ЧИСЛЕННОЕ ОПИСАНИЕ РАСПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ *н*-ПАРАФИНОВ В ВАКУУМНОМ ГАЗОЙЛЕ И ИХ РЕАКЦИОННОЙ СПОСОБНОСТИ В ПРОЦЕССЕ ГИДРОКРЕКИНГА

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В настоящее время процесс гидрокрекинга тяжелого нефтяного сырья является одним из основных процессов, позволяющих повысить глубину переработки нефти и получать компоненты моторных топлив высокого качества, в том числе компонентов дизельного топлива с улучшенными низкотемпературными свойствами. В данной статье представлен обзор существующих подходов к моделированию и разработанных моделей процесса гидрокрекинга тяжелого нефтяного сырья. Объектом исследования является процесс гидрокрекинга вакуумного газойля. В работе предложена схема химических превращений в процессе гидрокрекинга и математическая модель процесса. Отличительной особенностью предложенной схемы химических превращений и модели является учет реакций гидрокрекинга индивидуальных н-парафинов. Содержание индивидуальных н-парафинов в сырье процесса (вакуумном газойле) по числу атомов углерода в молекуле предложено определять исходя из распределения случайной величины, используя в качестве функции плотности вероятности функцию Гаусса. Реакционная способность индивидуальных н-парафинов в реакции гидрокрекинга учитывается в модели через термодинамические характеристики реакций гидрокрекинга каждого отдельного н-парафина, определенные с использованием квантово-химических методов. Расчет детального состава целевого продукта процесса – дизельного топлива – с учетом содержания индивидуальных н-парафинов позволяет определить его предельную температуру фильтруемости, которая в наибольшей степени зависит от содержания н-парафинов. Разработанная детальная модель процесса гидрокрекинга вакуумного газойля включает уравнения для расчета изменения концентрации реагирующих компонентов и уравнение для расчета изменения температуры процесса. Предложенный подход к моделированию процесса гидрокрекинга позволит оптимизировать процесс с учетом детального состава для получения максимального выхода низкозастывающего дизельного топлива.

Ключевые слова: вакуумный газойль, гидрокрекинг, парафин, математическая модель

NUMERICAL DESCRIPTION OF THE DISTRIBUTION OF *n*-PARAFFINS CONTENT IN VACUUM GAS OIL AND THEIR REACTIVITY IN THE HYDROCRACKING PROCESS

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Currently, the process of hydrocracking of heavy petroleum feedstocks is one of the main processes that makes it possible to increase the depth of oil refining and to obtain high-quality motor fuel components, including diesel fuel components with improved low-temperature properties. In this paper, a review on the existing modelling approaches and models of the heavy oil feedstock hydrocracking process is presented. The object of the research is the process of vacuum gasoil

hydrocracking. The work proposes the scheme of chemical transformations in the process of hydrocracking and the model of the process. The distinctive feature of the proposed chemical transformations scheme and a model is taking into account the hydrocracking reactions of individual n-paraffins. It is proposed to determine the content of individual n-paraffins in the feedstock of the process (vacuum gas oil) by the number of carbon atoms in the molecule based on the probability distribution, using the Gaussian function as a probability density function. The reactivity of individual n-paraffins in the hydrocracking reaction was taken into account via thermodynamic characteristics of the reactions of each individual n-paraffin determined using quantum-chemical methods. The calculation of the detailed composition of the target diesel product including the content of n-paraffins provides determination of cold filter plugging point, which is influenced by the content of n-paraffins to the most extent. The developed detailed model of vacuum gasoil hydrocracking process includes the equations for calculation of changes in concentrations of reacting component and change in the temperature of the process. The proposed approach to the modelling of the hydrocracking process makes it possible to optimize the process taking into account the detailed composition to get the maximum yield of low freezing diesel fuel.

Keywords: vacuum gas oil, hydrocracking, paraffin, mathematical model

INTRODUCTION

Due to the increasing volume of unconventional heavy oil production, oil refining is faced with the need to process an increasing volume of heavy oil feedstock [1]. The process of heavy oil feedstock hydrocracking is one of the most important processes in modern oil refining. In this process, in the high-concentrated hydrogen gas medium, under the action of a bifunctional catalyst, less valuable straight-run heavy oil fractions are converted into more valuable fuel products [2]. The most valuable target product is diesel fuel, which has a fairly high cetane number and a relatively low contents of sulfur and aromatics [3, 4].

