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Development of a Mathematical Model of the Diesel Fractions Isodewaxing Process

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Abstract

The chemistry of the diesel oil fractions isodewaxing process on the catalysts containing noble metals (Pt, Pd) was studied. The process of isodewaxing is intended for the production of diesel fuel with improved cold-flow properties, corresponding to the winter and arctic grades. The thermodynamic parameters of the reactions were determined. The mechanisms of coke formation on the catalyst surface were studied. A scheme of chemical transformations was devel-oped, taking into account target and side reactions, as well as the mechanisms of coke formation. Based on the identi-fied patterns, a mathematical model of the process was developed. The model is sensitive to the composition of the pro-cessed feedstock and can be used to predict the cold filter plugging point, the yield of low-freezing diesel fuel, and the catalyst activity in the isodewaxing process. Using the developed model, predictive calculations of the cold filter plug-ging point and the yield of low-freezing diesel fuel, as well as predictive calculations of the decrease in catalyst activity during the processing of raw materials of various compositions, were carried out. Hydrotreated and unhydrotreated diesel fractions were considered as the raw materials. The effect of the hydrogen-containing gas consumption on the activity of the catalyst was shown.

Keywords: *Diesel fuel; Isodewaxing; Cold filter plugging point; Mathematical model.*

1. Introduction

Currently, there is a tendency towards the development of the Arctic territories and the development of the economic potential of regions located in cold climate zones. In this regard, the demand for diesel fuel corresponding to winter and Arctic grades in terms of low-temperature properties is constantly increasing [1-3].

In industry, catalytic processes, aimed to convert diesel oil fractions into diesel fuels, which have improved low-temperature properties, such as hydrodewaxing and isodewaxing, have proved to be the most efficient [4-6]. Improvement of the diesel fuel low-temperature properties is achieved through the conversion of long-chain unbranched paraffins, the content of which determines the low-temperature properties of the fuel, on bifunctional catalysts [7-8]. Previously, the process of hydrodewaxing of diesel fuels, proceeding on a Ni-containing catalyst, was studied in detail. Namely, the chemistry of the process, the thermodynamics and kinetics of the occurring reactions, the mechanisms of catalyst deactivation were studied. An unsteady mathematical model and computer modeling system of this process were developed [9-10]. The target reaction in the process of hydrodewaxing on a Ni-containing catalyst is the selective hydrocracking of normal paraffins due to which the low-temperature properties are improved, but the yield of the target product (diesel fuel) is significantly reduced, the yield of by-products (gas and gasoline increases), the proportion of naphthenic and aromatic hydrocarbons in its composition, which have a low cetane number, are increased [8]. Despite the fact that the isodewaxing process takes place on a more expensive catalyst containing Pt or Pd, it has an undeniable advantage over the hydrodewaxing process: due to the fact that the target reaction in the process is the isomerization, not hydrocracking, a higher yield of the target diesel fuel is achieved. Thus, the isodewaxing process is promising for the production of low-freezing diesel fuels [11-12].

Mathematical modeling of the diesel fuel isodewaxing process is an urgent task. The developed mathematical model can be used as a tool to study the influence of the composition of raw materials and technological parameters on the yield and properties of the obtained product, the degree of catalyst deactivation, as well as to optimize technological modes on existing and new, currently actively introduced into industry, low-freezing diesel production units.

2. Chemistry and reaction thermodynamic parameters of diesel fractions isodewaxing process

The main reaction in the isodewaxing process, leading to an improvement in the low-temperature properties of diesel fuel, is the hydroisomerization reaction of long-chain n-paraffins. In the isomerization reaction, methyl-substituted isomers are most likely formed, ethyl- and propyl-substituted isomers are formed in small amounts [13].

In the process, selective hydrocracking of paraffins also proceeds to an insignificant extent with the formation of diesel range paraffins with a shorter chain, which have better low-temperature properties compared to long-chain n-paraffins presented in the feedstock.

In the process of isodewaxing, side reactions of oligomerization occur, which reduce the selectivity of the process. For the oligomerization reactions to occur, the presence of olefins in the reaction mixture is required. Olefins are formed in the isomerization reaction at the dehydrogenation stage and at the stage of carbocation deprotonation. Heavy hydrocarbons formed in the oligomerization reaction are difficult to desorb from the catalyst surface and can lead to its coking [14]. During isodewaxing process, in the presence of hydrogen, olefins undergo hydrogenation. In addition, the hydrogenation of polyaromatic hydrocarbons occurs [15].

