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INFLUENCE OF FEEDSTOCK AND HYDROGEN-CONTAINING GAS FLOW RATES ON THE EFFICIENCY OF MIDDLE DISTILLATES CONVERSION IN THE PROCESS OF CATALYTIC DEWAXING

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Abstract

This work considers the influence of feed rate and hydrogen-containing gas flow rate on the yield and quality of the diesel fraction obtained in the process of catalytic dewaxing of middle distillate fractions using the mathematician model. It is shown that the yield of the diesel fraction and its low-temperature properties depend on the feed rate and hydrogen-containing gas flow rate. An increase in the feed rate from 240 to 360 m^3/h leads to an increase in the yield of the diesel fraction from 58% to 63%. Moreover, a decline of its low-temperature properties by 1-4°C (at T =300°C) and 4-7°C (at T = 340°C) due to an increase in the contact time of the raw material with the catalyst. The increase of the hydrogen-containing gas flow rate from 5000 to 50000 m^3/hr, on the contrary, leads to a decrease in the yield of the diesel fraction by 3-5%. In addition, it leads to improvement of diesel fractions low-temperature properties by 3-4°C for different feedstock compositions, which is associated with increased hydrocracking reactions leading to formation of lighter hydrocarbons with lower meanings of freezing temperature and cold filter plugging point.

Keywords: diesel fraction; fuel; low-temperature properties; catalytic dewaxing; model; hydrogen; feed rate.

1. Introduction

Currently, the demand for diesel fuel of winter and arctic grades, which correspond to the requirements for low-temperature properties (freezing temperature, cloud point) is constantly increasing. This is due to such factors as developing north regions (more than 2/3 of Russian Federation territory), increase in the proportion of diesel powered passenger car traffic (growth by 6 % a year), the relevance of increasing the depth of petroleum refining because of the growth of export duty on heating oil and heavy residue [1-3].

Solving this problem is possible by increasing the proportion of hydrogenation processes [4-6] in general structure of a refinery, such as hydrotreating, dewaxing, hydrocracking, as well as by developing methods of informational support, which allow decreasing in operating costs of this processes.

Today, 5 grades of winter and arctic diesel, having cold filter plugging point from –32 to –52°C, are produced in Russia according to the State Standard 55475-2013 [7]. One of the widespread processes of winter and arctic diesel fuel production is the process of catalytic dewaxing. The main transformations of hydrocarbons occur on the surface of Ni-Mo catalyst in the medium of hydrogen-containing gas at the temperature of 350-400°C [8-9].

The efficiency of catalytic dewaxing depends on the variety of factors, such as technological conditions (temperature, pressure, feedstock flow rate, flow rate of hydrogen-containing gas) [10]. Hydrogen plays a key role in the process, because it is a reagent in the target reactions of of hydrocracking and hydroisomerization. Increasing the flow rate of hydrogen-containing gas in the reactor hydrocracking of paraffins passes with higher conversion. The equilibrium of hydrogenation of formed olefins shifts to the products.

The aim of this work is to study the influence of flow rates of feedstock and hydrogen-containing gas on the efficiency of middle distillate fraction conversion in the process of catalytic dewaxing under change of feedstock composition using the mathematical model of the process.

2. Research object and methods

The object of the research is the feedstock of middle distillates catalytic dewaxing process of different compositions (Table 1). Low temperature properties of the feedstock are shown in Table 2.

Table 1. Compositions of feedstock of middle distillates catalytic dewaxing process

	Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5
n-Paraffins (C10-C27)	16.12	17.09	16.46	14.86	19.19
n-Paraffins(C5-C9)	0.69	0.58	2.22	0.6	1.15
Olefins	1.09	2.10	0.45	1.98	2.5
Naphthenes	29.19	35.00	38.34	39.85	38.91
i-Paraffins	30.00	24.36	21.89	22.70	18.25
Monoaromatic hydrocarbons	21.68	19.68	19.4	18.82	18.82
Polyaromatic hydrocarbons	1.23	1.09	1.2	1.12	1.12
Hydrogen sulphide	0.0016	0.0975	0.0333	0.0703	0.0555

Table 2. Low-temperature properties of middle distillates catalytic dewaxing process

	Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5
Freezing temperature (Tf), °C	−11°C	−20°C	−17°C	−7°C	−15°C
Cloud point (Tc), °C	−1°C	−11°C	−7°C	−8°C	−6°C

As a tool of research the developed earlier mathematical model of catalytic dewaxing process [11-12] was applied. The model represents the system of differential equations of mass and heat balance:

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

Initial and boundary conditions are as follows: $z = 0$: $C_i = C_{i,0}$; $T = T_0$; $V=0$: $C_i = C_{i,0}$; $T = T_0$, where z is total volume of processed feedstock date of fresh catalyst load, m^3; G is feedstock flow rate, m^3/h; C_i is i^{th} component content in feedstock, mol/m^3; V is the volume of catalyst bed, m^3; a_j is catalyst activity in j^{th} reaction; ρ is the density of mixture, kg/m^3; C_p^m is the specific heat capacity of mixture, J/kg·K; Q_j is the heat effect of j^{th} reaction, J/mol; T is temperature, K; W_j is the rate of j^{th} reaction; m is the number of reactions.

Using the developed mathematical model of the catalytic dewaxing process the influence of technological conditions (flow rates of feedstock and hydrogen-containing gas) on the yield and quality of obtained diesel fraction.

3. Results and discussion

Studying the influence of technological parameters (flow rates of feedstock and hydrogen-containing gas) on the efficiency of middle distillates catalytic dewaxing was performed using the developed mathematical model [11-12] and initial data (Table 1, 2). The research results are presented in Fig. 1-7.

3.1. Dependency of the yield and quality of diesel fraction on the flow rate of feedstock in the process of middle distillates catalytic dewaxing

The feedstock flow rate is an essential parameter, which influences the residence time of feedstock and catalyst, and, consequently, the conversion degree of hydrocarbons [13-14]. As a result of studying the influence of change of feedstock flow rate at the dewaxing unit in the range from 240 to 360 m^3/h it was established that the yield of diesel fraction increases from 56 to 63 % depending on the feedstock composition. This is explained by decrease in the residence time of feedstock and catalyst, and, therefore, decrease in the yield of gases and light hydrocarbons of gasoline range. The results are presented in Fig. 1**.**

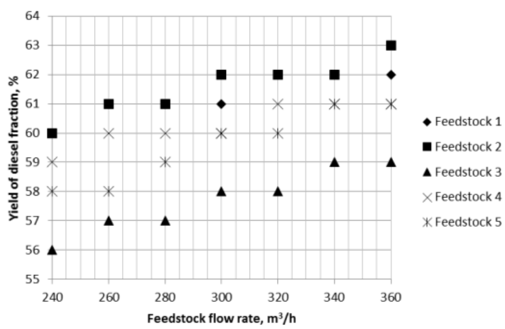

Fig. 1. The dependency of the yield of diesel fraction on the feedstock flow rate

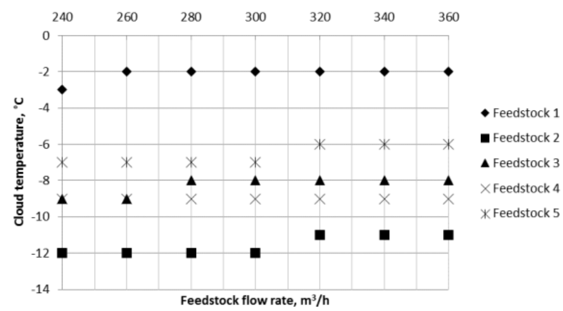

Fig. 2. The dependency of the cloud point of diesel fraction on the feedstock flow rate

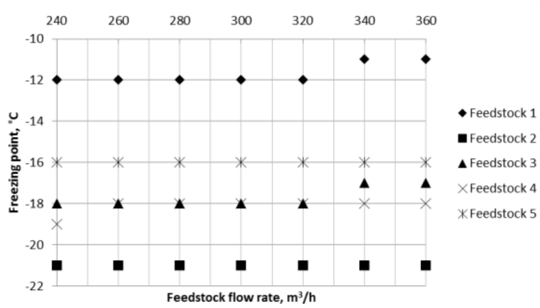

Fig. 3. The dependency of the freezing point of diesel fraction on the feedstock flow rate