To increase the production of high-margin products, improve their quality, reduce the production costs of oil refineries (consumption of energy resources, auxiliary materials, reagents, fuel additives, extending the service life of expensive catalysts), computer systems based on mathematical models are widely used for modeling, planning and optimization of production processes. Mathematical models developed based on the fundamental laws of processes are of the greatest value, because they are universal and can be used for various industrial objects in a wide range of parameters [5-7].

To date, a number of mathematical models of the hydrocracking process were developed. Stangeland developed a method of discrete grouping for modeling of the kinetics of transformations in the hydrocracking process, based on ordinary differential equations with a product distribution function [8]. This function is based on the boiling points of each pseudo-component characterizing the fraction. The model includes three parameters A, B, and C. Parameter A contains the reaction rate constants, while the distribution of yields is described by parameters B and C. An assumption is made about the first order of reactions, which simplifies the model. The authors [9] improved the kinetic model of the two-stage vacuum gas oil hydrocracking process that was proposed by Stangeland. Feedstock and products were divided into 23 pseudo-components and it was assumed that the reactions are pseudo-homogeneous and have the first order. Each group of components is characterized by a range of boiling points. Almeida and Guirardello presented a five-component model for hydroconversion of a vacuum residue [10]. For the kinetic model, 26 coefficients were estimated. The reactions between the micro-carbon residue and the light residue were assumed to be reversible, while the other reactions were assumed to be irreversible. In this model, thermal and catalytic reactions were considered as occurring in parallel. Using the true boiling points and the number of carbon atoms as the basis for determining hydrocarbon fractions, Balasubramanian and Pushpavanam developed a kinetic

model for vacuum gas oil hydrocracking based on discrete grouping [11]. In this kinetic model, three different stoichiometric components (arbitrary splitting, symmetrical and exponential) were used to determine the nature of the reactions and the distribution of product yields. So, an arbitrary splitting was proposed for both bases of the model – the true boiling points and the number of carbon atoms, an exponential form was proposed for the true boiling points of the group model, a symmetric form was proposed in the group model for the number of carbon atoms. To simulate hydrocracking reactions, the model includes five groups (gases, gasoline, kerosene, gas oil, residue). Krishan and Balasubramanian proposed an analytical solution for the kinetic model based on the complete stoichiometric discrete group model [12]. In this study, the general basis of the true boiling points of the discrete hydrocracking model was taken into account for cracking reactions occurring between groups. The authors made the assumption that cracking is a binary process in which only two products are formed in each cracking reaction. Also, the assumption is made that the cracking reactions are irreversible and have the first order. Using the method of the group first-order kinetics, the authors [13] developed a model that describes the hydrocracking of vacuum gas oil in a laboratory reactor filled with a zeolite catalyst. The proposed model divides the stream into 4 groups: vacuum gas oil, distillate, naphtha and gas. The model contains 12 kinetic parameters, which are determined from experimental data. In this study, three reaction routes and one activation energy coefficient were omitted. Thus, the number of coefficients is reduced to five. The study [14] presents a group model for the hydrocracking of a vacuum residue from Maya oil. The model includes 4 group components: products with the boiling point > 450 °C, products with the boiling point < 450 °C, gas and coke. Kinetic parameters were estimated based on experimental data obtained in a batch reactor at three temperatures (400 °C, 425 °C and 450 °C) and four residence times (10, 30, 60 and 90 min). The authors [15] used a computer algorithm to develop a scheme of elementary stages, including carbenium ions for the hydrocracking of paraffins, taking into account all reactions of each molecule. Due to the molecular approach, the number of kinetic parameters that describe the kinetics of hydrocracking is limited. The model based on the single event method was improved by Vynckier and Froment for the complex feedstock and includes a description of group coefficients in order to formulate reaction rate equations [16]. Topil'nikov and Sosna created a scheme of transformations and a mathematical model of the paraffin hydrocracking based on the literature

