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STUDYING THE INFLUENCE OF TEMPERATURE AND PRESSURE OF HYDRO-DEWAXING PROCESS ON THE QUALITY AND YIELD OF DIESEL FUEL

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Abstract

This work considers the influence of technological modes of the hydrodewaxing unit (temperature within the range of 300-360°C and pressure within the range of 6.5-8.0 MPa) on the yield of diesel fraction and its low-temperature properties using the mathematical model of the process. The dependencies of the yield, freezing temperature and cold filter plugging point of diesel fraction, obtained with the use of the mathematical model, are presented. It was shown that increase in the temperature and pressure in the hydrodewaxing reactor leads to decrease in the yield of diesel fraction. Meanwhile its low-temperature properties are improved. This is due to physical-chemical regularities of transformations of middle distillate fraction hydrocarbons in the reactions of hydrocracking and hydrogenation.
Keywords: diesel fraction; fuel; low-temperature properties; hydrodewaxing; model; temperature; pressure.

1. Introduction

In recent years, the demand for diesel fuel has kept steadily growing [1-3]. Diesel fuel consumption growth is due to increase in the number of diesel-engined passenger vehicles and fleet renovation of lorries and buses, among which diesel-engined ones comprise 97.8 % and 62.4 % correspondingly [4].

According to the results of 2013 year, the amount of 71.2 million tons of diesel fuel was produced in Russia. This is by 4.6 % more than the amount of diesel fuel produced in 2012 year. According to estimates of Moscow Oil and Gas Centre EY by the year 2020 the consumption of diesel fuel in Russia will comprise 42.7 million tons per year (growth to the current level will comprise 7.4 million tons). Export supply of diesel fuel will grow from 36 million tons to 51 million tons [5].

According to Wood Mackezie, by the year 2020 existing structure of consuming different types of motor fuel will not change, meanwhile diesel fuel will play more and more significant role [5]. Herewith, the consumption of gasoline will decrease by 9 million tons (average decrease is by 1.7 % per year in the period from 2013 to 2020), the demand for diesel fuel will increase by 32 million tons (average growth is by 1.4 % per year) (Tab. 1).

Table 1.Balance of diesel fuel in Russia [2]

	2013 (million tons)	2020 (million tons)	Growth
Production	71.2	94.1	22.9
Domestic consumption	35.3	42.7	7.4
Export	35.9	51.4	15.15

Currently, in Russia diesel fuels are produced according to following state standards: 305-2013, 52368-2005, 55475-2013. These standards specify such indicators as cloud point, cold filter plugging point, freezing temperature, cetane number, sulfur and polyaromatic cyclic compounds contents [6]. The main document, according which diesel fuel is currently produced is State standard 52368-2005. In accordance with this document 5 classes of diesel fuel are produced for the use in regions with cold and arctic climate conditions [7-10]. The cold filter plugging point varies from –20 °C to –44°C from class to class (Tab. 2), which is determined by the content of n-paraffins.

Table 2. Specifications of diesel fuel of winter and arctic classes according to State standard 52368-2005

Indicator	The value for the class				
	0	1	2	3	4
Cold filter plugging point, no more than, oC	–20	–26	–32	–38	–44
Cloud point, no more than, oC	–10	–16	–22	–28	–34

The basic processes for diesel fuel production include [11-12]:

- distillation;
- catalytic dewaxing;
- hydrocracking;
- hydrotreating.

Catalytic dewaxing is the most widespread process for production of diesel fuel, which meets required quality of the product. The main transformations occur on the surface of Ni-Mo-containing catalyst in hydrogen-containing medium at the temperature of 330-370°C [13]. Herewith, he reactions of hydrocracking, hydroisomerization, hydrogenation of unsaturated hydrocarbons occur, as well as mercaptan hydrogenation with formation of hydrogen sulphide, aromatization and coke formation.

