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PREDICTION OF RESOURSE BASE INCREASE OF CATALYTIC DEWAXING BY A MATHEMATICAL MODELING METHOD

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Abstract

Climatic conditions in Russia generate a great need for high-quality waxy diesel fuels. To solve this problem it was proposed to increase the resource base of a catalytic dewaxing process for production of winter and arctic marks of diesel fuels by adding a middle fraction of (C14-C20) hydrocarbons using a method of mathematical modeling. The paper presents the method for selection of this particular faction. The mathematical model was evaluated and its value was assessed. The assumptions were confirmed by the calculations which showed that the resource base can be extended by addition of (C_{14}-C_{20}) n-paraffins into a paraffin extraction unit. And, it will improve the potential of hydrocarbons usage in an enterprise and increase the production of winter and arctic marks of diesel fuels in the catalytic dewaxing unit.

Keywords: diesel fuel; catalytic dewaxing; low-temperature characteristics; mathematical model.

1. Introduction

Production of diesel fuel of winter and arctic marks is an urgent task of the state, since the development of the strategically important northern and arctic regions depends on its solution. The climatic conditions in these regions cause a large demand for high-quality waxy diesel fuels. However, today there is a shortage in the winter and arctic marks of diesel fuel with the desired low temperature properties in Russia [1-3].

Low-temperature properties of diesel fuel are determined with hydrocarbon composition. N-paraffins characterized by a high melting temperature have the greatest influence on low temperature properties of diesel fuel. Isoalkanes have lower cloud point and maximum filtration temperature, therefore, they are important components in the preparation of waxy fuels. Thus, the main aim of the production of diesel fuel with the improved low temperature properties is to determine the optimum feed composition providing a high yield at the required quality [5-6].

The research process of catalytic dewaxing of diesel fuel led to the creation of a complex mathematical model of the dewaxing process describing the processes occurring inside the reactor, and the relationship between the structural units of all chemical-engineering system.

The aim of this work is to increase the resource base of the production of diesel fuels of winter and arctic marks in the process of catalytic dewaxing due to the addition of a middle fraction of (C_{14}-C_{20}) hydrocarbons on base of the mathematical modeling method.

The fraction of C_{14}-C_{20} hydrocarbons has an acceptable value of pour point and cetane number of diesel fuels for production of winter and arctic marks (Fig. 1-2).

The maximum value is observed for the conversion of n-paraffins having from 14 to 20 carbon atoms in a hydrocarbon chain. It means that the n-paraffins of this composition can be potential feedstock for the production of diesel fuels of winter and arctic marks in the dewaxing process (Fig. 3).

At the present time in Russia diesel fuel is manufactured according to the current standards (GOST 305-2013, GOST 52368-2005, GOST R 55475-2013) normalizing such indicators for diesel fuels, as cloud point, filterability, pour point, cetane number and content of sulfur and polycyclic aromatic hydrocarbons [4]. The main document is GOST R 52368-2005 according which, five marks of diesel fuel used in a cold and arctic climate are produced (0, 1, 2, 3, 4 with maximum filtration temperature from -20°C to -44°C).