data [17]. To simplify the system and reduce the number of equations, all isomers having the same molecular weight and the number of methyl substituents were combined into groups. When compiling the system of kinetic equations, the following groups were considered (for carbocations, paraffins and olefins: N(s) – straight-chain, MB(s) – monobranched secondary, MB(t) – monobranched tertiary, DB(s) – dibranched secondary, DB (t) – dibranched tertiary, TB(s) – tribranched secondary, TB(t) – tribranched tertiary, P – paraffins, O – olefins). Further, the authors developed a kinetic model of the n-paraffin hydrocracking based on the proposed groups of components, the theory of the activated complex, and the principle of a single event [18]. Based on the activated complex theory, it was assumed that the reaction rates of isomers with the same number of methyl substituents constituting a group of components are equal. In addition, the model takes into account the gas-liquid equilibrium using the Langmuir isotherm. The authors [19] developed a model for the hydroconversion of a vacuum residue in a slurry phase. The model consists of 21 groups representing hydrocarbons, takes into account the consumption of hydrogen and calculates reaction rates through molar concentrations. In addition, vapor-liquid mass transfer and vapor-liquid equilibrium are taken into account. The authors [20] used the support vector machine, the group kinetic model and data obtained at the Tehran refinery, Iran to predict the yield of hydrocracking products. Several key parameters were used to evaluate the behavior of the support vector machine, including the minimum calculated quadratic correlation coefficient. The output variables of the model were optimized for hydrocracking products. The kinetic parameters and root-mean-square errors were calculated for 4-component kinetic model. The study [21] presents a mathematical model based on the gradient boosting machine learning method, which predicts the value of the sediment content in the atmospheric residue of a tar hydrocracking unit, which can be used as a tool for continuous monitoring of the indicators of the resulting product and operational process control, which will reduce the quality margin and maintain maximum plant conversion and economic efficiency, as well as reduce unwanted equipment contamination and increase equipment run times. Fan and Long modeled an industrial hydrocracking unit using the Aspen HYSYS program [22]. According to a data set from one of the Chinese refineries, key parameters to which product yield is sensitive have been optimized. It is shown that a model that predicts the yield of certain products describes industrial data well. Based on the corrected model, the influence of the

properties of feedstock on the distribution of products was studied. The calculation results show that there is a linear correlation between feedstock and mass yield of products, which indicates that the calculation results can be used directly as delta base values for a linear programmable model used in production planning. The authors [23] simulated the hydrocracking unit using the Aspen HYSYS software. The model can be used to predict failures in the operation of a hydrocracking unit.

Thus, the models based on the grouping of reactants by fractions, as well as more detailed models, which are based on the aggregation of the reactants by groups: paraffins, naphthenes, aromatic hydrocarbons, were developed for the hydrocracking process. The detailed models (especially single event models) describe product characteristics (yield, PNA distribution) far more accurate than models, based on lumping approach. The first models then can be used for predicting of compositions in terms of individual molecules. Also, these models provide the detailed kinetic description of the individual molecules and can be applied as a research tool. Some drawbacks of the detailed models include their complexity, requirements of large computational resources, expensive analytical methods, as well as large number of parameters to be estimated from experimental data, which make them inapplicable for industrial objects. The models developed according to the lumping approach are useful for practical applications, for example, for the design and operation of the industrial hydrocracking units. But, in these models the chemistry of the process is not fully taken into account. The developed models do not take into account n-paraffin distribution and their reactivity in the target hydrocracking reaction. Thus, the numerical description of distribution of n-paraffins mass contents and their reactivity in the target hydrocracking reaction is a useful contribution to the methodology of the modeling of the hydrocracking process and. From the practical point of view, the developed model can be used not only for prediction of the yield of diesel fuel, but also its crucial operational characteristics such as cold flow properties and the cetane number.

In our previous work, we developed an approach for modeling of the petroleum distillates hydroprocesses, based on the chemical transformations of hydrocarbons, the reactivity of n-paraffins in the target reaction of hydroprocesses – the hydrocracking reaction, as well as the non-stationary nature of the processes due to catalyst deactivation and changes of feedstock composition [24]. The developed approach was applied for modeling of the catalytic hydrodewaxing process. A mathematical model was created in several main stages. An analysis of experimental data on the

composition of feedstock and products, as well as existing knowledge about the chemistry and mechanism of the process. On the basis of the analysis, a scheme of chemical transformations was drawn up. A method for recalculating of the feedstock fractional composition into a group composition was developed. Functional dependences of the long-chain n-paraffins content in the feedstock on the number of carbon atoms in the molecule were revealed. The relationships of n-paraffins reactivity in the target reaction (hydrocracking reaction) under the conditions of the industrial hydrodewaxing process were established. A system of equations of a non-stationary mathematical model of the process was compiled, taking into account the distribution of n-paraffin mass content in the feedstock and their reactivity in the target reaction.