In the process of diesel fractions isodewaxing, olefins and polyaromatic hydrocarbons are coke precursors. Naphthenes are also slightly contribute to coke-generation.

Table 1 shows the reactions of the diesel fractions isodewaxing process, taken into account for the purpose of developing a mathematical model, as well as their thermodynamic parameters.

Table 1. Reactions of the diesel fractions isodewaxing process

№	Reaction	Δ*G*, kJ/mol	Δ*H*, kJ/mol
1.	Isomerization of HM n-paraffins	−5.44	−2.03
2.	Hydrocracking of HM n-paraffins	−88.82	−61.58
3.	Oligomerization of LM olefins	−10.43	−94.80
4.	Hydrogenation of HM olefins	−62.76	−132.79
5.	Hydrogenation of LM olefins	−70.76	−134.28
6.	Hydrogenation of polyaromatic hydrocarbons	−82.13	−44.95

Thermodynamic properties were calculated using the quantum-chemical method of the density functional theory DFT, the theoretical approximation is the B3LYP model, the 3-21G basis at the process temperature of 320°C and a pressure of 4 MPa. Fig. 1 shows the scheme of chemical conversions in the process of diesel fractions isodewaxing process.

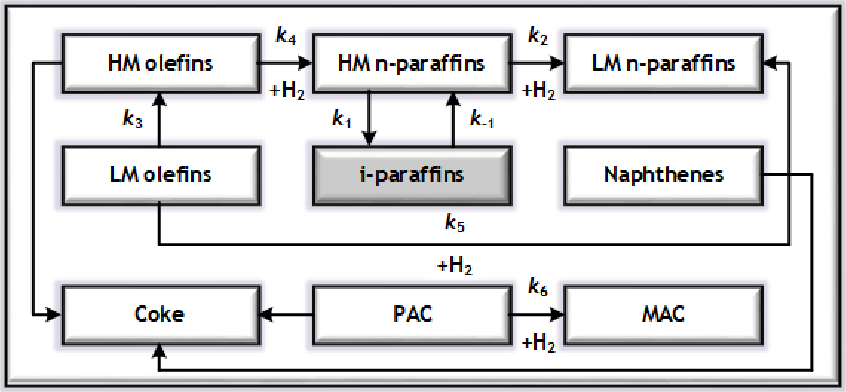

Figure 1. The scheme of chemical conversions in the process of diesel fractions isodewaxing process

In Fig. 1 and further in the kinetic model, the following symbols are adopted: k_j is the rate constant of the forward reaction, k_{-j} is the rate constant of the reverse reaction, where *j* is the number of the reaction (Table 1); HM n-paraffins are unbranched high molecular weight paraffins C_{12}-C_{27}; LM n-paraffins are unbranched low-molecular weight n-paraffins C_5-C_{11}; i-paraffins are branched paraffins C_{12}-C_{27}; HM olefins are high molecular weight olefins C_{12}-C_{27}; LM olefins are low molecular weight olefins C_5-C_{11}; MAC are monoaromatic hydrocarbons; PAC are polyaromatic hydrocarbons.

3. Kinetic model of the diesel fractions isodewaxing process

The kinetic model of the diesel fractions isodewaxing process is a system of differential equations, which describes changing the concentrations of reactants over time:

$$\begin{cases} \frac{dC_1}{dt} = -k_1 \cdot C_1 + k_{-1} \cdot C_3 - k_2 \cdot C_1 \cdot C_8 + k_4 \cdot C_4 \cdot C_8 \\ \frac{dC_2}{dt} = k_2 \cdot C_1 \cdot C_8 + k_5 \cdot C_5 \cdot C_8 \\ \frac{dC_3}{dt} = k_1 \cdot C_1 - k_{-1} \cdot C_3 \\ \frac{dC_4}{dt} = 2 \cdot k_3 \cdot C_5^2 - k_4 \cdot C_4 \cdot C_8 \\ \frac{dC_5}{dt} = -2 \cdot k_3 \cdot C_5^2 - k_5 \cdot C_5 \cdot C_8 \\ \frac{dC_6}{dt} = k_6 \cdot C_7 \cdot C_8 \\ \frac{dC_7}{dt} = -k_6 \cdot C_7 \cdot C_8 \\ \frac{dC_8}{dt} = -k_2 \cdot C_1 \cdot C_8 - k_4 \cdot C_4 \cdot C_8 - k_5 \cdot C_5 \cdot C_8 - k_6 \cdot C_7 \cdot C_8 \end{cases} \qquad (1)$$

Initial conditions: $t = 0$, $C_i = C_{i0}$. Integration limit up to $t = \tau$ ($\tau = 3600 \cdot V_{cat}/V_{feed}$).

