

At the first stage in order to regulate the asphaltene phase transitions, the studies of asphaltene phase transitions were conducted in the model system of toluene-heptane. The threshold concentration of heptane was set 49% at which asphaltene starts to aggregate from the solution.

When threshold concentration of heptane is fixed in the model asphaltene solution, asphaltene particles from the solution does not fall. At higher concentrations of heptane particle aggregation rate is considerably reduced. It is shown that the dispersant additive stabilizes the growth of asphaltene aggregates up to 200 nm.

The next stage was the analysis of additives influence on the paraffin compositions in the model system and oil based on rheological properties by devices "CRYSTAL" (developer IPC SB RAS, Tomsk, Russia).

It has been found that by adding the additive to the model solution, viscosity range of paraffin 6.1% reduced to 86 mPa.s. When the paraffin content increases to 10%, the viscosity increases.

However, the influence of the additive on viscosity in oil systems is weakly expressed.

The results of determining the temperature of solidification are shown in Table.

Table

<i>Temperature of solidification</i>					
	Temperature of solidification, °C				
Concentrations of additive	-	0,03 %	0,06 %	0,5 %	1 %
Samples (Wax)					
Paraffin (1%)	<-40	-	-	-	-
Paraffin (4%)	-8.4	-7	-5	-	-
Paraffin (6%)	3.8	2.2	2.1	-	-
Парафин (10%)	7.9	11.3	11.8	-	-
Oil 1 (1.1%)	-15.7	-14	-	-26.8	-25.4
Oil 2 (4.4)	-30.4	-31	-31	-35.0	-
Oil 3 (13.27)	14.8	12.3	12.1	12.0	-

The following conclusions have been made:

1. The regulation of the phase transition for asphaltene was studied using succinimide additive. It is shown that the additive prevents coarsening for asphaltene fraction, lowering the strength of the forming particles.

2. As a result of research work, it has been found that the succinimide dispersant additive in model solutions under cooling in a series of paraffin with additives prevents nucleation in case of low paraffin concentrations.

3. In real oil systems, additive helps to reduce the temperature of solidification only when the entry at high additive concentrations (0.5-1%). With this increase in the content of paraffin oil more than 6%, depressant properties decreases.

References

1. Zang V., Takanoashi T., Sato S., Kondo T., Saito I., Tanako R. Energy and Fuels. 2003. V.17. P. 101.
2. Mullins O.C., Sheu E.Y., Hammami A. (Eds.) - New York: Springer, 2007.

APPLICATION OF DISTILLATES CATALYTIC HYDRODEWAXING MATHEMATICAL MODEL

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Modernization of petroleum refining industry is being a priority direction of Russian economy development at present. Implementation of state of the art technologies of middle and heavy petroleum distillates enhanced processing provides both increasing in petroleum refining depth and producing end products that meet the latest Euro standards to quality of motor fuels. Particularly, the process of catalytic hydrodewaxing, which is widely implementing on Russian petroleum refineries these days, provides straight run diesel fractions and atmospheric gasoil processing in order to produce marketable diesel fuel components that meet the Euro-5 standard. Moreover, in winter time the processing unit produces diesel fuel with improved low temperature properties. This allows using obtained diesel fuels in severe winter and arctic weather conditions of the Russian Federation north climate zones.

With that, while implementing new technologies, the methods of available resources and industrial power sustainable use should be developing. One of the techniques, which are effectively applied to forecast resource efficiency modes of refining processing units operation, is optimization by means of computer modelling systems application [1]. The advantages of such systems are predicated by the fact that they are based on physical-chemical laws of complex, multifactorial re-refining processes. In this work the catalytic hydrodewaxing processing unit optimal operation modes forecasting was made depending on feedstock consumption using computer modelling system.

To develop the mathematical model the thermodynamic analysis of hydrodewaxing reactions was performed; kinetic model of the process was developed; kinetic parameters of the model were estimated.