The efficiency of the hydrodewaxing unit is influenced by such parameters as temperature and pressure. Thus, the aim of this work is to study influence of temperature and pressure of the dewaxing process on the quality and yield of diesel fuel.

2. Object of research

The object of research is the industrial hydrodewaxing unit (Fig. 1). This unit is aimed to produce environmentally friendly summer, winter and arctic classes of diesel fuel having low content of sulphur and polyaromatic compounds, which meet European standards of diesel fuel EN 590:2004 (Russian State standard 52368-2005). The unit allows involving in production atmospheric gasoil and upgrading visbreaking gasoline, which give additional amount of feedstock for catalytic reforming and isomerization units. As a result of hydrodewaxing process diesel fractions, gasoline and hydrocarbon gas are produced.

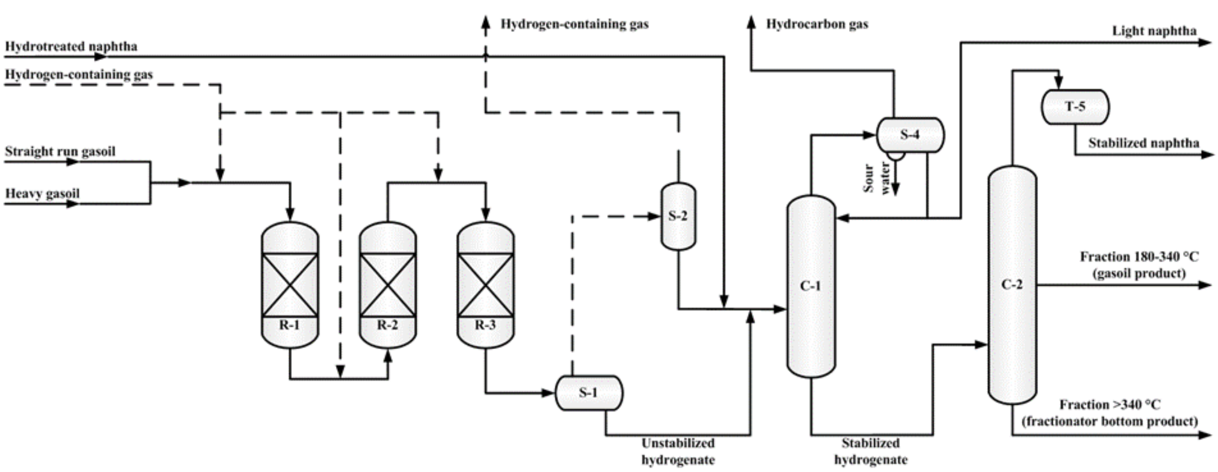

Figure 1 - Flow diagram of hydrodewaxing unit:
R-1 and R-2 – hydrotreating reactors; R-3 – hydrodewaxing reactor; S-1 – high pressure separator; S-2 – low pressure separator; C-1 – stabilizer; C-2 – fractionator; T-5 – reflux tank

In the process hydrogenation of sulpur-, nitrogen-, oxygen-containing and polyaromatic hydrocarbons occur, as well as hydrocracking of long chain paraffins in order to improve low temperature properties of diesel fuels.

Deep hydrodesulphurization and dewaxing of the feedstock are provided by increased pressure and by means of using modern catalysts [14].

The main parts of catalytic dewaxing unit are:

- reactor block, which is aimed for hydrotreating and hydrodewaxing;
- stabilization block, which is aimed for product stabilization;
- fractionation block, which is aimed for separating stable hydrogenate into fractions (gasoline, diesel and residue).

3. Initial data and research method

The composition of feedstock for hydrodewaxing unit changes constantly. In this research five feedstock compositions were studied. The compositions and low temperature properties of the considered feedstock are presented in Table 3 and Table 4 respectively.

Table 3. Composition of the feedstock for hydrodewaxing unit

Hydrocarbons	Feedstock, wt.%				
	1	2	3	4	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 compounds	21.68	19.68	19.4	18.82	18.82
Polyaromatic compounds	1.23	1.09	1.2	1.12	1.12

Table 4. Low temperature properties of the feedstock for hydrodewaxing unit

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

The mathematical model, which describes the industrial hydrodewaxing process, is a 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.

