

## Development of a Mathematical Model of the Vacuum Oil Distillates Hydrocracking Process Taking into Account Catalyst Deactivation by Coke

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### **Abstract**

A mathematical model of the vacuum oil distillates hydrocracking process, which takes into account catalyst deactivation by coke, was developed. The mathematical model was implemented in the form of a computer modelling system. Using the developed computer modelling system, predictive calculations of the decrease in the catalyst activity during the working cycle were carried out for various compositions of the feedstock. The influence of the ratio Hydrogen-containing gas / Feedstock on the rate of catalyst deactivation during the working cycle was shown.

**Keywords:** *Vacuum distillate; Hydrocracking; Mathematical model.*

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## **1. Introduction**

The process of hydrocracking of vacuum oil distillates takes a leading role in the oil refining, as the process that allows converting heavy oil fractions into light oil products with high added value [1-3]. Diesel fuel obtained in the hydrocracking process as one of the most valuable target products meets strict requirements of standards and provides meeting the growing demand for diesel fuels [4-6].

One of the most significant problems of any technology of hydrocarbon feedstock processing is catalyst deactivation, which leads to a decrease in the degree of feedstock conversion, deterioration of the product quality, an increase in operating costs of the production, the need to develop measures for the disposal of a catalyst that has undergone irreversible deactivation, which makes it impossible to regenerate [7-8]. This problem is especially relevant for the processing of heavy oil feedstock, including vacuum distillates, containing thermally unstable reactive components, which form coke deposited on the active sites of the catalyst during thermocatalytic processing [9-11].

At present, the problem of reducing the rate of catalyst deactivation in hydroprocessing of oil feedstock and extending their service life is being successfully solved by the development of new highly active and selective catalysts that provide the maximum yield of high-quality light oil products with improved properties [1,4,9].

However, at currently operating industrial vacuum oil distillates hydrocracking units, it is possible to reduce the catalyst deactivation rate by means of optimal control of the process parameters depending on the feedstock composition and the current catalyst activity, which can be implemented using non-stationary mathematical models developed on the basis of fundamental physicochemical laws of the processes and technological laws of the processes behaviour in industrial conditions [12-15].

Previously, for the purpose of modelling the process of vacuum oil distillates hydrocracking, the authors proposed a formalized scheme of chemical transformations during the process, carried out a thermodynamic analysis of the ongoing reactions, developed equations for the kinetic model of the process and a software algorithm for their solution [16].

The aim of this work is to develop a mathematical model of the vacuum oil distillates hydrocracking process, taking into account the previously identified patterns of the process and catalyst deactivation by coke.

## 2. The regularities of catalyst deactivation by coke in vacuum oil distillates hydrocracking process

Heavy oil feedstock contains hydrocarbon components with high molecular weight, namely aromatic and heteroaromatic compounds, which lead to the blocking of active sites of the catalyst due to the formation and deposition of coke on their surface [17]. Coke deposition on the catalyst reduces its active specific surface area as well as the average pore diameter and volume. Effective diffusion strictly depends on the coke content, since the more coke is deposited on the catalyst, the more difficult it is to enter the catalyst pores where chemical transformations take place. As a result, there is a decrease in the efficiency factor, which largely has a negative effect on the processing of vacuum oil distillates containing components with high molecular weight [18].

Coke has a complex structure. The primary products in the process of coke formation, the so-called coke precursors, can under the influence of process parameters, such as temperature and time, undergo a reaction on the catalyst surface, forming coke. To prevent this process, it is necessary to hydrogenate the coke precursors, which will reduce their content on the catalyst surface. At the industrial conditions, in fact, the composition and properties of the feed will determine how quickly the catalyst will be deactivated by coke. At the same time, increasing the temperature in order to maintain the required degree of conversion may not be enough to reduce the rate of coke deposition. In addition, at high temperatures, the metal particles of the catalyst sinter, which also leads to a decrease in the specific surface area. When the maximum allowable temperature is reached, at which the degree of catalyst deactivation does not decrease or even increases, the catalyst is removed, regenerated or replaced [17].

The characteristics of coke deposits on catalyst depend on the conditions of formation and can vary widely in chemical composition, structure, dispersion, and distribution on the catalyst surface. Most researchers divide the types of coke deposits into two: amorphous coke (C/H ratio 0.5-1.0) and graphite-like coke (C/H ratio 1.5-2.0) [19-20]. Amorphous coke is removed in the hydrogen environment, while the formation of graphite-like coke is irreversible.

