

Prediction of the Catalyst Activity in the Process of Vacuum Gas Oil Hydrocracking Using a Mathematical Model

*Nataliya S. Belinskaya**, *Mikhail N. Chernyshov*, *Roman D. Popov*

National Research Tomsk Polytechnic University, Russia

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Abstract

The article presents a mathematical model of the vacuum gas oil hydrocracking process, which takes into account chemical transformations of the grouped components, including n-paraffins C₂₂-C₄₀, i-paraffins C₂₂-C₄₀, n-paraffins C₅-C₂₁, i-paraffins C₅-C₂₁, naphthenes, aromatics, resins, hydrocarbon gas, and the reactions of coke formation and its accumulation on the catalyst surface during the operation cycle. The model also includes the equation for calculation of temperature profile during the process and the equation for calculation of the catalyst activity depending on the content of coke accumulated. The results on the influence of the hydrogen-containing gas consumption and the feedstock flow rate on the coke content on the catalyst, the activity of the catalyst and the temperature profile in the catalyst layers, obtained by calculations using a model, are presented. It is shown that hydrogen-containing gas consumption has optimal values depending on the feedstock flow rate, which ensure the maintenance of the maximum possible catalyst activity and the required depth of feedstock conversion. The optimal consumption of hydrogen-containing gas is determined at different feedstock flow rates. The increase in the feedstock flow rate by 20 m³/h from 220 m³/h to 240 m³/h requires increasing in the hydrogen-containing gas consumption by 500 kg/h from 9500 kg/h to 10000 kg/h. Maintaining hydrogen-gas consumption higher than optimal is impractical because it leads to decrease in the temperature of the process lower than favorable for the target reactions thus decreasing the depth of feedstock conversion with simultaneous increasingly more lower influence on the coke formation and increased operational costs.

Keywords: hydrocracking; Vacuum gas oil; Mathematical model; Catalyst activity; Catalyst deactivation.

1. Introduction

Currently, oil refining is faced to the tasks of increasing oil conversion ratio over 90% and the production of motor fuels while simultaneously reducing the yield of marine fuels, fuel oil and heavy residues [1-2]. Therefore, the capacities of secondary refining processes, including the vacuum gas oil hydrocracking process, is constantly increasing [3-5].

For the industrial hydrocracking process, supported bifunctional catalysts are most widely used: the hydrogenation function is provided by molybdenum or tungsten sulfides promoted by nickel sulfides; the cracking function is provided by zeolites, amorphous aluminosilicates or their mixtures [6-9].

During the operation of hydrocracking catalysts, their activity gradually decreases, and, as a consequence, the depth of conversion of vacuum gas oil into gasoline and diesel fractions reduces [10]. The main reason for the decrease in the activity of hydrocracking catalysts is the deposition of coke on their surfaces, which requires their replacement or regeneration [11-14]. Industrial hydrocracking units are large-scale facilities and are characterized by a large volume of catalyst loading into the reactor. That is why the operations to replace or regenerate catalysts are very expensive. Given this, predicting the activity of catalysts depending on the technological parameters of the process is an essential science and technology task, which will help reduce the costs of enterprises by maintaining optimal technological parameters that

allow extending the service life of catalysts while maintaining the depth of feedstock conversion at high level, and reducing downtime for replacement and regeneration of the deactivated catalysts.

It is difficult to assess the current catalyst activity when an industrial unit is operating since this requires unloading the catalyst from the reactor and results in downtime. The current activity of the catalyst can be estimated by calculation using a mathematical model of the physicochemical processes occurring in the reactor, including the process of coke formation [15].

The aim of this work is mathematical modeling of the coke formation and reduction of catalyst activity in the hydrocracking of vacuum gas oil process.

2. Experimental

The object of the study is the process of vacuum gas oil hydrocracking. Boiling range of the feedstock is 300 – 570°C. The process runs in a hydrogen-containing gas medium in a trickle bed reactor where the feedstock-gas mixture passes through 5 catalyst layers at severe technological conditions: high pressure (15 – 18 MPa) and high temperature (340 – 440°C).

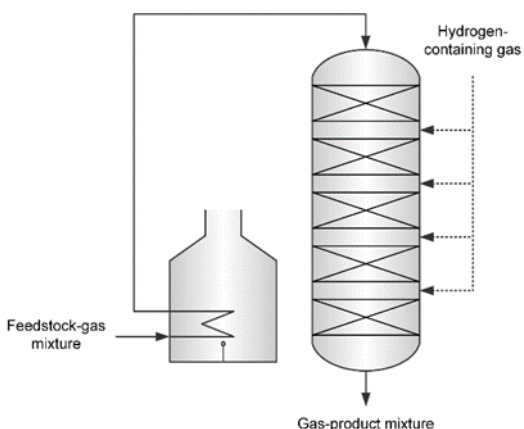


Figure 1. Simplified scheme of the hydrocracking process.