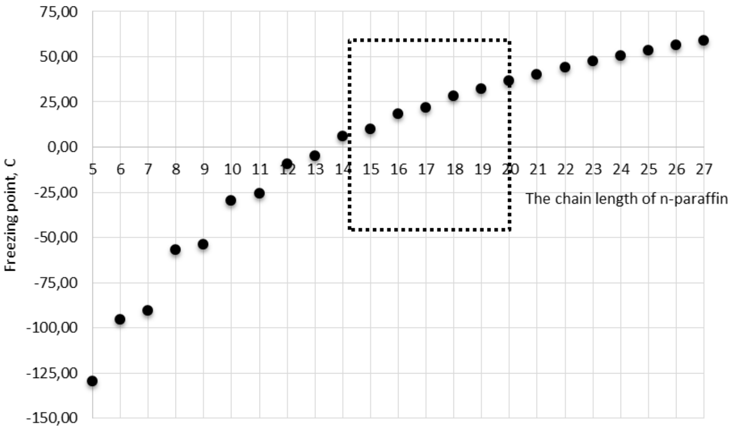

Fig. 1. The solidification temperature dependence of the n-paraffin chain length

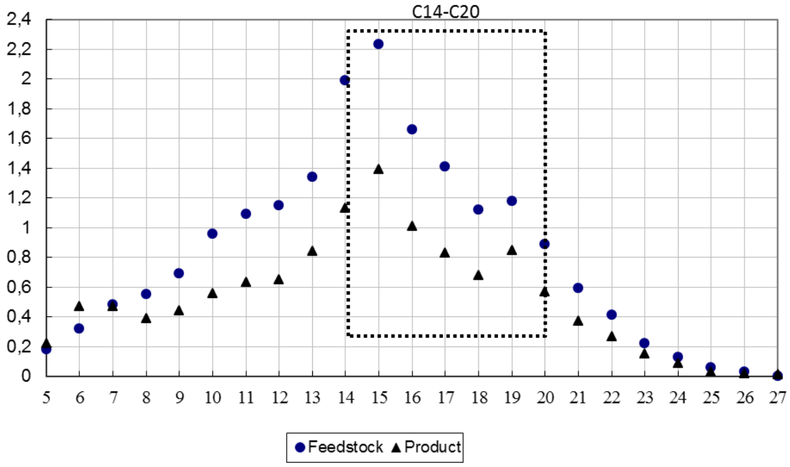

Fig. 2. The content of n-paraffins in the feedstock and the product

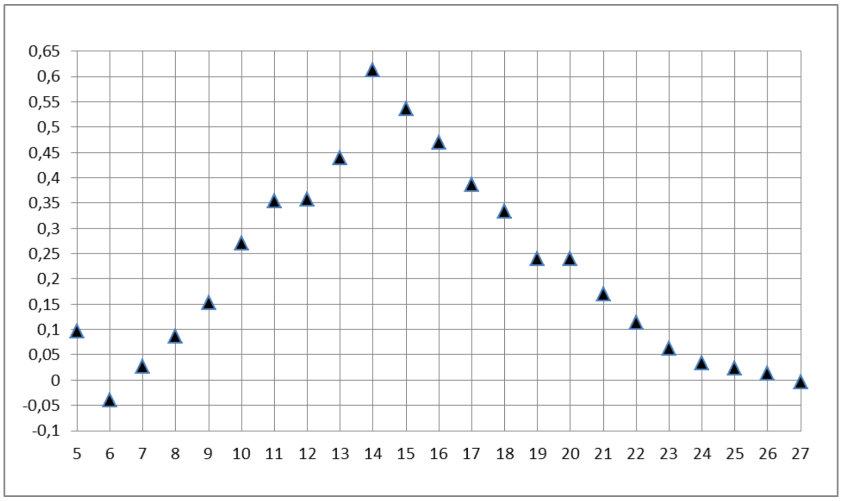

Fig. 3. Change in conversion of hydrocarbons of the length of their chains

A catalytic dewaxing unit with a block of paraffin separation «Parex» was studied in the research.

In the catalytic dewaxing process the main hydrocarbon conversion occurs on Ni-containing catalyst in a hydrogen atmosphere at a temperature of 350-400°C. The process results in hydrocracking reactions, hydroisomerisation, hydrogenation of unsaturated hydrocarbons, hydrogenation of mercaptans with the formation of hydrogen sulfide, flavoring and coking products. After the reactor unit the product is fed into the stabilization and rectification unit where light hydrocarbons, hydrogen sulfide and water are separated, and the obtained stable hydrogenate is divided into the products.

Based on the developed mathematical model of catalytic dewaxing [7-8] the influence of addition of a middle fraction of (C_{14}-C_{20}) hydrocarbons from the paraffin isolation unit into the dewaxing feedstock on the yield and the quality of the diesel fuel were investigated. The experimental data of the industrial catalytic dewaxing units L-24-10/2000 as well as the n-paraffin separation unit "Parex" were used as initial data for the research based on the mathematical model. The hydrocarbon compositions of the feedstock and the products are shown in Tab. 1, 2.