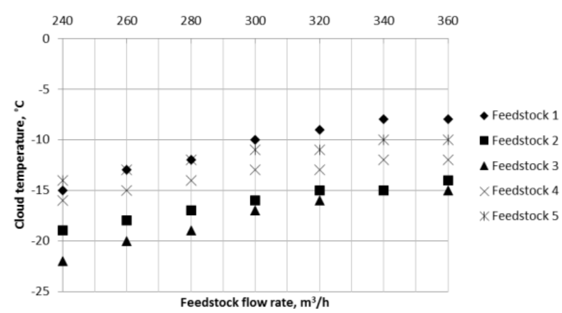

Fig. 4. The dependency of the cloud point of diesel fraction on the feedstock flow rate

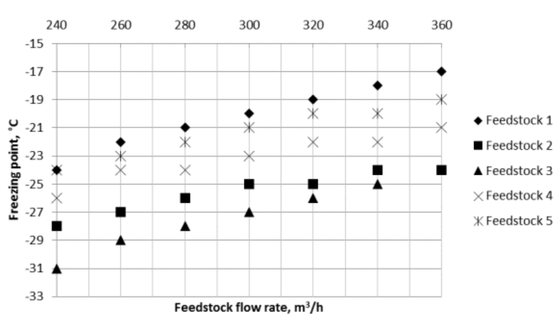

Fig. 5. The dependency of the freezing point of diesel fraction on the feedstock flow rate

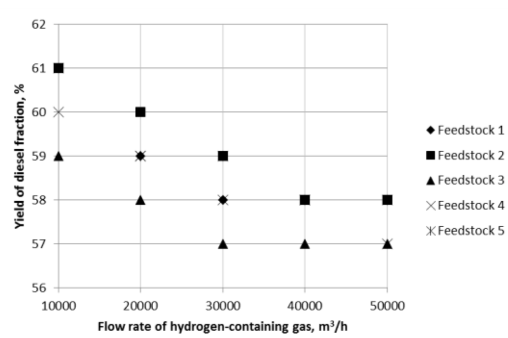

Fig. 6. The dependency of the yield of diesel fraction on the flow rate of hydrogen-containing

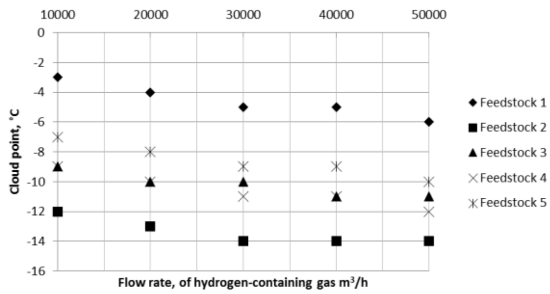

Fig. 7. The dependency of the cloud point of diesel fraction on the flow rate of hydrogen-containing gas

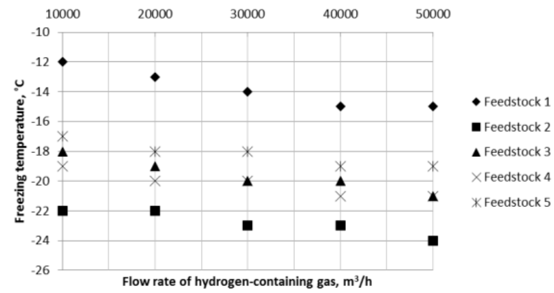

Fig. 8. The dependency of the freezing point of diesel fraction on the flow rate of hydrogen-containing gas

Herewith, among the considered feedstock samples the highest yield of diesel fraction is observed for sample 2, the lowest yield of diesel fraction is observed for sample 3. This is due to different hydrocarbon composition, namely, sample 2 contains the highest amount of target n-paraffins (C_{10}-C_{27}) and i-paraffins at low amount of naphthenes and aromatics. Meanwhile, feedstock sample 3 contains more aromatic components in comparison to paraffins.

The study of the influence of feedstock flow rate on the quality of obtained diesel fraction in terms of low-temperature properties (cloud point, freezing point) was performed at the following technological conditions: the pressure of 7.0 MPa, the temperature of 300 °C, the flow rate of hydrogen containing gas of 8000 m^3/h. The feedstock flow rate was varied from 240 to 360 m^3/h. The results are presented in Fig. 2, 3.

Thus, at the temperature in the reactor equal to 300 °C increase in the feedstock flow rate from 240 to 360 m^3/h leads to the change in quality indicators of diesel fraction, namely, the cloud point and freezing point increase by 1-2 °C on the average.