The processes of catalytic hydrodewaxing and hydrocracking are similar. Namely: the processes proceed in a hydrogen medium on bifunctional catalysts; feedstocks are fractions of complex compositions, the determination of which is a labor-consuming and expensive procedure. In these processes, the target reaction is the selective hydrocracking of n-paraffins. The most valuable target product is diesel fuel. Similar mechanisms of catalyst deactivation are observed. Similar process technologies are used for the processes. Processes due to the changing composition in the feedstock and deactivation of the catalyst have non-stationary nature. Thus, the identified earlier regularities and the approach to modeling of petroleum distillates hydroprocesses, developed on the example of the hydrodewaxing process, can be applied for the modeling of the heavy oil feedstock hydrocracking process. Also, for the hydrocracking process, the simplest group scheme of transformations and the simplest kinetic model was developed, as well as a program code was compiled for solving the equations of this model [25, 26]. From the scientific point of view, this model does not fully reflect the regularities of the hydrocracking process and a more detailed study of the physicochemical laws and the development of a mathematical model according to the approach described above are the vital tasks.

Taking into account the fact that one of the target reactions in the hydrocracking process is the hydrocracking of n-paraffins, the reactivity of n-paraffins in this reaction under industrial conditions and its numerical description is of the greatest interest. This is because the total content of n-paraffins and the distribution of n-paraffins content by the number of carbon atoms determine to the greatest extent the cetane number and low-temperature properties of the resulting diesel fuel, as well as the effectiveness of additives that

improve the low-temperature properties of diesel fuel [27, 28].

The aim of this work is to reveal and numerically describe the relationships between *n*-paraffins content in the feedstock of the hydrocracking process (vacuum gas oil) and their chain length. It allows us to establish relationships between the reactivity of *n*-paraffins in the target reaction of hydrocracking and the number of carbon atoms in the molecule at different position of bond cleavage in order to develop a detailed mathematical model of the vacuum gas oil hydrocracking process.

EXPERIMENTAL

The object of research is the process of vacuum gas oil hydrocracking. The most common technology of the hydrocracking process is two-stage hydrocracking. In the two-stage variant, hydrotreatment, feedstock hydrogenation and partial hydrocracking are carried out in the first stage, while the main hydrocracking proceeds in the second stage. In this case, a higher depth of conversion of heavy feedstock is achieved [29]. The feedstock of the hydrocracking process is vacuum gas oil with a boiling range of 350-500 °C. The following main products are obtained in the process: liquefied hydrocarbon gas, light gasoline fraction, heavy gasoline fraction, kerosene, diesel fuel. By-products include hydrocarbon gas, hydrogen sulfide, ammonia, unconverted residue.

Hydrocracking catalysts are bifunctional, that is, they have both acidic active sites, on which cracking and isomerization reactions occur, and metal active sited, on which hydrogenation-dehydrogenation reactions occur. Zeolites, aluminosilicates and aluminum oxide are used as the acid components. The metals from group VIII (nickel, cobalt) and group VI (molybdenum, tungsten) are used as hydrogenating components [30].

The process kinetic description is based on the chemical transformations scheme. The level of detail of chemical transformations in the modeling of a particular process largely depends on the possibility and complexity of determining the compositions of feedstock and products. The feedstock of the hydrocracking process is a heavy fraction of vacuum gasoil, which detail composition is determined via a complex procedure [31]. Therefore, the development of a detailed scheme of chemical transformations, taking into account all the stages of the reaction mechanisms, is inappropriate for this process. Simplified chemical transformation schemes based on combining reactants into groups, and reactions into groups of reactions, describe the chemical nature of complex oil refining processes with a fairly high accuracy. The group composition of heavy oil fractions, including vacuum gas oil, is determined using liquid adsorption chromatography, high temperature gas chromatography, and multi-dimensional chromatography.