Table 1. The feedstock composition of the catalytic dewaxing process

Component	Content, wt. %
N-paraffins C_5-C_9	1,15
N-paraffins C_{10}-C_{27}	19,90
Iso-paraffins	18,31
Naphthenes	38,91
Olefins	2,50
Monoaromatic hydrocarbons	18,82
Polyaromatic hydrocarbons	1,12

Table 2. The composition of the product flow in the paraffin separation unit «Parex»

Component	Content, wt. %
N-paraffins C_5-C_9	1,1
N-paraffins C_{10}-C_{13}	41,5
N-paraffins C_{14}-C_{20}	55,8
Monoaromatic hydrocarbons	1,6

The compositions of the product flows of the catalytic dewaxing unit obtained by mixing dewaxing feedstock and (C_{14}-C_{20}) hydrocarbons of the paraffin isolation unit «Parex» in various ratios are shown in Tab. 3.

Table 3. The hydrocarbon composition of the streams obtained by mixing dewaxing feedstock and hydrocarbons of the unit «Parex» (consumption of dewaxing feedstock 280 m^3/h)

	Consumption of added paraffins, m^3/h		
	70	80	90
Component		Content, wt.%	
N-paraffins C_5-C_9	1,14	1,13	1,13
N-paraffins C_{10}-C_{27}	27,08	27,88	28,63
I-paraffins	14,65	14,24	13,86
Naphthenes	31,13	30,26	29,45
Olefins	2	1,94	1,89
Monoaromatic hydrocarbons	15,38	15,00	14,64
Polyaromatic hydrocarbons	0,9	0,9	0,9

It can be seen from Table 3-5 that addition of (C_{14}-C_{20}) hydrocarbons from the unit «Parex» into the dewaxing feedstock composition increases the content of (C_{14}-C_{20}) n-paraffin of feedstock of the unit from19.90% to 28.61%, thus expanding the resource base of the dewaxing unit in order to increase the yield of diesel fuels of different marks.

To describe the industrial process of catalytic dewaxing in the fixed-bed reactor, a model of a plug flow reactor as a system of differential equations of mass balance and thermal balance for each component was used:

$$\begin{cases} G\cdot\dfrac{\partial C_i}{\partial z}+G\cdot\dfrac{\partial C_i}{\partial V}=\sum\limits_{j=1}^{m}a_j\cdot W_j \\ G\cdot\dfrac{\partial T}{\partial z}+G\cdot\dfrac{\partial T}{\partial V}=\dfrac{1}{\rho\cdot C_p^{см}}\sum\limits_{j=1}^{m}Q_j\cdot a_j\cdot W_j \end{cases}$$

The initial conditions are: $z = 0$: $C_i = C_{i,0}$; $T = T_0$; $V = 0$: $C_i = C_{i,0}$; $T = T_0$,
Catalyst activity:

$$a_j = A_j\cdot e^{-\alpha_j\cdot C_K}$$

The kinetic parameters of the model, such as a pre-exponential factor of the Arrhenius equation (k_0) and activation energy of the reaction (E_a), were evaluated by solving the inverse kinetic equation by means of selection of the kinetic parameter values to ensure minimum deviation between the calculated and experimental parameters. They can be effective due to such kinetic parameters, i.e., the reaction behavior for all intermediate stages is taken into account.

Table 4 shows the kinetic parameters of the catalytic dewaxing reactions for the Ni-containing zeolite catalyst operated in the industrial unit with the Co-Mo hydrotreating catalyst.

Table 4. Kinetic parameters of the model of the catalytic dewaxing process (at a temperature of 355°C)