At higher temperature in the reactor due to higher catalyst deactivation degree, the influence of feedstock flow rate becomes more essential. In such a way at the temperature of 340 °C the increase in feedstock flow rate from 240 to 360 m^3/h leads to increase in the cloud point and freezing point by 4-7 °C on the average (Fig. 4-5).

The simultaneous increase in the temperature in the dewaxing reactor from 300 to 340 °C and feedstock flow rate leads to increase in the cloud point and freezing point of the product (diesel fraction), which is explained by the shift of equilibrium of exothermic hydrocracking reaction to reverse direction.

3.2. Dependency of the yield and quality of diesel fraction on the flow rate of hydrogen containing gas in the process of middle distillates catalytic dewaxing

Studying the influence of the flow rate of hydrogen-containing gas on the yield and quality of diesel fraction in middle distillates catalytic dewaxing was performed using the mathematical model of the process at the following technological conditions: the pressure of 7 MPa, the temperature of 300°C, the feedstock flow rate of 240 m^3/h. The flow rate of hydrogen-containing gas was varied from 5000 to 50000 m^3/h. The results of the study are presented in Fig. 6-8.

Thus, for different feedstock compositions decrease in the yield of diesel fraction is observed at increase of flow rate of hydrogen-containing gas. This is due to the intensification of hydrocracking reactions, leading to the formation of light hydrocarbons of gasoline range and gases.At the change of flow rates of hydrogen-containing gas from 5000 to 50000 m^3/h the yield of diesel fraction decreases by 3-5 %.

The research allowed revealing that increase in the flow rate of hydrogen-containing gas in the process of middle distillates catalytic dewaxing leads to improving the cloud point and freezing point of obtained product (diesel fraction).In such a way, at increasing flow rate of hydrogen-containing gas from 5000 to 50000 m^3/h for feedstock 1, which cloud point is equal to −1°C and freezing point is equal to −11°C, the cloud point of the product varies from −2 to

−6°C, freezing point varies from −12 to −15°C; for feedstock 2, which cloud point is equal to −11°C and freezing point is equal to −20°C, the cloud point of the product varies from −12 to −14°C, freezing point varies from −21 to −24°C; for feedstock 3, which cloud point is equal to −7°C and freezing point is equal to −17°C, the cloud point of the product varies from −8 to −11°C, freezing point varies from −18 to −21°C; for feedstock 4, which cloud point is equal to −8°C and freezing point is equal to −17°C, the cloud point of the product varies from −9 to −12°C, freezing point varies from −18 to −21°C; for feedstock 5, which cloud point is equal to −6°C and freezing point is equal to −15°C, the cloud point of the product varies from −7 to −10°C, freezing point varies from −16 to −19°C.

3.3. Determination of optimal conditions of summer, winter and arctic grades of diesel fuelm using the matehamatical model of the process

To determine optimal conditions for production of diesel fuel of different grades, such as summer grade diesel fuel (the freezing point of −22°C), winter grade diesel fuel (the freezing point of −37°C) and arctic grade diesel fuel (the freezing point of −48°C), the calculations were performed using the mathematical model. The temperature was varied in the range of 300 – 365°C, the feedstock flow rate was varied in the range of 240 – 360 m^3/h, the flow rate of hydrogen-containing gas was varied in the range of 5000 – 50000 m^3/h. The results of calculations are presented in Tables 3-5.

Table 3. Optimal regimes for production of summer grade diesel fuel

		Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5
Temperature,	°C	340	340	330	320	345
Flow rate of hydrogen-containing gas,	m^3/h	13000	7500	10000	12000	12000
Feedstock flow rate,	m^3/h	330	300	320	356	335
Yield of diesel fraction,	%	63	63	63	63	63
Cloud point,	°C	−13	−12	−13	−13	−13
Freezing point,	°C	−22	−22	−22	−22	−22

Table 4. Optimal regimes for production of winter grade diesel fuel

		Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5
Temperature,	°C	350	350	350	355	355
Flow rate of hydrogen-containing gas,	m^3/h	13000	12000	11000	16000	15000
Feedstock flow rate,	m^3/h	300	205	270	270	270
Yield of diesel fraction,	%	58	58	58	58	58
Cloud point,	°C	−28	−18	−28	−28	−25
Freezing point,	°C	−37	−37	−37	−37	−37