In the equations of the kinetic model, the following symbols are adopted: C_{i0} is initial concentrations of the reacting components, mol/m^3; C_i is current concentration of reacting components, mol/m^3, where *i* is the number of the reagent (1 is for HM n-paraffins ; 2 is for LM n-paraffins; 3 is for i-paraffins; 4 is for HM olefins; 5 is for LM olefins; 6 is for MAC; 7 is for PAC; 8 is for hydrogen); *t* is time, s; *τ* is the residence time, s; V_{cat} is the volume of the catalyst bed, m^3; V_{feed} – feedstock consumption, m^3/h.

The amount of coke is calculated based on the amount of olefins, polyaromatic hydrocarbons and naphthenes in the reaction mixture, which are coke precursors.

The catalyst activity is calculated through the content of coke as follows:

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

where A_j, α_j – deactivation coefficients; C_{coke} – content of coke and coke-generating compounds deposited on the catalyst surface, %wt.

The kinetic model is implemented in the form of a program containing a module for loading the initial data, a module for recalculating the content of components from % wt. to mol/m^3, a module containing a mathematical model and an algorithm for solving the equations of a mathematical model, a module for calculating the low-temperature properties of the obtained diesel fuels, a module for outputting calculation results.

4. Results and discussion

Using the developed model of the diesel fractions isodewaxing process, predictive calculations of the influence of the feedstock composition and technological parameters on the cold filter plugging point (CFPP) and the yield of the obtained low-freezing diesel fuel, as well as on the activity of the catalyst were carried out.

For the calculations, two feedstock compositions were used: the composition of the unhydrotreated diesel fraction (DF-1) and the composition of the hydrotreated diesel fraction (DF-2).

Table 2. Compositions of the isodewaxing process feedstocks

Component of the feedstock	Content, % wt.	
	DF-1	DF-2
n-paraffins	34.5	23.2
i-paraffins	34.9	40.3
Naphthenes	10.2	18.2
MAC	5.2	9.7
PAC	12.7	7.1
Olefins	0.7	1.0
Heteroatom compounds	1.8	0.5
Sum	100.0	100.0
CFPP, °C	−6	−11

The predictive calculation of the cold filter plugging point and the yield of low-freezing diesel fuel for two feedstock compositions were carried out (Fig. 2 and Fig. 3, respectively). Technological parameters at which the calculation was carried out: temperature at the isodewaxing reactor is 320 °C, pressure is 4 MPa, feedstock consumption is 280 m^3/h; the consumption of hydrogen-containing gas is 25000 m^3/h.

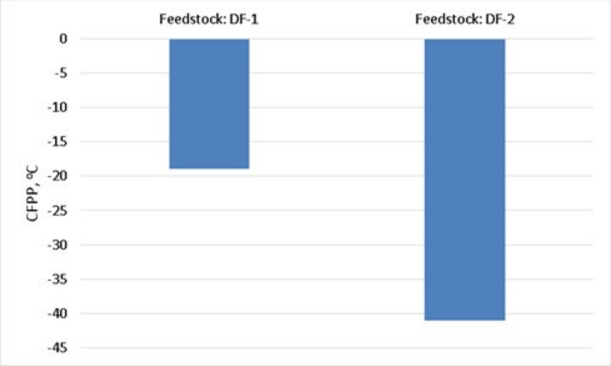

Figure 2. The CFPP of diesel fuel obtained in the process of isodewaxing

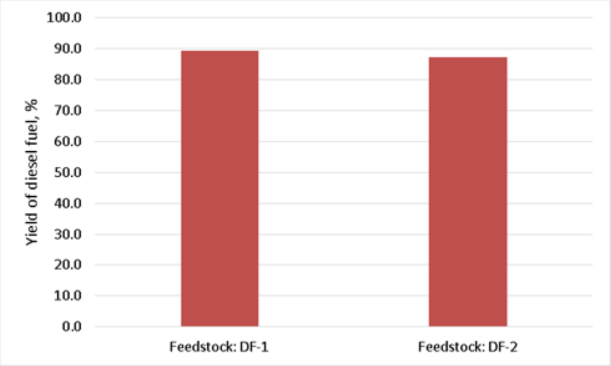

Figure 3. The yield of diesel fuel obtained in the process of isodewaxing

The product obtained from the feedstock DF-2 has a significantly better CFPP in comparison with the product obtained from the feedstock DF-1, because initially, the composition of the feedstock DF-2 contains a greater amount of i-paraffins, while the degree of conversion of n-paraffins for two different feedstock compositions is approximately the same.