№	Reaction	E_a, kJ/mole	k_0	k_j
1.	Hydrocracking n-paraffins C_{10}–C_{27}	140	$5,12\cdot10^{9}$ $l\cdot s^{-1}\cdot mole^{-1}$	$1,16\cdot10^{-2}$ $l\cdot s^{-1}\cdot mole^{-1}$
2.	Dehydration n-paraffins C_5-C_9	110	$1,04\cdot10^{6}$ s^{-1}	$7,37\cdot10^{-4}$ s^{-1}
3.	Isomerization of olefins	130	$6,07\cdot10^{8}$ $l\cdot s^{-1}\cdot mole^{-1}$	$9,33\cdot10^{-3}$ $l\cdot s^{-1}\cdot mole^{-1}$
4.	The cyclization i-paraffins	180	$6,47\cdot10^{10}$ s^{-1}	$6,90\cdot10^{-5}$ s^{-1}
5.	Hydrogenation of monoaromatic hydrocarbons	140	$5,00\cdot10^{5}$ $l\cdot s^{-1}\cdot mole^{-1}$	$7,34\cdot10^{-7}$ $l\cdot s^{-1}\cdot mole^{-1}$
6.	hydrogenation of polyaromatic hydrocarbons	140	$3,28\cdot10^{7}$ $l\cdot s^{-1}\cdot mole^{-1}$	$7,45\cdot10^{-5}$ $l\cdot s^{-1}\cdot mole^{-1}$
7.	Formation of coke	190	$2,39\cdot10^{12}$ s^{-1}	$3,75\cdot10^{-4}$ s^{-1}
8.	Formation of mercaptans	120	$2,95\cdot10^{6}$ $l\cdot s^{-1}\cdot mole^{-1}$	$3,08\cdot10^{-4}$ $l\cdot s^{-1}\cdot mole^{-1}$
9.	Hydrogenation of mercaptans	80	$3,67\cdot10^{7}$ $l\cdot s^{-1}\cdot mole^{-1}$	$8,14$ $l\cdot s^{-1}\cdot mole^{-1}$

2. Experimental

For this process to be described by a model of the catalytic dewaxing process it is necessary to take into account not only kinetics of hydrocarbon reactions, but also a hydrodynamic mode of a catalytic reactor, i.e. the reactor in which the process takes place.

The adequacy of the model was verified by comparing the experimental data of industrial isomerization unit L-24-10/300 with the calculated values (Tab. 5).

Table 5. The adequacy check of the model according to experimental data

Hydrocarbons	Hydrocarbon content in the product, wt.% estimated	experimental
N-paraffins C_5-C_9	1,05	1,15
N- paraffins C_{10}-C_{20}	18,56	19,90
I-paraffins	19,25	18,31
Naphthenes	39,50	38,91
Olefins	2,0	2,50
Monoaromatic hydrocarbons	18,86	18,82
Polyaromatic hydrocarbons	1,02	1,12

The adequacy check of the reactor model has shown its sensitivity to the hydrocarbon composition of the feedstock and the low deviation of the calculated and experimental values within 5%, which allows using it for optimization calculations.

The developed mathematical model was implemented as a computer program. Using the software, a user can interact with the program through the interface, introduce initial data and select a type of calculation. The algorithm for solving the system of equations of the kinetic process model is realized by means of these calculations. The model parameters (numerical characteristics of flows and reactions) are read from the database.

Fig. 4 is a schematic representation of the interaction between a user and a designer of the model on the stages of its development and testing.