The catalyst activity is determined as:

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

where A_j, α_j are the coefficients, which characterize catalyst deactivation; C_K – coke content, wt.%.

The validation of the model was performed by the comparison of experimental data, obtained at the industrial dewaxing unit, with calculated values (Tab. 5).

Validation of the model showed that it is sensitive to hydrocarbon composition of the feedstock and deviations of calculated values from experimental are low (no higher than 5 %), which is comparable with the error of chromatography method of analysis. Thus the model can be used for studying and optimization of the process.

Table 5. Validation of the model

Hydrocarbons	Content in product, % wt. calculated	experimental
N-paraffins (C10-C27)	1.05	1.15
N-paraffins (C5-C9)	18.56	19.90
Olefins	19.25	18.31
Naphthenes	39.50	38.91
I-paraffins	2.00	2.20
Monoaromatic compounds	18.86	18.82
Polyaromatic compounds	1.02	1.12

4. Results and discussion

Studying of the influence of technological modes (temperature and pressure) on the efficiency of middle distillates hydrodewaxing process (C_5-C_{27}) was carried out using the mathematematical model of the process. The results of research are presented in Fig. 2-7.

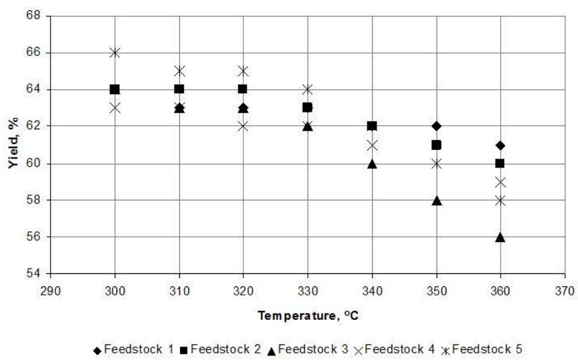

Figure 2. Dependency of the yield of diesel fraction on the temperature for different feedstock compositions

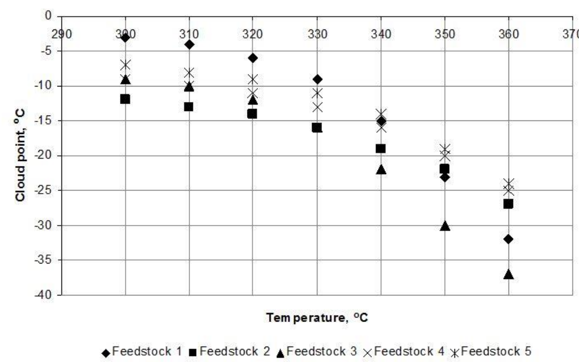

Figure 3. Dependency of cloud point of diesel fraction on the temperature for different feedstock compositions

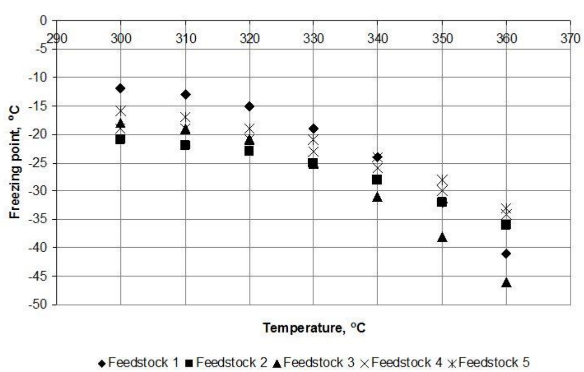

Figure 4. Dependency of freezing point of diesel fraction on the temperature for different feed-stock compositions