## 3. Mathematical model of the vacuum oil distillates hydrocracking process, which takes into account catalyst deactivation by coke

The mathematical model, developed on the basis of physicochemical laws, taking into account the catalyst deactivation by coke, is a system of differential equations of the material balance by components and the heat balance equation:

$$\begin{cases} G \cdot \frac{\partial C_i}{\partial z} + G \cdot \frac{\partial C_i}{\partial V} = \sum_{j=1}^m a_j \cdot W_j \\ G \cdot \frac{\partial T}{\partial z} + G \cdot \frac{\partial T}{\partial V} = \frac{1}{\rho \cdot C_p^{mix}} \sum_{j=1}^m Q_j \cdot a_j \cdot W_j \end{cases} \quad (1)$$

Initial conditions:  $z = 0$ :  $C_i = C_{i,0}$ ;  $T = T_0$ ;  $V = 0$ :  $C_i = C_{i,0}$ ;  $T = T_0$ , where  $z$  is the volume of processed feedstock from the moment of loading the fresh catalyst,  $m^3$ ;  $G$  is feedstock consumption,  $m^3/h$ ;  $z = G \cdot t$  ( $t$  is the catalyst operation time from the moment of loading the fresh catalyst, h);  $C_i$  is the concentration of the  $i^{th}$  component,  $mol/l$ ;  $V$  is the volume of the catalyst bed,  $m^3$ ;  $a_j$  is the catalyst activity in the  $j^{th}$  reaction;  $\rho$  is the density of the mixture,  $kg/m^3$ ;  $C_p^{mix}$  is the specific heat capacity of the mixture,  $J/(kg \cdot K)$ ;  $Q_j$  is the thermal effect of the  $j^{th}$  reaction,  $J/mol$ ;  $T$  is the temperature,  $K$ ;  $W_j$  is the rate of the  $j^{th}$  reaction,  $mol/(l \cdot s)$ ;  $m$  is the number of reactions.

The catalyst activity is calculated through the amount of coke and coke-generating structures

$$a_j = A_j \cdot e^{-\alpha_j C_{coke}} \quad (2)$$

$A_j$ ,  $a_j$  are the deactivation coefficients;  $C_{coke}$  is the amount of coke and coke-generating structures on the catalyst surface, %wt.

#### 4. Computer modelling system of the vacuum oil distillates hydrocracking process

A computer modelling system of the vacuum oil distillates hydrocracking process was developed using the Pascal programming language and implemented in the Delphi 7 programming environment. The computer modelling system includes the following blocks: database, knowledge base, mathematical model of the process, software package, interface.

The database of the developed computer modelling system contains: data on the chemistry of the process and the mechanisms of the reactions occurring in the process; thermodynamic characteristics of the reactions (change in enthalpy, change in Gibbs energy, change in entropy during reactions); kinetic parameters of the reactions (activation energy, preexponential factor in the Arrhenius equation); the characteristics of the reactor (the volume of the loaded catalyst); composition and properties of the feedstock, composition of hydrogen-containing gas (HCG), technological parameters of the process. The knowledge base of a computer modelling system allows collecting, accumulating and processing of the information about the process.

#### 5. Results and discussion

Using the developed model of the vacuum oil distillates hydrocracking process, predictive calculations of the influence of the feedstock composition and the ratio of HCG / Feedstock on the catalyst deactivation rate were carried out. For calculations, two feedstock compositions were used (Table 1).

Table 1. Feedstock compositions of the vacuum oil distillates hydrocracking process

Components of the feedstock	Content, %wt.	
	VD-1	VD-2
Saturated hydrocarbons	61.45	68.26
Aromatic hydrocarbons	30.58	25.81
Resins	7.97	5.93
Sum	100.00	100.00

VD-1 represents vacuum distillate of composition No. 1; VD-2 represents vacuum distillate of composition No. 2. Fig. 1 shows the results of a predictive calculation of the catalyst activity in the hydrocracking process for two compositions of vacuum distillate.

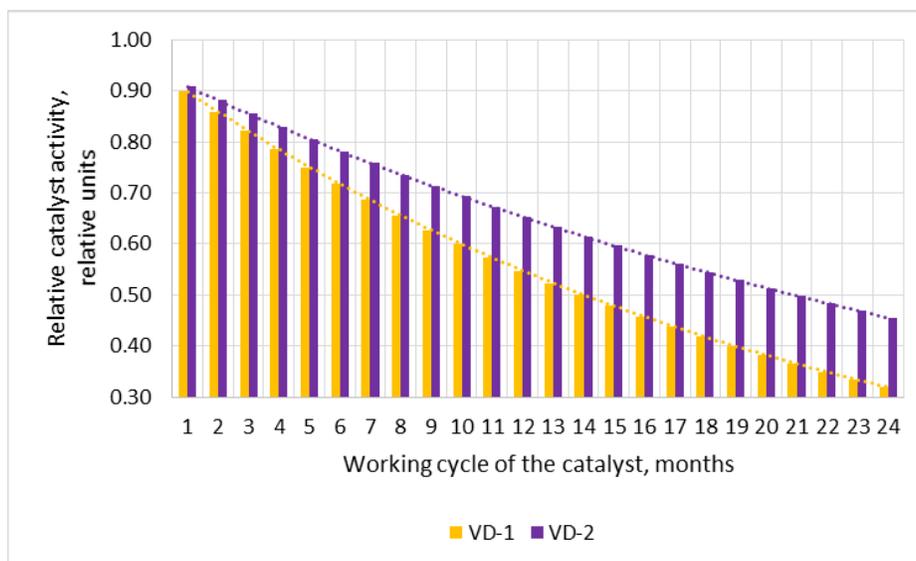


Figure 1. Decrease in the catalyst activity in the hydrocracking process during the working cycle for two feedstock compositions

As can be seen from Fig. 1, when processing feedstock VD-1, the relative catalyst activity after 2 years of operation is 30 % lower than when processing feedstock VD-2. This is due to the fact that the vacuum distillate of composition No. 1 contains by 4.77 %wt. less aromatic hydrocarbons, which are precursors of coke and by 2.04 % wt. fewer resins, which are also coke precursors and they block the active surface of the catalyst.

