assembled in the following sequence(fig.2): line of controlled supply of water vapor and atmospheric air - heat exchangers (tube space) - furnace - hydrotreating reactor - heat exchangers (tube space) - air-cooled refrigerator - absorber for capturing combustion products - release of purified steam-air mixture into atmosphere [3-5].

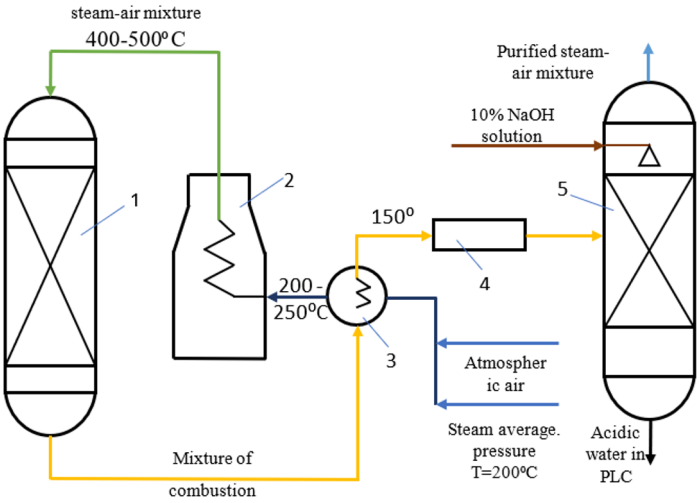

Fig. 2. Technological diagram of hydro catalyst regeneration leaning with steam-air mixture: 1 – reactor; 2 – furnace compartment; 3- heat exchanger; 4 – air-cooled refrigerator; 5- gas purification absorber; I – medium pressure water vapor); II – atmospheric air; III – solution of (NaOH)-alkali; IV – "Acidic water" into the sewer system (PLC), V – Purified water vapor into the atmosphere.

Table 1. Comparison of Regeneration Methods for Hydrotreating Catalysts

The name of indicators	When regenerating using the classical method in %	When regenerating with a steam-air mixture in %
Energetic resources: - electricity - inert gas nitrogen - oxygen - fuel gas - water resources	 29930 kWh/ton 54200 m3/t. 3650 m3/t. 24.455 t/t 136 m3/hour.	 10200 kWh/t. not consumed 800 m3/t. 11.135 t/t. 73 m3/hour.
Regeneration time	At least 7 days	No more than 3-4 days
Amount of toxic and harmful gases (CO, CO2, SO, SO2) released into the environment:	At least 10% of emitted gases are released into the environment	There is no release of toxic and harmful gases.
Failure of the catalyst as a result of unwanted strong burnout of coke in the catalyst bed.	At more than 500 C, grain sintering occurs in the catalyst layers	Simplified control of coke combustion in catalyst beds
The influence of oxygen contained in steam on the oxidation of the catalyst.	Catalyst oxygen saturation is insufficient	The high oxygen content in the steam-air mixture saturates the catalyst well
Consumption of NaOH reagent used to neutralize combustion products CO, CO2, SO, SO2.	Due to insufficient contact with combustion products, a lot of alkali is consumed	Good contact of alkali with combustion products is ensured, alkali consumption is reduced by 10%.
Relation to corrosion of water-cooled refrigerators, separators, and their connecting pipelines operating in a NaOH environment.	Participate in the process and are subject to corrosion	Do not participate in the process due to the inclusion of a packed absorber in the circuit
Availability of additional stages of work during regeneration.	After catalyst regeneration, it is necessary to sift the catalyst and blow off burnt coke	There is no need for sifting and purging of burnt coke due to the participation of an absorber-neutralizer in the process

Advantage of the proposed technology:

1. Energy, material and technical resources are saved in large quantities - electricity, inert gas nitrogen, oxygen, fuel gas, water resources, etc.
2. The time required for the process is reduced, making the work of workers easier.
3. The amount of toxic and harmful gases released into the environment is greatly reduced.
4. Failure of the catalyst as a result of unwanted strong burnout of coke in the catalyst bed is prevented.
5. The use of NaOH reagent is significantly reduced.
6. Corrosion losses of process equipment operating in a caustic NaOH environment are reduced [1-3].

4 Conclusion

It should be noted that the method proposed in the study for restoring hydrotreating catalysts with a steam-air mixture has many advantages over the classical method, that the use of this method in technology allows increasing the service life of equipment, pipelines and devices by reducing corrosion, saving energy, material and technical resources and time, spent on the process, preserves people's health and the environment from pollution by emitted harmful and toxic gaseous substances.

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