For the purpose of hydrocracking process modeling, the following key components were identified: *n*-paraffins C_{22}-C_{40}, *n*-paraffins C_5-C_{21}, *i*-paraffins C_{22}-C_{40}, *i*-paraffins C_5-C_{21}, hydrocarbon gas, naphthenes, aromatic hydrocarbons, resins, coke, hydrogen. The reactions are combined into the following key reactions: hydrocracking of C_{22}-C_{40} *n*-paraffins (individually for each *n*-paraffin), isomerization of *n*-paraffins C_{22}-C_{40}, cracking of i-paraffins C_{22}-C_{40}, isomerization of *n*-paraffins C_5-C_{21}, hydrocracking of naphthenes, hydrogenation of aromatic hydrocarbons, formation of coke from aromatic hydrocarbons, formation of coke from resins. Reactions without the participation of hydrogen are of the first order, reactions with the participation of hydrogen are of the second order. Fig. 1 shows the chemical conversion scheme in hydrocracking process.
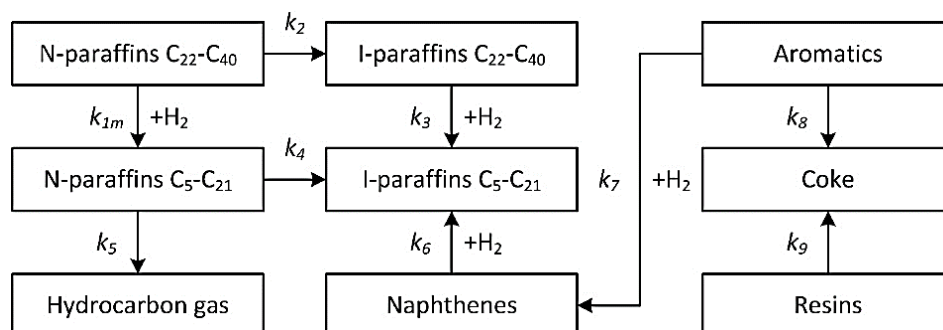

Fig. 1. The scheme of chemical transformations in the process of vacuum gas oil hydrocracking. m – the number of the reaction in the array of *n*-paraffin hydrocracking reactions (m = 1-19 assigned accordingly to the number of carbon atoms in *n*-paraffin molecule x = 22-40); k_{1m} – the array of rate constants of hydrocracking reactions of individual *n*-paraffins C_{22}-C_{40}; k_2 – k_9 – rate constants of the reactions

Рис. 1. Схема химических превращений в процессе гидрокрекинга вакуумного газойля. m – номер реакции в массиве реакций гидрокрекинга *н*-парафинов (m = 1-19 назначается соответственно числу атомов углерода в молекуле *н*-парафина x = 22-40); k_{1m} – массив констант скоростей реакций гидрокрекинга индивидуальных н-парафинов C_{22}-C_{40}; k_2 – k_9 – константы скоростей реакций

Сравнение значений массового содержания *н*-парафинов в вакуумном газойле, рассчитанных по уравнению (1), и экспериментальных значений, полученных по [32]. Общее массовое содержание *н*-парафинов составляет 18,40 % мас.

Table. **Comparison of the values of *n*-paraffins mass content in vacuum gas oil, calculated by equation (1), and the experimental values obtained by [32]. The total mass content of *n*-paraffins is 18,40 %wt.**

Number of carbon atoms in the *n*-paraffin molecule									
22		23		24		25		26	
N-paraffin content, %wt.									
calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
1.44	1.45	1.47	1.55	1.44	1.50	1.36	1.30	1.23	1.09
Number of carbon atoms in the *n*-paraffin molecule									
27		28		29		30		31	
N-paraffin content, %wt.									
calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
1.07	0.98	0.89	0.82	0.71	0.70	0.55	0.61	0.41	0.38
Number of carbon atoms in the *n*-paraffin molecule									
32		33		34		35		36	
N-paraffin content, %wt.									
calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
0.29	0.30	0.2	0.25	0.13	0.19	0.08	0.10	0.05	0.07
Number of carbon atoms in the *n*-paraffin molecule									
37		38		39		40			
N-paraffin content, %wt.									
calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.		
0.03	0.03	0.02	0.02	0.01	0.01	0.00	0.01		

