OPTIMIZATION OF DIESEL FUEL CATALYTIC DEWAXING PROCESS CONSIDERING THE CATALYST DEACTIVATION

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The Government of Russia currently adopts the rules focused on the modernization of fuel and energy complex of the country. The main changes of the oil and gas sphere are being made in the sector of oil refinery, particularly enhancing the feed conversion ratio and improving the products quality. The priority goal represents new solutions of the catalysis and catalytic processing of the heavy feedstocks. As the large portion of Russian territories has a specific winter and arctic climate, there is much tension around the issue of producing low pour point fuels.

Deterioration of diesel fuel low-temperature properties is associated with the presence of unbranched high-molecular alkanes that have the positive values of freezing and cloud points, and naphthene hydrocarbons with long side chains [1]. These components can be extracted with the application of various chemical and physical methods, such as low-temperature crystallization, urea dewaxing, depression of the end boiling point, using the depressive additives etc. According to the ecological demands and the question of efficiency, it is economically advisable to implement the technology of catalytic dewaxing. This process has not got widespread use yet owing to the lack of effective and cheap catalytic systems. So, it is necessary to develop the actual operating dewaxing units applying the methods of system analysis.

During the process of catalytic dewaxing of straight-run diesel fraction and atmospheric gasoil the advance of the cold flow properties takes place due to the reactions of selective hydrocracking of unbranched paraffins. The bifunctional catalyst HYDEX-G is represented by nickel supported on the acid carrier. The latter is a pentasil zeolite of ZSM-5 type. Thus, the catalyst contains metal and acid active sites to conduct the reactions of hydrogenation-dehydrogenation and cracking-isomerization correspondingly.

The method of mathematical modelling has been successfully used to develop the mathematical description of hydrodewaxing process taking into account the interconnected equipment of reactor and stabilizer column [2]. The model was created drawing on the industrial unit data including the operating conditions, changing feed composition concerning hydrocarbon group distribution, flow rate of the hydrogen-containing gas and its content, etc. The main chemical-physical laws of proceeding chemical reactions have provided a background for the model development. Its adequacy has been approved by comparing the data computed with the model and experimental data from the unit.

One of the most important issues when operating the catalytic processes is catalyst deactivation, which takes place as the reactions of coke formation proceed. To forecast the industrial unit operation for a long-term period, it is viable to consider the factors of non-stationarity, such as the loss of activity and varying feed composition. So, the objective of the work is to accomplish the existing model by adding the deactivation function to the symbolic description.

During the research of the actual hydrodewaxing unit it was revealed that within the period of four-year industrial catalyst operation slight decrease of diesel fraction yield from 90 to 44 % wt. has been occurring, and the gasoline fraction yield has been increasing from 8 to 20 % at the same time (Table1).

Table 1

Fraction yield during the period of 2012-2016

Year	2012	2013	2014	2015	2016
Yield of diesel fraction, %	74 – 90	63 – 88	52 – 65	54 – 60	44 – 52
Yield of gasoline fraction, %	8 – 10	10 – 12	15 –18	18 – 20	20 – 21
Yield of residue fraction >340 °C	5 – 15	10 – 25	25 – 30	30 –35	35 – 40

The decreased volume of the diesel fraction and enhanced yield of light gasoline fraction indicates the intensification of cracking reactions, as they lead to the formation of light hydrocarbons with the number of carbon atoms from C_1 to C_4. Also the increased volume of the high-boiling fraction from 5 to 40 % shows the reduction of feed conversion degree, therefore, the catalyst deactivation is observed. This process occurs as the ratio of metal and acid active sites on the catalyst surface is being changing due to the coke deposition, sulfur poisoning or sintering of the particles. As a consequence, one type of reactions predominates over another.