In the process of vacuum oil distillates hydrocracking, hydrogen in the composition of HCG participates not only in the target reactions, but also hydrogenates compounds that are precursors of coke. Fig. 2 shows the results of the predictive calculation of the catalyst activity depending on the HCG / Feedstock ratio (for three ratios: 1000 Nm<sup>3</sup>/m<sup>3</sup>, 1500 Nm<sup>3</sup>/m<sup>3</sup>, 2000 Nm<sup>3</sup>/m<sup>3</sup>).

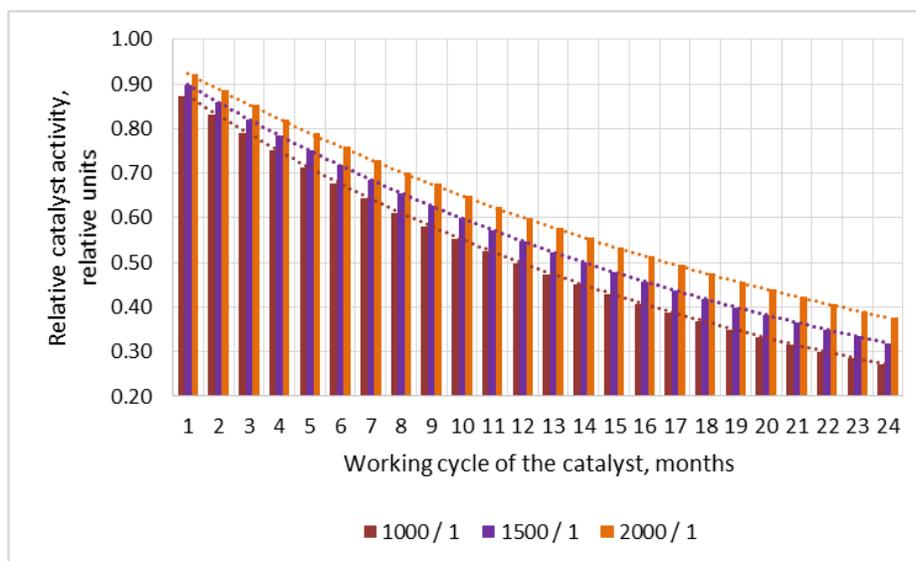


Figure 2. Influence of the HCG / Feedstock ratio on the rate of catalyst deactivation in the vacuum oil distillates hydrocracking process

As can be seen from Fig. 2, an increase in the HCG / Feedstock ratio allows the catalyst resource to be saved by an average of 15 % with an increase in the HCG/Feedstock ratio by every 500 Nm<sup>3</sup>/m<sup>3</sup>.

## 6. Conclusion

A mathematical model of the process of vacuum oil distillates hydrocracking, which takes into account the deactivation of the catalyst by coke, was developed. On the basis of this model, a computer modelling system of the process was developed. Model calculations show that when processing feedstock with a higher content of aromatic hydrocarbons and resins, which are precursors of coke deposited on the catalyst, over 2 years of catalyst operation, its activity decreased by 30 % more than when processing feedstock with a lower content of aromatic hydrocarbons and resins. It is shown that it is advisable to maintain HCG consumption at the highest possible level, as far as it can be provided by fresh HCG resources and economic considerations, since this allows saving the catalyst resource by an average of 15 % with an increase in the ratio of HCG / Feedstock by every 500 nm<sup>3</sup> / m<sup>3</sup>.

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## Symbols

$A_j, a_j$	deactivation coefficients;
$C_{\text{coke}}$	content of coke and coke-generating compounds deposited on the catalyst surface, %wt;
$C_{i0}$	initial concentrations of the reacting components, mol / m <sup>3</sup> ;
$C_i$	current concentration of reacting components, mol / m <sup>3</sup> ;
$i$	the number of the reagent;
$j$	the number of the reaction;
$k_j$	the rate constant of the forward reaction;
$k_{-j}$	the rate constant of the reverse reaction;
$t$	time, s;
$V_{\text{cat}}$	the volume of the catalyst bed, m <sup>3</sup> ;
$V_{\text{feed}}$	feedstock consumption, m <sup>3</sup> /h;
$\tau$	the residence time, s.

## Abbreviations

HCG	hydrogen-containing gas;
VD-1	vacuum oil distillate of composition No. 1;
VD-2	vacuum oil distillate of composition No. 2.

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