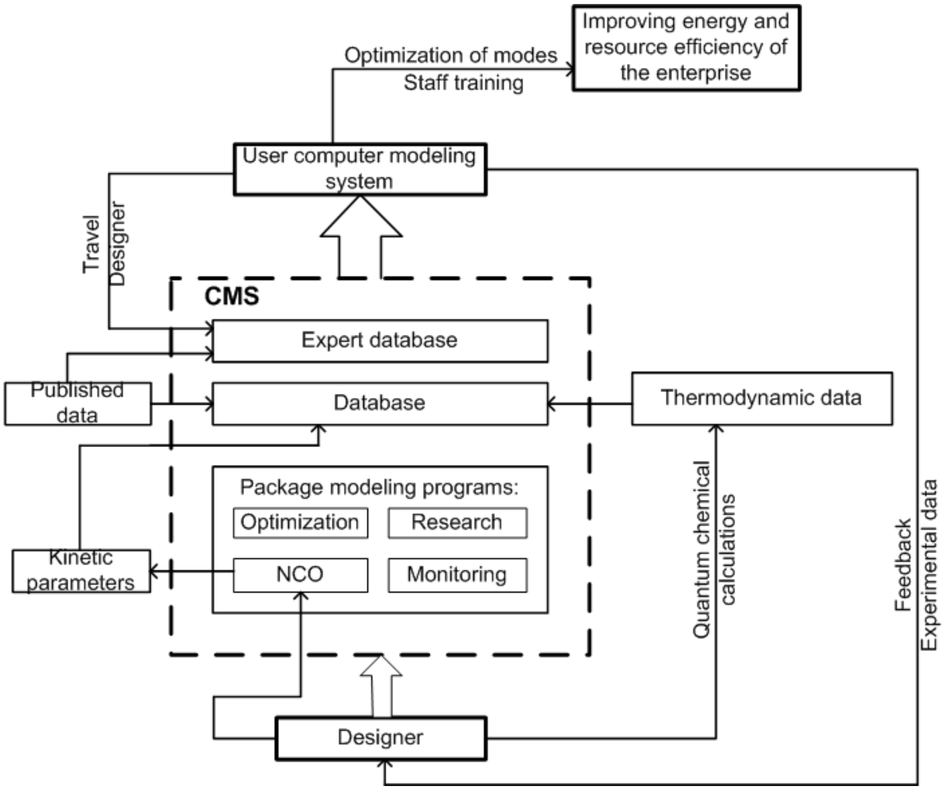

Fig.4. Interaction of a user and a software designer

3. Results and discussion

The study of influence of the feedstock composition obtained by mixing the feedstock of the dewaxing process and an additional fraction of (C_{14}-C_{20}) hydrocarbons of the paraffin separation unit «Parex» on the quality of the diesel fuel of winter and arctic marks was conducted under the following constant process parameters (Tab. 6).

Table 6. Technological parameters

Inlet temperature in the reactor R-3, °C	352
Inlet pressure in the reactor R-3, MPa	7,1
Hydrogen-containing gas flow rate in the reactor R-3, m^3/h	30 607
Maximum filtration temperature for winter diesel fuel marks, °C	-26
Maximum filtration temperature for arctic diesel fuel marks, °C	-44

The results are shown in Fig. 5, 6. The results showed that depending on the amount of the added fraction of hydrocarbons (C_{14}-C_{20}) from 70 to 90 m^3/hour in the dewaxing feedstock, the diesel fuel production increased by 25-32% (60-77 m^3/hr) for producing winter fuel and by 52-68 m^3/h for arctic fuel of the given fuel quality.

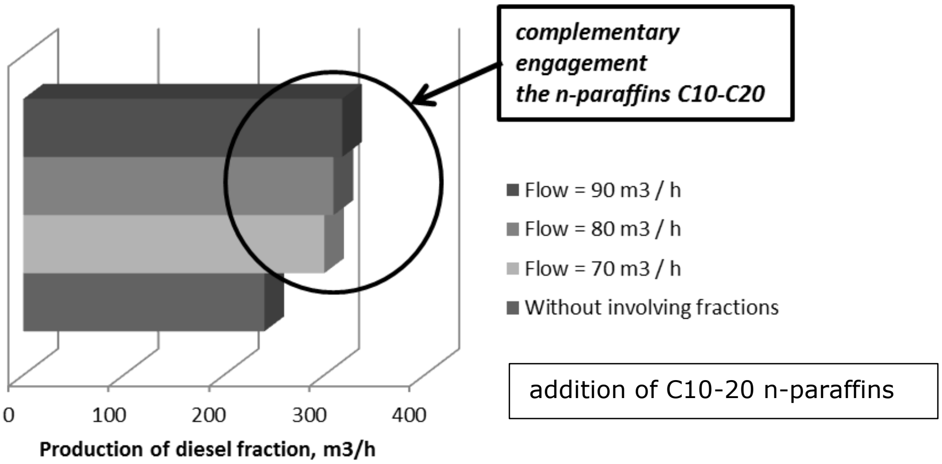

Fig. 5. Production of winter diesel fuel depending on the amount of the added fractions of (C_{14}-C_{20}) hydrocarbons