As the load of the fresh catalyst demands a sizeable portion of expenses, the unit optimization in order to maintain the catalytic activity plays an important role. The main methods of its controlling involve mixing with the hydrogen containing gas and increasing the temperature inside the reactor. First one is applied since adding the hydrogen ensures the reactions of hydrogenation of polyaromatic compounds and olefins which predicts the coke formation. The second method is used according to the reactions kinetic laws and rate constants. But the optimal temperature cannot exceed the range of 355-375°C as it leads to the acceleration of coking. The main task of controlling the dewaxing catalyst deactivation process is determination of optimal hydrogen containing gas-feed ratio under the conditions of changing flow rate, feed composition and temperature inside the reactor.

Mathematical model of the dewaxing reactor corresponds to the hydrodynamic flow regime of the plug-flow reactor. The mass balance is calculated according to the volume of the refined feed, catalyst bed volume and feed component concentrations inside the reactor. Also the model takes into account the deactivation factor as a proportion of reaction rate constant at any time to the reaction rate constant at the initial moment of the time when the fresh catalyst had been

charged [3,4].

The created model allowed carrying out some computations in order to define the temperature inside the reactor that compensates the loss of activity of the catalyst (Table 2).

Table 2

Calculation of the deactivation compensating temperature

Date	Yield of fraction 240-340 (DF), %	CFPP, °C	T_{in} R-3 (actual), °C	T_{in} R-3 (comp.), °C	ΔT, °C
25.01.2016	41.4	-34	341	318	23
27.01.2016	41.8	-37	352	332	20
29.01.2016	41.5	-44	360	345	15
05.02.2016	43.0	-41	369	350	19

The quality of the product is determined by the cold filter plugging point (CFPP). Accepting the required diesel fraction yield and quality, it was established that temperature inside the reactor without losing activity is on the average lower than actual temperature to 19°C. This difference provided the opportunity to calculate the deactivation degree throughout the period of four years, and it amounted to 32%.

Also the model showed that during the same period the coke deposition on the catalyst surface totaled about 12.8 % wt. which is shown in the Fig.

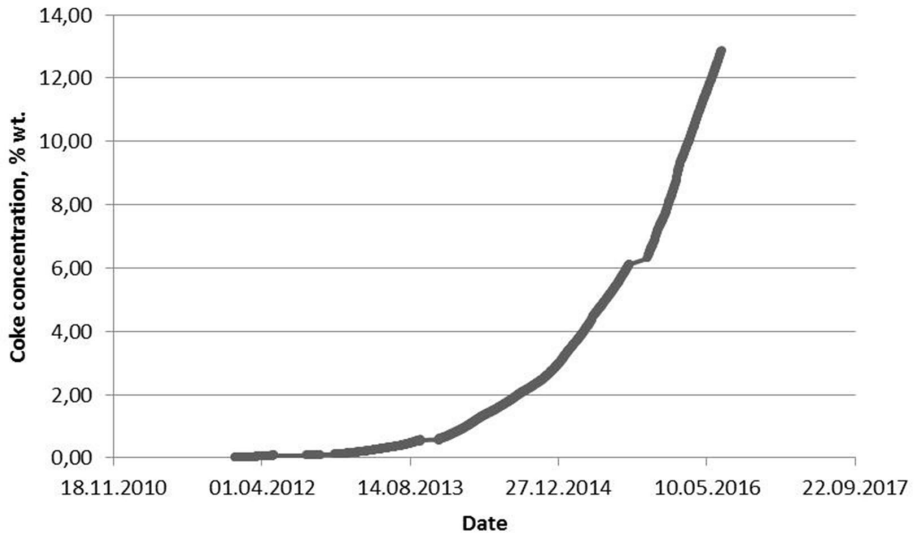

Fig. Concentration of coke deposited from 2012 to 2016

The developed and advanced mathematical model of the catalytic dewaxing process considers the non-stationarity factors. As this model is based on the fundamental kinetic and thermodynamic laws of the reactions being conducted inside the reactor, it works as a reliable tool to predict the system behavior in situ. Therefore, it is possible to determine the optimal technology of catalyst operation under dynamic conditions of the industrial unit.

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