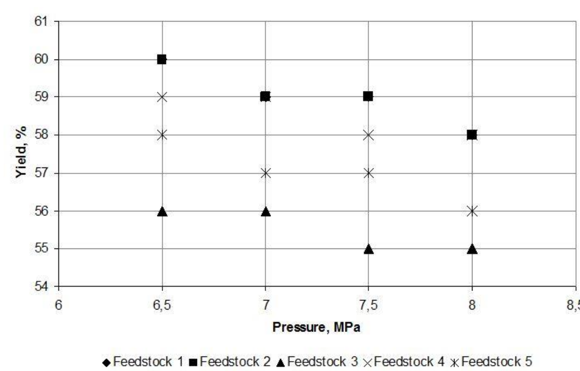

Figure 5. Dependency of the yield of diesel fraction on the pressure for different feedstock compositions

4.1. The dependency of yield and quality of diesel fraction on the temperature of hydrodewaxing process

The key parameter of the hydrodewaxing process is the temperature. It influences on the rate of high molecular weight n-paraffins hydrocracking, low molecular weight n-paraffins and olefins cracking, and, as a consequence, on the the conversion of feedstock and quality of diesel fraction (cloud point, freezing point).

The research results, obtained using the model (Fig. 2), showed that while the temperature model in the reactor changes the yield of diesel fraction changes as well.

The maximum yield of diesel fraction equal to 66 % is observed for feedstock 5 at the temperature of 300 °C, which is on average by 2 % higher than for other feedstock compositions. This is because of higher content of n-paraffins C_{10}-C_{27}, which give hydrocarbons of diesel range in the reaction of hydrocracking. Increase in the temperature from 300 to 360 °C the yield of diesel fuel decreases, which is explaind by acceleration of hydrocracking reaction leading to formation lighter hydrocarbons of gasoline range and gases.

Studying of the temperature influence on the quality of diesel fraction (cloud point and freezing point) showed that increase in the temperature provides improving of low temperature properties (Fig. 3, 4).

At increase in temperature of the hydrodewaxing process from 300 to 360 °C for feedstock 1 cloud point changes from –3 to –32°C while freezing point changes from –12 to –41°C; in case of feedstock 2 cloud point decreases from –12 to –27°C, freezing point decreases from –21 to –36°C; in case of feedstock 3 cloud point and freezing point are improved by 28°C; in case of feedstock 4 the changes in cloud point and freezing point comprise 15-16°C; for feedstock 5 depression of cloud point and freezng point constitute 17°C.

The obtained regularities are explained by acceleration of hydrocracking reactions at increasing temperature resulting in formation light hydrocarbons, which have lower cloud and freezing points. This allows controlling the process for production of diesel fuel meeting specifications for different classes from summer class to arctic class.

4.2. The dependency of yield and quality of diesel fraction on the pressure of hydrodewaxing process

Pressure is a key parameter, which influences the equilibrium of high molecular weight n-paraffins hydrocracking, low molecular weight n-paraffins and olefins cracking, and, as a consequence, on the the conversion of feedstock. The results of studying the influence of pressure on the yield and quality of diesel fraction (cloud point, freezing point) are presented in Fig. 5-7.

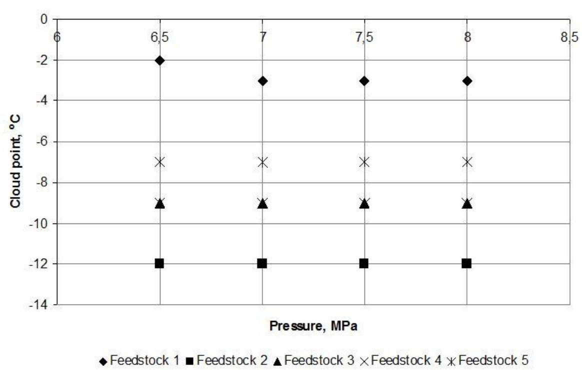

Figure 6. Dependency of cloud point of diesel fraction on the pressure for different feedstock compositions