Before the hydrocracking process, the feedstock undergoes demetallization (on the first catalyst layer) and hydrotreating (on the second catalyst layer) to remove metals, sulfur and nitrogen compounds, as well as to hydrogenate aromatic hydrocarbons (dearomatization). Hydrocracking occurs on three catalyst layers (catalyst layers 3, 4, 5), where cracking and hydrogenation reactions occur, resulting in the formation of products with lower boiling point ranges than the feedstock (Fig. 1). Catalyst layers 2, 3, 4 and 5 are supplied with circulating hydrogen-containing gas.

Several models have been developed for the hydrocracking process so far. These models provide prediction of the product yields depending on the feedstock composition and technological parameters [16-21]. However, insufficient attention has been paid to modeling of the catalyst deactivation by coke in the hydrocracking process.

To develop a mathematical model of the hydrocracking process, the following groups of reactions were taken into account: hydrocracking and isomerization of high molecular weight n-paraffins C₂₂-C₄₀, hydrocracking of i-paraffins C₂₂-C₄₀, hydrocracking and isomerization of low molecular weight n-paraffins C₅-C₂₁, hydrocracking of i-paraffins C₅-C₂₁, hydrodeacyclization of naphthenes, hydrogenation of aromatic hydrocarbons. The content of n-paraffins by the number of carbon atoms in the molecule is determined using normal distribution [22]. Reactions that produce coke include: coke formation from aromatic hydrocarbons and coke formation from resins.

The change in the concentrations of reacting substances is calculated according to the law of mass action:

$$\frac{dC_i}{dt} = \pm \sum k_j \cdot C_{r_1}^{v_1} \cdot C_{r_2}^{v_2}, \quad (1)$$

where C_i is the concentration of the i^{th} substance, mol/l; t is time, s; k_j is the rate constant of the j^{th} reaction; C_{r_1} , C_{r_2} are the concentrations of the initial substances participating in the reactions, mol/l; v_1 , v_2 are stoichiometric coefficients; «+» means that the substance is formed in the reaction; «-» means that the substance is consumed in the reaction.

The reaction rate constant is calculated using the Arrhenius equation:

$$k_j = a_{cat} \cdot k_{0j} \cdot e^{\frac{-E_a}{RT}}, \quad (2)$$

where a_{cat} is catalyst activity, relative units; k_{0j} is preexponential factor; E_a is activation energy, $\text{J}\cdot\text{mol}^{-1}$; R is the universal gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T is temperature, K.

Catalyst activity is calculated as follows:

$$a_{cat} = A \cdot e^{-\alpha \cdot C_c}, \quad (3)$$

where A , α are empirical deactivation coefficients; C_c is the content of coke accumulated on the catalyst, %wt.

Spent catalysts of vacuum gas oil hydrocracking process were studied by thermogravimetric analysis and differential scanning calorimetry to determine of the content of coke accumulated on the surface of the catalyst during the operating cycle. The contents of coke are 3,96 %wt., 5,52 %wt. and 6,61 %wt. for catalyst layers 3, 4, 5 respectively.

The change in temperature in the reactor during the process is determined as follows:

$$\frac{dT}{dt} = \frac{\pm \Delta H_j \sum k_j \cdot C_{r1}^{v1} \cdot C_{r2}^{v2}}{C_{p_{mix}} \cdot \rho_{mix}}, \quad (4)$$

where ΔH_j is the heat of j^{th} reaction, $\text{J}\cdot\text{mol}^{-1}$; $C_{p_{mix}}$ is the heat capacity of the mixture, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; ρ_{mix} is the density of the mixture, kg/m^3 .

3. Results and discussion

Hydrogen is of key importance in the hydrocracking process [23]. Hydrogen is necessary for the hydrogenation of olefins, which are formed as intermediates in the target hydrocracking reactions, as well as for the saturation of aromatic compounds and cracked products. Hydrogen also has a significant effect on reducing the rate of hydrocracking catalyst deactivation by eliminating of the reactions leading to coke formation [24].