Fig. 4 shows the results of the predictive calculation of the catalyst activity for two feedstock compositions for the catalyst operation period of 12 months.

As can be seen from Fig. 4, when processing feedstock DF-1, the relative activity of the catalyst after 12 months of operation is 4% lower than when processing feedstock DF-2. This is due to the fact that the unhydrotreated diesel fraction contains a larger amount of polyaromatic hydrocarbons, the compounds from which the formation of coke, deactivating the catalyst, is most likely.

As noted above, olefins in the reaction mixture of the isodewaxing process participate in oligomerization reactions, in which, in turn, coke-generating compounds are formed that block the catalyst surface. In addition, in the isodewaxing process, coke is formed from polyaromatic compounds. In the process of isodewaxing, hydrogen in the composition of a hydrogen-containing gas (HCG) participates not only in target reactions that make it possible to obtain components with improved low-temperature properties, but also hydrogenates compounds that are coke precursors. Fig. 5 shows the results of the predictive calculation of the catalyst activity depending on the flow rate of the hydrogen-containing gas.

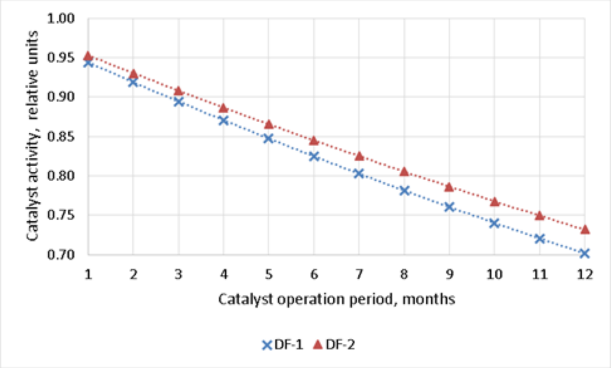

Figure 4. Change in the activity of the isodewaxing catalyst within 12 months for two feedstock compositions

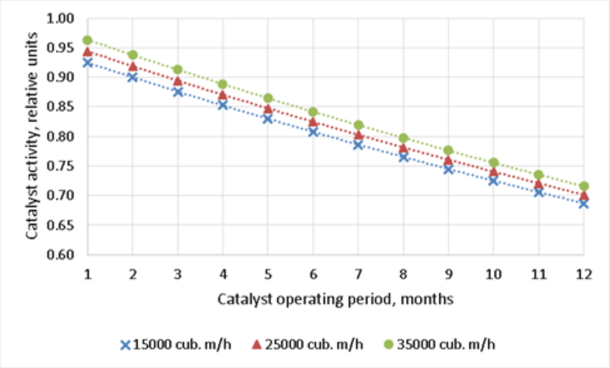

Figure 5. Influence of the hydrogen-containing gas consumption on the activity of the catalyst

As can be seen from Fig. 5, an increase in the consumption of hydrogen-containing gas makes it possible to save the catalyst resource by an average of 2% with an increase in the flow rate by each 10000 m^3/h.

5. Conclusion

The developed model is sensitive to the composition of the processed feedstock and can be used to predict the CFPP, the yield of low-freezing diesel fuel, and the activity of the catalyst in the diesel fractions isodewaxing process. Model calculations show that preliminary hydrotreating of feedstock prior to processing in the isodewaxing process allows saving the catalyst resource by an average of 4% per year of operation by reducing the content of polyaromatic hydrocarbons, which are hydrogenated in hydrotreating. It was also been shown that it is advisable to maintain the flow rate of the hydrogen-containing gas and the partial pressure of hydrogen at the highest possible level, as far as it can be provided by the resources of fresh hydrogen-containing gas and economic considerations, since this makes it possible to save the catalyst resource by an average of 2% with an increase in the flow rate of hydrogen-containing gas by each 10000 m^3/h.

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Symbols

A_j, a_j	*deactivation coefficients;*
C_{coke}	*content of coke and coke-generating compounds deposited on the catalyst surface, %wt;*
C_{i0}	*initial concentrations of the reacting components, mol / m^3;*
C_i	*current concentration of reacting components, mol / m^3;*
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_{cat}	*the volume of the catalyst bed, m^3;*
V_{feed}	*feedstock consumption, m^3/h;*
τ	*the residence time, s.*

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