In order to reveal and numerically describe the relationships between the mass content of *n*-paraffins and their chain length, the compositions of heavy oil fractions presented in [32-37] were analyzed. It was found that the distribution of the mass content of *n*-paraffins in petroleum distillates by the number of carbon atoms in the molecule obeys the normal distribution (Gauss distribution) with a deviation to the right (positive distribution):

$$C_{i(w)npar}(x) = C_{(w)npar} \cdot \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}, \quad (1)$$

$C_{i(w)npar}$ – the mass content of individual *n*-paraffins, %wt.; $C_{(w)npar}$ – the total mass content of *n*-paraffins, %wt.; x – total number of carbon atoms in *n*-paraffin molecule; σ – the standard deviation of the distribution; μ – mode of the distribution (σ and μ are determined using experimental data on the feedstock composition: $\sigma = 5$, $\mu = 23$).

The calculation error does not exceed the error of experimental methods for determining the mass content of *n*-paraffins in petroleum distillates. Thus, equation (1) accurately enough describes qualitative and quantitative relationships between the mass content of *n*-paraffins in vacuum gas oil and the chain length for the purpose of developing a detailed mathematical model.

One of the target reactions of the vacuum gas oil hydrocracking process is the hydrocracking of *n*-paraffins. For a numerical description of *n*-paraffins reactivity in hydrocracking reactions, the probability of reactions involving *n*-paraffins with a different number of carbon atoms in the molecule and the probability of C–C bond cleavage at different position in *n*-paraffin molecule (v_m) were determined.

The reactivity and bond cleavage probabilities were determined on the basis of the thermodynamic characteristics of hydrocracking reactions under industrial process conditions (the temperature of 360 °C, the pressure of 16 MPa). The reactions include hydrocracking of *n*-paraffins C_{22}-C_{40}. For each of *n*-paraffin C_{22}-C_{40} hydrocracking reactions the products, that are considered, include *n*-paraffins, formed by cleavage of bonds from the one located at the first atom in the chain to the central bond of the molecule. To determine the thermodynamic parameters, it is possible to use reference books, but the number of components described in them is limited and there is no possibility of studying the influence of pressure. For the substances and technological conditions, which are not presented in the reference books, the thermodynamics studies are most often carried out using quantum chemical calculation methods implemented in specialized software. The models of n-paraffins and hydrogen molecules were built in GaussView. To calculate the thermodynamic properties of these molecules, the quantum-chemical method of the DFT theory, implemented in

the Gaussian software product [38] (the B3LYP model (Becke's density functional theory (B3)), Lee Yang and Par correlation (LYP)), basis 3-21G) were used. This method was chosen after comparison of the reference values [39] and the results of calculations of thermodynamic parameters for low molecular weight *n*-paraffins (from C_5H_{12} to C_9H_{20}) and hydrocracking reactions of these *n*-paraffins by the methods which are most commonly used in computational chemistry, such as semiempirical method PM3 and nonempirical method DFT [40]. The values calculated by DFT (B3LYP model) were more accurate and the calculation error does not exceed 7% compare to the reference values. The use of this method also reflects other works in the literature on studying *n*-paraffins, for example [41]). The change in the Gibbs energy during the reactions was calculated according to the Hess's law.

The revealed dependences of the change in the Gibbs energy in the *n*-paraffin hydrocracking reactions upon bond cleavage at different position in the molecule and obtained on their basis the probability functions of bond cleavage at different position in *n*-paraffin hydrocracking reaction are presented in Fig. 2 and Fig. 3 respectively for *n*-paraffin $C_{40}H_{82}$. Dependences for the reactions of *n*-paraffins with the number of carbon atoms in the molecule from 22 to 39 have the similar form.
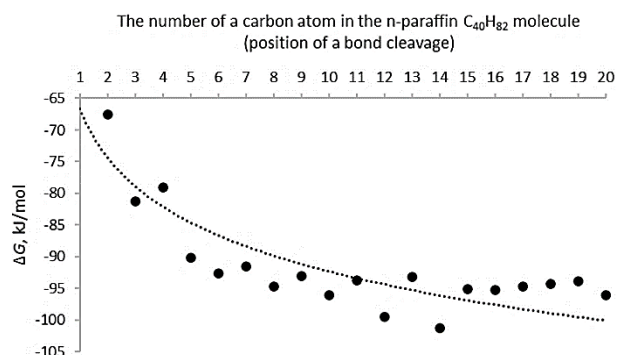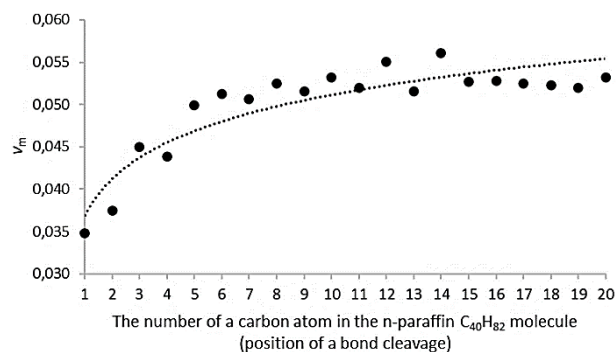