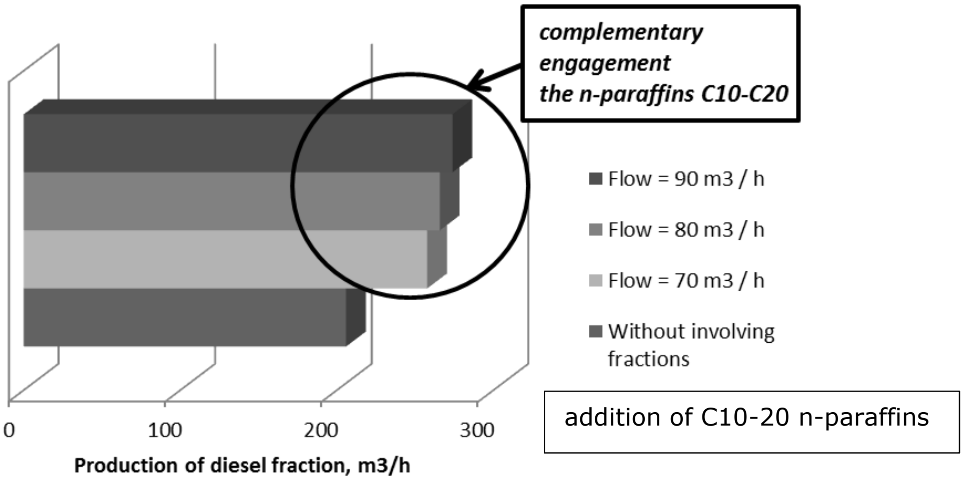

Fig. 6. Production of arctic diesel fuel depending on the amount of the added fractions of (C_{14}-C_{20}) hydrocarbons

Thus, the calculations carried out on the mathematical model of the catalytic dewaxing process showed that the resource base of the unit can be extended by addition of the (C_{14}-C_{20}) n-paraffin fraction separated in the paraffin separation unit. It allowed us to increase the use of the whole volume of hydrocarbon feedstock in an enterprise and increase the production of diesel fuels of winter and arctic marks in a catalytic dewaxing unit. The optimal parameters of the unit should be determined to provide the required yield of diesel fuel while maintaining the quality of the low-temperature properties.

To conclude, addition of (C_{14}-C_{20}) n-paraffin in an amount of 70 to 90 m^3/h in the dewaxing feedstock can increase the yield of diesel fuel by 25-32 % by increasing the content of the main components. The conversion of these components in hydrocracking reactions allows producing target components of diesel fractions.

4. Conclusions

Application of the proposed mathematical model of a catalytic dewaxing process takes into account the impact of technological modes of the unit operation and the composition of the feedstock depending on the desired quality of the obtained diesel fuel of winter and arctic marks.

The study based on the mathematical model has shown that the resource base of the catalytic dewaxing process for the production of diesel fuels of winter and arctic marks can be extended by addition of a middle fraction of hydrocarbons (C_{14}-C_{20}) from the paraffin extraction unit «Parex» that allows us to increase the content of (C_{14}-C_{20}) n-paraffins from 19.90% to 28.61% in the feedstock of the unit. In addition, depending on the amount of (C_{14}-C_{20}) hydrocarbons added from 70 to 90 m^3/hour in the dewaxing feedstock there was an increase of the yield of diesel fraction by 25-32% (60-77 m^3/h) for winter fuel and 52-68 m^3/h for arctic fuel of the given quality. The use of the model allowed determining the optimal temperature condition of the catalyst operation under changes of the composition and consumption of feedstock in the unit. Moreover, it is necessary to maintain the temperature of 355-357°C for the production of winter fuels, and 363-365°C for the production of arctic fuels. Thus, an increase in the amount of an additional fraction from 70 to 90 m^3 hour results in the increased temperature of the reactor by 2°C, and the increased yield of the diesel fraction by 8%.

Redistribution of feedstocks and product flows between a catalytic dewaxing unit and a paraffin separation unit can increase the whole potential of hydrocarbon feedstock and its processing in the case of a single production.

Symbols

z	*the amount of refined feedstock after loading of fresh catalyst, m^3;*
G	*feedstock consumption, m^3 / h;*
z	*$G \bullet t$ (t – catalyst operating time after loading, h);*
C_i	*concentration of the i th component, mol/L;*
V	*bed volume of catalyst, m^3;*
a_j	*catalyst activity in j th reaction;*
ρ –	*density of mixture in kg / m^3;*
$C_p^{см}$	*specific heat capacity of mixture, J / (kg • K);*
Q_j	*heating effect of j th reaction J/mole;*
T	*temperature, K;*
Wj	*rate of j th reaction, mole / (l • s),*
m	*the number of reactions.*
Aj, αj	*decontamination factor;*
C_K	*concentration of coke,% by weight.*

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