Table 5. Optimal regimes for production of arctic grade diesel fuel

		Feedstock 1	Feedstock 2	Feedstock 3	Feedstock 4	Feedstock 5
Temperature,	°C	350	350	350	355	355
Flow rate of hydrogen-containing gas,	m^3/h	20000	7717	12595	15945	16352
Feedstock flow rate,	m^3/h	230	126	190	180	195
Yield of diesel fraction,	%	58	56	56	56	56
Cloud point,	°C	−40	−28	−37	−37	−37
Freezing point,	°C	−48	−48	−48	−48	−48

The optimal conditions for production of summer grade diesel fuel, having the freezing temperature equal to −22°C and the yield is equal to 63 %, depend on the feedstock composition. Thus, among the considered feedstock samples, the most suitable is feedstock 4, which allows to achieve maximum yield of diesel fraction at the highest feedstock flow rate (356 m^3/h) and the lowest temperature (320°C).

The optimal conditions for production of winter grade diesel fuel, having the freezing point equal to −37 °C, ensure the maximum yield of diesel fraction at the level of 58 %. Among the considered feedstock samples, the most suitable is feedstock 1, which allows obtaining maximum yield of diesel fraction at the highest feedstock flow rate equal to 300 m^3/h and the lowest temperature equal to 350°C.

The optimal conditions for production of arctic diesel fuel, having freezing temperature equal to −48 °C, ensure the yield of diesel fraction at the level of 58 %. Thus, among the considered feedstock samples, the most suitable feedstock is feedstock 1, which allows achieving maximum yield of diesel fraction at the highest feedstock flow rate equal to 230 m^3/h and the lowest temperature of 350°C.

4. Conclusions

1. Applying the mathematical model of catalytic dewaxing process allows evaluating the influence of the flow rates of feedstock and hydrogen-containing gas on the yield and low-temperature properties of diesel fraction at conversion of middle distillate fractions of different compositions and selecting optimal conditions for production of fuel of required quality.
2. Increase in the feedstock flow rate at the middle distillates catalytic dewaxing unit from 240 to 360 m^3/h leads to increase in the yield of diesel fraction from 56 to 63 % depending on the feedstock composition. This is due to the decrease in the residence time of feedstock and catalyst, and, consequently, decrease in the yield of gases and light hydrocarbons of gasoline range.
3. Increase in the flow rate of hydrogen-containing gas from 5000 to 50000 m^3/h provides the decrease in the yield of diesel fraction by 3-5 % for different feedstock compositions. This is due to intensification of hydrocracking reactions, leading to the formation of light hydrocarbons of gasoline range and gases.
4. Low-temperature properties of diesel fraction depend on temperature and feedstock flow rate. Thus, increase in the feedstock flow rate from 240 to 360 m^3/h leads to the deterioration of low-temperature properties. This is explained by decrease in residence time of feedstock and catalyst and, consequently, increase in the cloud point and freezing point. Herewith, the influence of feedstock flow rate increases with the rise of temperature in the reactor. Thus, at the temperature of 300°C increase in feedstock flow rate from 240 to 360 m^3/h leads to increase in cloud point and freezing point by 1-2°C on the average. Meanwhile, at higher temperature leads to increase in cloud point and freezing point by 3-7 °C for different feedstock compositions at rising feedstock flow rate.
5. The flow rate of hydrogen-containing gas influences low-temperature properties of diesel fraction in the following way: change in the flow rate of hydrogen-containing gas from 5000 to 50000 m^3/h leads to decrease in cloud point and freezing point by 3-4°C, which is due to intensification of hydrocracking reaction, leading to formation of lighter hydrocarbons, having lower cloud point and freezing point, due to shift of equilibrium of dehydrogenation stage of formed olefins in the forward direction.
6. Studying the process of middle distillates catalytic dewaxing using the mathematical model allowed determining optimal conditions of the process for production of diesel fuel of different grades: summer grade diesel fuel, having the freezing point of −22°C, winter grade diesel fuel, having the freezing point of −37°C, and arctic grade diesel fuel, having the freezing point of −48°C, at the maximum yield of the product at the level of 58-63 % for different feedstock composition.

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