According to the mechanism of the hydrodewaxing process the list of possible reactions was proposed. Based on the calculation of the change in Gibbs free energy for each reaction the list of spontaneous reactions ($\Delta G < 0$) was created. Based on the list of spontaneous reactions occurred in the hydrodewaxing process, the kinetic model was developed. The model represents a system of differential equations with reactant concentrations changing over the residence time. As the process of hydrodewaxing operates under excess of hydrogen-containing gas the dilution of the feedstock by hydrogen containing gas is accounted for in the mathematical model. The estimation of reactions rate constants was made by solving the inverse kinetic problem using a large array of full-scale experimental data obtained from the actual industrial hydrodewaxing unit operating in its normal mode.

Validation of the developed mathematical model was carried out by comparison of calculated concentrations of hydrocarbons groups in the end product and actual operational values of the full-scale unit. The absolute error of calculated concentrations does not exceed 1.7 %, 2.5 %, 0.8 %, and 0.7 % for n-paraffins C_{10} – C_{27} , iso-paraffins, olefins, and monoaromatic components respectively. This proves the applicability of the developed mathematical model for studying and optimization of the industrial process.

The purpose of the hydrodewaxing is to convert long chain n-paraffins (from 10 to 27 carbon atoms) into short chain iso-paraffins (from 5 to 9 carbon atoms) in order to produce winter grade and arctic diesel fuel [2]. Low temperature characteristics of diesel fuel depend on concentration of long chain n-paraffins [3]. As lower concentration of long chain paraffins is than lower cloud point and freezing temperature are.

The temperature is a key factor that defines the reaction rate in the hydroisomerization process. Using developed mathematical model the influence of operating temperature in the range of 345–405 °C on n-paraffins C_{10} – C_{27} concentration in the end product was studied depending on the feedstock consumption into the reactor in the range of 160–320 m^3/h (Fig. 1). The pressure and hydrogen containing gas consumption were adopted as 6,799 MPa and 25951 m^3/h respectively.

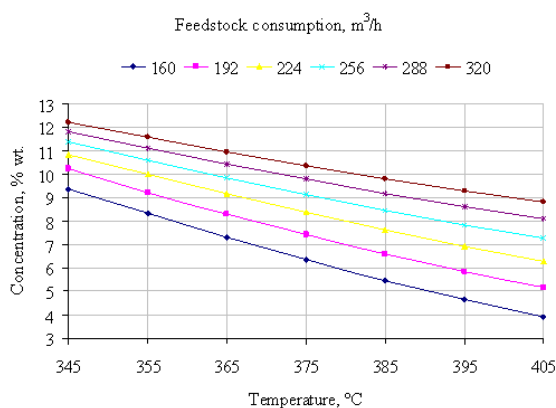


Fig. 1. The influence of operating temperature on n-paraffins C_{10} – C_{27} concentration depending on feedstock consumption

As it can be seen from Figure 1, if the feedstock consumption rises the temperature that is needed to achieve required n-paraffins C_{10} – C_{27} concentration in the end product increases as well. According to the full-experiment data n-paraffins C_{10} – C_{27} concentration in the end product is required to be at the level 9 wt. % to obtain winter grade and arctic diesel fuel components. To define the operating temperature that enables maintenance of given n-paraffins C_{10} – C_{27} concentration in the end product (9 wt. %) the forecasting calculation of temperature was performed depending on the feedstock consumption into the reactor (Fig. 2).

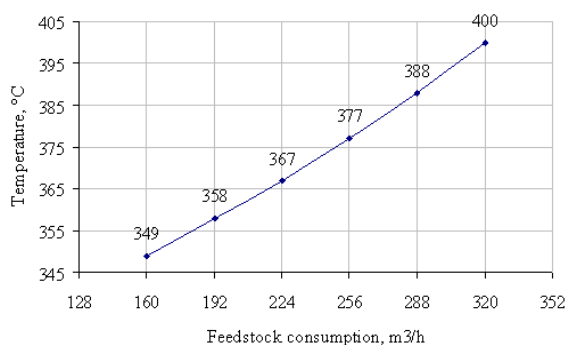


Fig. 2. The temperature required to maintain n-paraffins C_{10} – C_{27} concentration at the level 9 wt. % depending on feedstock consumption

In the hydrodewaxing process it is crucial to maintain the excess of hydrogen in circulating gas as fresh hydrogen injected simultaneously with the feed is intensively consumed in chemical reactions of hydrocracking. The hydrogen circulation rate is as higher as heavier the feed is and higher conversion degree is as well as lighter obtained products are. The hydrogen consumption rate significantly influences the exploitation expenses as well. For these reasons optimal hydrogen containing gas maintenance depending on the feedstock consumption is vital in order to achieve cost-effectiveness and resource efficiency of the plant.