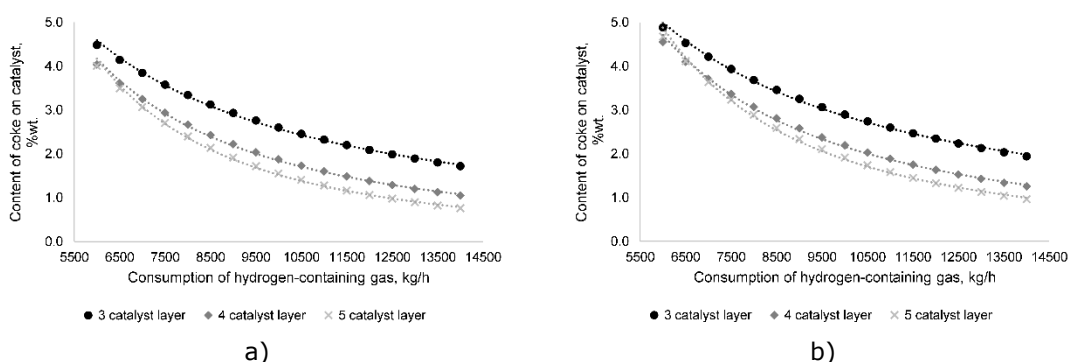


Figure 2. The content of coke on the catalyst (model calculations): a) at the feedstock flow rate of $220 \text{ m}^3/\text{h}$; b) at the feedstock flow rate of $240 \text{ m}^3/\text{h}$.

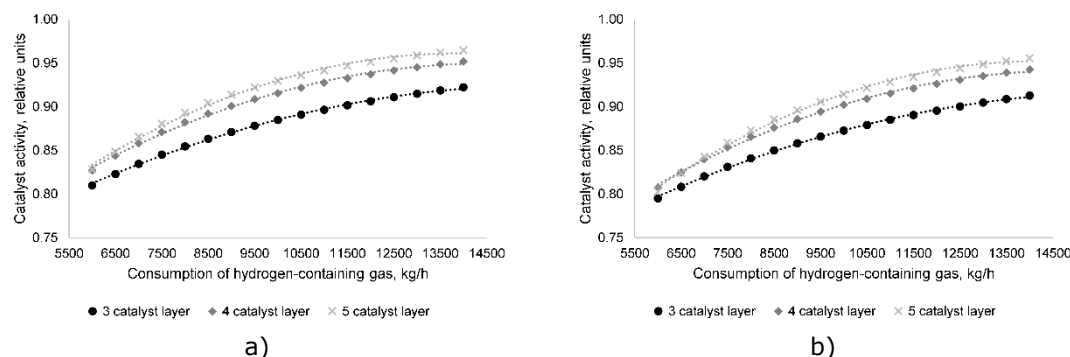


Figure 3. Catalyst activity (model calculations): a) at the feedstock flow rate of $220 \text{ m}^3/\text{h}$; b) at the feedstock flow rate of $240 \text{ m}^3/\text{h}$.

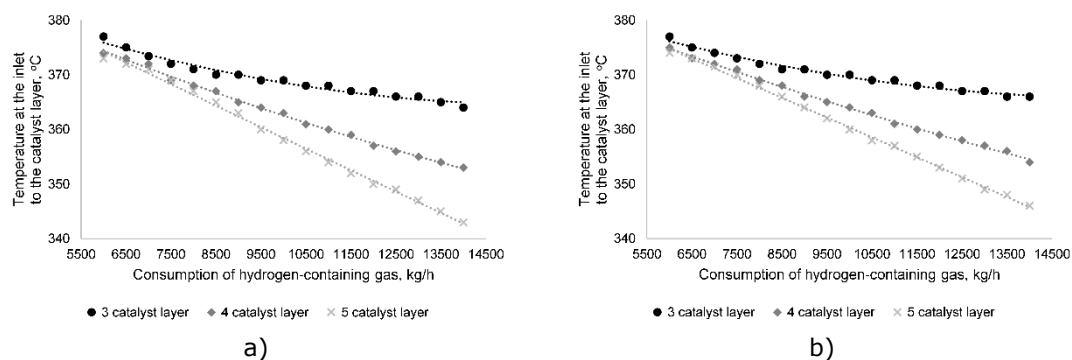


Figure 4. Temperature at the inlet to the catalyst layer (model calculations): a) at the feedstock flow rate of 220 m³/h; b) at the feedstock flow rate of 240 m³/h.

Using the developed mathematical model, a study was carried out on the influence of hydrogen-containing gas consumption on coke formation and a decrease in the activity of hydrocracking catalysts. The calculation was carried out for a catalyst operating cycle of 5 years for two feedstock flow rates – 220 m³/h and 240 m³/h.