Fig. 3. Probability of bond cleavage at different position in hydrocracking reaction of *n*-paraffin $C_{40}H_{82}$

Рис. 3. Вероятность разрыва связи в разных положениях в реакции гидрокрекинга *н*-парафина $C_{40}H_{82}$

Fig. 2. Change in the Gibbs energy in hydrocracking reactions of *n*-paraffin $C_{40}H_{82}$ at different position of bond cleavage

Рис. 2. Изменение энергии Гиббса в реакциях гидрокрекинга *н*-парафина $C_{40}H_{82}$ при различном положении разрыва связи

The reaction rate constant is determined by the values of the energy and entropy factors. The energy factor (activation energy) characterizes the energy barrier that molecules must overcome for a reaction. The entropy factor characterizes the probability of a reaction occurring in a collision. Paraffin hydrocracking reactions are structurally sensitive. Therefore, the entropy component included in the equation for calculating the Gibbs energy is different for paraffins with different chain lengths.

Numerically, the probability of bond cleavage at a particular position in the *n*-paraffin molecule is incorporated into the model of the hydrocracking process in the form of a bond cleavage probability matrix developed on the basis of the thermodynamic probability of bond cleavage at different position. In the equations of the model, the reaction rate is multiplied by the probability of reactions, which makes it possible to reflect the regularities of the reactivity of paraffins.

RESULTS AND DISCUSSION

Taking into account the revealed relationships on *n*-paraffin mass content distribution in vacuum gasoil and their reactivity in the target reaction, mathematical model of the vacuum gas oil hydrocracking process is written as follows:

$$\begin{cases} \frac{dC_i}{d\tau} = \sum_{l=1}^{p_1} \sum_{i=1}^{s_1} \pm a_{cat}(\tau) \cdot k_l \cdot C_i(\tau) + \sum_{n=1}^{p_2} C_{H_2} \sum_{i=1}^{s_2} \pm a_{cat}(\tau) \cdot k_n \cdot C_i(\tau) + \\ + \sum_{npar=1}^{s_3} C_{H_2} \sum_{m=1}^{p_3} \sum_{x=x_1}^{x_n} \sum_{x'=x'_1}^{x'_n} \pm a_{cat}(\tau) \cdot k_{1m}(x) \cdot C_{npar}(x) \cdot v_m(x,x') \\ \frac{dT}{d\tau} = -\frac{1}{C_p^{mix}} \sum_{j=1}^{p_4} \Delta H_j \cdot a_{cat}(\tau) \cdot k_j \cdot C_j(\tau) \end{cases} \quad (2)$$

C_i – the contents of reacting substances, mol/l; C_{npar} – the contents of *n*-paraffins, mol/l; k_l – the rate constants of the reactions, in which hydrogen does not participate; k_n – the rate constants of the reactions, which involve hydrogen; k_{1m} – the array of rate constants of hydrocracking reactions of individual *n*-paraffins C_{22}-C_{40}; v_m – the probability of bond cleavage in different positions in the molecule in hydrocracking of