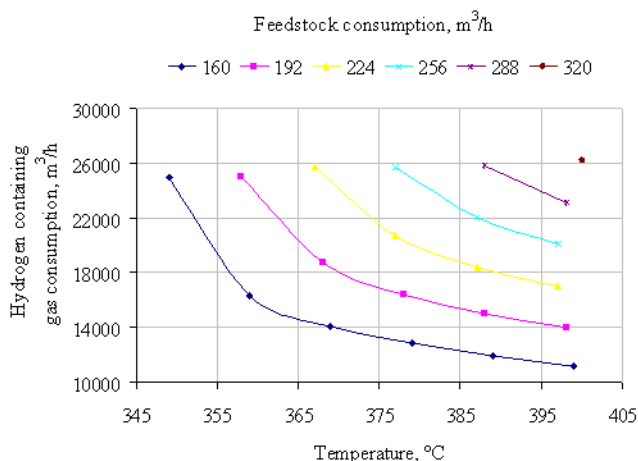


Fig. 3. The temperature and hydrogen containing gas consumption required to maintain *n*-paraffins C_{10} – C_{27} concentration at the level 9 wt. % depending on feedstock consumption

So, the higher the temperature in the reactor is the lower hydrogen containing gas consumption is required to obtain the product that meets desired low temperature properties.

The process should be operated at optimal ratio between temperature and hydrogen containing gas consumption depending on feedstock consumption to save resource of the plant.

References

1. Dolganova I.O., Dolganov I.M., Ivashkina E.N., Ivanchina E.D., Romanovskiy R.V. Development of approach to modelling and optimization of non-stationary catalytic processes in oil refining and petrochemistry // Polish Journal of Chemical Technology. – 2012. – Vol. 14. – Issue 4. – pp. 22–29.
2. Mihalyi R.M., Lonyi F., Beyer H.K., Szegedi A., Kollar M., Pal-Borbely G., Valyon J.. *n*-Heptane hydroconversion over nickel-loaded aluminum- and/or boron-containing BEA zeolites prepared by recrystallization of magadiite varieties // Journal of Molecular Catalysis A: Chemical. – 2013. – Vol. 367. – pp. 77–88.
3. Ovchinnikova A.V., Boldinov V.A., Esipko E.A., Prozorova I.S.. Effect of *n*-paraffins on the low-temperature properties of aviation diesel fuels // Chemistry and Technology of Fuels and Oils. – 2005. – Vol. 41 (6). – pp. 462–467.

HARDNESS SPREADING PARAMETERS FOR PIPELINE CONDITION ASSESSMENT

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Ensuring reliable and safe operation of pipelines is the most important task for oil and gas transportation companies. This is solved mainly by decreasing the corrosion damageability of pipes, however, pipeline failure is not only caused by corrosion.

During the pipeline operation, the metal of a pipe is experiencing degradation resulting from the accumulation of scattered damages of various origins, which form crack-type flaws. This causes deterioration of the performance of the pipe or its failure in terms of functioning parameters.

One of the most serious factors responsible for pipeline failures is irreversible changes in structure and physico-mechanical properties of the pipeline material under the action of various temperature and force effects, corrosion, aging, chemical interaction with the product being transported [1].

Clearly, the degradation distribution depends on the origin of the material, its structural state and operating conditions, as well as loading mode. Reliability of pipeline is defined by the current condition of metal and its mechanical properties (including tensile strength and yield strength).

Hardness measuring is widely used for pipeline condition assessment, since hardness value correlates, to a certain extent, with characteristics of all mechanical properties of a certain material. This method includes measuring hardness of several zones of a pipe and calculating a mean value, which is compared to original hardness value of non-