When the consumption of hydrogen-containing gas increases from 6000 kg/h to 14000 kg/h, due to greater elimination of coke formation reactions at a higher consumption of hydrogen-containing gas and a decrease in the temperature at the inlet to the catalyst layer due to a larger proportion of cold hydrogen-containing gas in the feedstock-gas mixture:

- the coke content on the catalyst decreases: by 3.15 wt.%, 3.48 wt.% and 3.86 %wt. for the 3rd, 4th and 5th catalyst layers, respectively (at the feedstock flow rate of 220 m³/h); by 3.34 %wt., 3.83 %wt. and 4.38 % wt. for the 3rd, 4th and 5th catalyst layers, respectively (at the feedstock flow rate of 240 m³/h) (Fig. 2);
- the rate of catalyst deactivation reduces: by 0.13 relative units, 0.14 relative units and 0.16 relative units for the 3rd, 4th and 5th catalyst layers, respectively (at the feedstock flow rate of 220 m³/h); by 0.13 relative units, 0.16 relative units and 0.18 relative units for the 3rd, 4th and 5th catalyst layers, respectively (at the feedstock flow rate of 240 m³/h) (Fig. 3).

The decrease in temperature at the inlet to the catalyst layer due to the larger proportion of cold hydrogen-containing gas in the feedstock-gas mixture is: 14°C, 23°C and 31°C for the 3rd, 4th and 5th catalyst layers (at the feedstock flow rate of 220 m³/h), respectively; 14°C, 22°C and 28°C for the 3rd, 4th and 5th catalyst layers, respectively (at the feedstock flow rate of 240 m³/h) (Fig. 4).

The ongoing operation of the hydrocracking unit at low consumption of hydrogen-containing gas leads to accelerated deactivation of catalysts and a reduction in their prescribed service life due to increased coke formation, therefore the hydrocracking process is carried out at a sufficiently high consumption of hydrogen-containing gas. Higher feedstock flow rate also requires maintaining higher consumption of hydrogen-containing gas. The increase in the consumption of hydrogen-containing gas at the industrial unit is limited by the design capacity of the equipment. In addition, increasing the consumption of hydrogen-containing gas has a significant impact on the process temperature. Therefore, it is advisable to maintain the consumption of hydrogen-containing gas in order, on the one hand, to maintain the activity of the catalyst at the highest possible level, and, on the other hand, to maintain the process temperature that ensures the pass of the target reactions of the hydrocracking process and the required depth of feedstock conversion.

At the feedstock flow rate of 220 m³/h, the optimal value of the hydrogen-containing gas consumption is 9500 kg/h, and at the feedstock flow rate of 240 m³/h, it is 10000 kg/h, because above these values, the temperature at the inlet to the 5th catalyst layer becomes lower than the prescribed process temperature (360°C), at which the depth of feedstock conversion becomes lower than required. In addition, the further increase in consumption of hydrogen-containing gas leads to much smaller decrease in the rate of coke formation and the rate of

catalyst deactivation (Fig. 2, Fig. 3); thus, the further proportional increase in the consumption of hydrogen-containing gas is impractical, because operating costs for its pumping increase, but a decrease in the deactivation rate does not lead to appropriate proportional compensation for this increase in costs.

4. Conclusion

The developed mathematical model of the vacuum gas oil hydrocracking process provides calculation of the amount of coke formed in the reactions, the catalyst activity based on the amount of coke accumulated on the surface of the catalyst during its operation cycle, as well as temperature profiles across the catalyst layers. The model adequately describes the qualitative patterns of the influence of technological parameters on the process and can be used at industrial hydrocracking units to quantify the optimal process parameters in order to maintain the maximum possible catalyst activity and the required depth of feedstock conversion.

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Symbols

A, a	deactivation coefficients;
a_{cat}	catalyst activity, relative units;
C_c	the content of coke accumulated on the catalyst, %wt.;
C_i	the concentration of the i^{th} substance, mol/l;
$C_{p_{mix}}$	the heat capacity of the mixture, $J \cdot mol^{-1} \cdot K^{-1}$;
C_r	the concentration of the initial substance participating in the reaction, mol/l;
i	the number of the reagent;
j	the number of the reaction;
E_a	activation energy, $J \cdot mol^{-1}$;
k_{0_j}	preexponential factor;
k_j	the rate constant of the j^{th} reaction;
R	the universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$;
t	time, s;
T	temperature, K;
ν_1, ν_2	stoichiometric coefficients;
ρ_{mix}	the density of the mixture, kg/m^3 ;
ΔH_j	the heat of j^{th} reaction, $J \cdot mol^{-1}$.

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To whom correspondence should be addressed: Dr. Nataliya S. Belinskaya, School of Earth Sciences & Engineering, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia, E-mail: belinskaya@tpu.ru