n-paraffins; τ – the residence time, s; T – the temperature of the process, K; C_p^{mix} – the heat capacity of the mixture, J/mol·K; j – the index of the reaction; ΔH_j – the change in Enthalpy of the reaction, kJ/mol; x – total number of carbon atoms in n-paraffin molecule; x' – the number of a carbon atom at which a bond breaks (the position of bond clevage) in the n-paraffin molecule; x_1, x_n – the number of carbon atoms in the shortest and the longest n-paraffin, respectively (in case of vacuum gas oil $x_1 = 22$, $x_n = 40$); x'_1 – the number of a carbon atom in the molecule, which represents the position of bond cleavage in the n-paraffin molecule between the first and the second carbon atom, $x'_1 = 1$; x'_n – the number of a carbon atom in the molecule, which represents the position of bond cleavage in the n-paraffin molecule in the center of the molecule; i – the index for the groups of hydrocarbons; $npar$ – the index for n-paraffins C_{22}-C_{40} (n-$par = 1 \div 19$ assigned accordingly to the number of carbon atoms in n-paraffin molecule $x = 22$-40); l – the number of a reaction in which hydrogen does not participate (according to the chemical transformation scheme $l = 2; 4; 5; 8; 9$); n – the number of a reaction, which involve hydrogen (according to the chemical transformation scheme $n = 3; 6; 7$); m – the number of a reaction in the array of n-paraffin hydrocracking reactions ($m = 1 \div 19$ assigned accordingly to the number of carbon atoms in n-paraffin molecule $x = 22$-40); p_1 – total number of reactions in which hydrogen does not participate; p_2 – total number of reactions, which involve hydrogen; p_3 – total number of hydrocracking reactions of n-paraffins; p_4 – total number of reactions; s_1 – the number of hydrocarbon groups participating in the reactions, in which hydrogen does not participate; s_2 – the number of hydrocarbon groups participating in the reactions, which involve hydrogen; s_3 – the number of n-paraffins participating in the hydrocracking reactions; a_{cat} – the relative catalyst activity (catalyst activity, determined relatively to the activity of the fresh catalyst, which is considered equal to 1).

Initial conditions: $\tau = 0$ $C_i = C_{i0}$ $T = T_0$.

The first term in the material balance equation describes the reactions, in which hydrogen does not participate, the second term describes the reactions, which involve hydrogen. The third term describes the hydrocracking reactions of n-paraffins, including consideration of initial contents of individual n-paraffins, which are determined according to the methodology explained in section 3.2 and consideration of n-paraffins behaviors (bond cleavage at different positions in the molecule) in hydrocracking reaction via multiplication of a reaction rate constant by the bond cleavage probability in different positions in the molecule of n-paraffin.

The process of vacuum gas oil hydrocracking is a complex industrial process. In this process a heavy oil feedstock with a complex composition is used, a huge number of multi-stage reactions occur, flows are characterized by a complex hydrodynamic structure, the contribution of heat transfer by different ways is difficult to assess, etc. A detailed description of all these phenomena is impractical and sometimes impossible. Therefore, in order to take into account the most important physical and chemical regularities of the process and for further applying of the model in practice for the industrial process, some assumptions were made during modeling. The industrial hydrocracking reactor is a vertical vessel with axial flow of the feedstock. Due to the fact that the height of the reactor is much greater than its diameter (the height is 38000 mm, the diameter is 2500 mm) the ideal plug flow regime is made as an assumption to describe the hydrodynamic structure of the flows in the reactor. The developed model is formalized and quasi-homogeneous. Therefore, the rate constants shall be regarded as effective, i.e. they are a combination of constants of all intermediate stages. The reaction rates were written according to the law of mass action. Thus, the model assumptions include: formalized chemical transformations scheme, normal distribution of mass content of n-paraffins in the feedstock, quasi-homogeneous reaction medium, the ideal plug flow regime, adiabatic operation.

CONCLUSIONS

The proposed approach to the development of a detailed mathematical model of the vacuum gas oil hydrocracking process is based on taking into account the regularities of n-paraffins mass content distribution and their reactivity in the target reaction. It is shown that the relationships between the mass content of n-paraffins and the number of carbon atoms in the molecule can be quite accurately described numerically using the normal distribution, the parameters of which are determined based on experimental data on the compositions of vacuum gas oils. Using quantum-chemical methods for calculations, the thermodynamic probability of bond cleavage at a different position in the n-paraffin molecule was determined, on the basis of which a matrix of bond cleavage probabilities was compiled, which describes the revealed regularities of n-paraffins reactivity in the model. The revealed regularities of the distribution of n-paraffins content and their reactivity will allow to predict not only the yield, but also the low-temperature properties of the obtained diesel fuel. The proposed mathematical model is a system of material and heat balance equations, which includes a description of reactions in which hydrogen

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does not participate, reactions involving hydrogen, and a detailed description of *n*-paraffin hydrocracking reactions.

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