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Study of the influence of catalyst activity on the reaction rate during hydrotreating of diesel fractions using mathematical modeling

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Abstract

The previously developed mathematical model takes into account the activity of the catalyst. The influence of the activity of the catalyst on the rate of the reactions occurring during hydrotreating, the resulting rate constants of the deactivation. The adequacy of calculations of the improved model is checked. It was found that the reduction of catalyst activity by only 30% significantly affects the reaction rate constants, the reactions are slowed down by 18 times. The quality of the product is reduced when the catalyst is deactivated. To compensate for the loss of catalyst activity, it is necessary to vary the technological parameters, in particular, to increase the temperature in the reactor.

Keywords: Hydrotreatment, hydrotreating, diesel fuel, mathematical model, simulation, catalyst, deactivation;

1. Introduction

In recent years, there has been a tendency to increase the amount of sulfur and high-sulfur oils entering the refinery. The products obtained during the primary processing of such oils do not meet the requirements for the quality of petroleum products, which are becoming tougher every year.

Hydrotreating process is used to bring diesel fuel to the specified quality. Hydrotreating is the most large-scale secondary process and is present at any refinery. The task of finding new effective methods of its management is relevant.

2. Materials and methods

Based on the results of thermodynamic analysis of reactions, a scheme for the conversion of hydrocarbons in the process of hydrotreatment of diesel fractions was previously compiled [1]. The scheme takes into account the conversion of olefins, saturated and aromatic hydrocarbons, the main representatives of sulfur-containing substances, as well as the reaction of coke formation, which have a significant impact on the process, on the quality of the target product.

3. Results and discussion

A mathematical model based on the proposed formalized scheme of the process is written based on the law of mass action and is a system of differential equations reflecting the change in the

concentration of reacting substances. In order for the model to accurately describe the actual process under industrial conditions, it is also necessary to take into account catalyst deactivation. Thus, the aim of the work is to take into account the activity of the catalyst with the operation time of the industrial installation on the rate constants of the reactions taking place in the hydrotreating process.

The integral activity of the catalyst was calculated by the formula:

Activity = $\Delta - (|t_{experiment} - t_{calculation}|)/\Delta$,

where Δ is the difference between the minimum and maximum temperatures of the process;

$t_{experiment}$ - the temperature obtained during the experiment; $t_{calculation}$ - temperature obtained in the calculation on the model.

The obtained data were taken into account when calculating the rate constants of the main reactions on the mathematical model. The calculated rate constants for catalyst deactivation are presented in table 1.

Table 1. Values of the reaction rate constants for the diesel hydrotreatment process

Designation of rate with constant	The value of the rate constant, c^{-1}	The value of the rate constant constant with regard to the deactivation of the catalyst, c^{-1}
k_1	0.3114	0.017381
k_2	0.1090	0.006084
k_{-2}	0.0218	0.001217
k_3	0.0722	0.004030
k_{-3}	0.0052	0.000290
k_4	0.0934	0.005213
k_5	0.0990	0.005526
k_{-5}	0.0078	0.000435
k_6	0.0012	0.000067

4. Conclusion

According to the industrial data of the L-24/10 hydrotreating unit operation, a regular decrease in catalyst activity is observed with an increase in the mass of the processed raw materials. In 1.5 years, more than 2.5 thousand tons of raw materials were processed, and activity decreased by 30% from the original and reached 0.67.

A decrease in the catalyst activity of only 30% significantly affects the reaction rate constants. Reactions are 18 times slower, to obtain a product of a given quality, it is required to change technological parameters, in particular, to raise the temperature.

In the future we plan to expand the scheme of transformations by taking into account the reactions of nitrogen-containing compounds that affect the rate of coke formation.

The practical value of the work lies in the creation and possibility of using an innovative software product that allows solving technological problems that actually arise in production, and it will allow refineries to optimize the operating mode of the hydrotreating unit at the lowest cost.

References

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