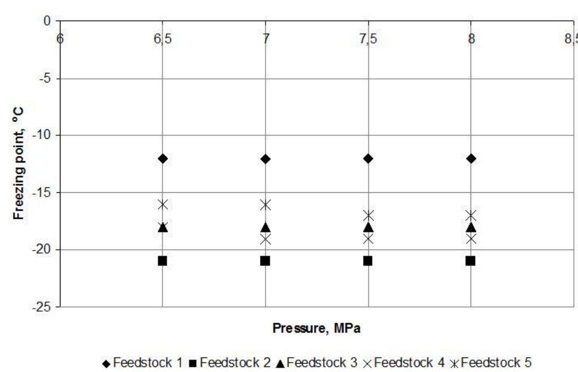

Figure 7. Dependency of freezing point of diesel fraction on the pressure for different feedstock compositions

Fig. 5 shows result of studying, which describe the dependency of yield of diesel fraction on the pressure for different feedstock. At the change of pressure from 6.5 to 8 MPa fall in the yield of diesel fraction by 3-5 % is observed. This is due to increase in the conversion level of the feedstock explained by shift of equilibrium of high molecular weight n-paraffin cracking, which pass with increase in volume, to products and formation of lighter hydrocarbons of gasoline range.

The change in the pressure in the hydrodewaxing reactor influences a lot on the quality characteristics of diesel fraction (cloud point, freezing point). The results of this research are presented in Fig. 6-7.

At increase in the pressure of the hydrodewaxing process cloud point and freezing point of obtained product (diesel fraction) decrease. Increase in the pressure from 6.5 to 8 MPa in case of feedstock 1 leads to change in cloud point from –14 to –17°C, freezing point changes from –23 to –26°C; in case of feedstock 2 low temperature properties change by 3°C; in case of feedstock 3 cloud point changes from –21 to 24°C, freezing point changes from –30 to –33°C; in case of feedstock 4 depression of cloud point and freezing point comprise 2-3°C; in case of feedstock 5 deppresion of low temperature properties comprises 2°C.

Decrease in the cloud point and freezing point of obtained diesel fraction as a result of increase in the pressure is explained by the shift of equilibrium of hydrocracking reaction to the product formation. As much as reaction of dehydrogenation of unsaturated hydrocarbons, formed as a result of cracking reactions, pass with decrease in the volume leading to decrease in the pressure in system, the increase in the pressure leads to the shift of equilibrium of these reactions to the product formation, namely lighter paraffins having low cloud point and freezing point.

5. Conclusions

1. Application of the mathematical of hydrodewaxing process allows estimating the influence of technological modes of the unit operation on the yield and low temperature characteristics of diesel fraction at the processing of feedstock having different composition for the production of diesel fuel of required amount and quality.
2. While temperature mode of the hydrodewaxing reactor changes from 300 to 360°C the yield of diesel fraction decreases by 4-8 %, meanwhile low temperature properties are improved (cloud point and freezing point decrease by 10-30°C) depending on the feedstock composition. The obtained regularities are explained by acceleration of hydrocracking reactions at increasing temperature resulting in formation light hydrocarbons, which have lower cloud and freezing points. This allows controlling the process for production of diesel fuel meeting specifications for different classes from summer class to arctic class.
3. Pressure is a key parameter, which influences the equilibrium of high molecular weight n-paraffins hydrocracking, low molecular weight n-paraffins and olefins cracking, and, as a consequence, on the the conversion of feedstock. At the change of pressure from 6.5 to 8 MPa fall in the yield of diesel fraction by 3-5 % is observed. This is due to increase in the conversion level of the feedstock explained by shift of equilibrium of high molecular weight n-paraffin cracking, which pass with increase in volume, to products. Herewith, low temperature properties are improved (cloud point and freezing point decrease by 2-3°C). This is explained by formation lighter hydrocarbons of gasoline range, having low cloud point and freezing point, as a result of the shift of equilibrium of olefin hydrogenation reaction.

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