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Studying the Regularities of Atmospheric Oil Distillates Catalytic Dewaxing Process Using the Method of Mathematical Modelling

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Abstract

In this paper, with the use of the method of mathematical modelling, the study was carried out on the regularities of the process of atmospheric oil distillates catalytic dewaxing, which is aimed at production of low-freezing diesel fuel. The influence of feedstock composition, flow rate, and process temperature on the yield of products and cold filter plugging point of the obtained diesel product was revealed. Prognostic calculation was carried out on the deactivation degree of the dewaxing catalyst for different feedstock compositions.

Keywords: *Diesel fuel; Catalytic dewaxing; Cold filter plugging point; Catalyst deactivation; Mathematical modelling.*

1. Introduction

Modernization of oil refineries is becoming a key requirement of the oil refining industry survival these days [1]. In the last decade, along the modernization of oil refineries, many units for diesel fuel production were retrofitted by addition of the catalytic dewaxing stage [2]. The process of catalytic dewaxing allow refineries to convert atmospheric distillates, including heavy ones, which have unsatisfying cold flow properties, into low-freezing components of diesel fuel, suitable for operation in the environmental conditions, characterized by low-temperatures [3-4]. Today, the demand for low-freezing diesel is constantly increasing due to the Artic region exploration and economic development of the northern regions [5-6]. Improving of diesel fuel cold flow properties in the process of catalytic dewaxing is due to hydrocracking and hydroisomerization of long straight chain paraffins in the medium of hydrogen-containing gas [7-8]. Due to the fact that diesel fuel catalytic dewaxing is a relatively new process in oil refining, studies of this process are of the utmost interest these days.

Modernization of oil refineries also assumes digital transformation of the enterprises, including digitalization of chemical conversion stages of the production cycle [9-10]. One of the directions of digitalization is creation of digital twins of industrial units [11-12]. Mathematical models, developed on the base of the physico-chemical regularities of the processes, can become basic modules of the digital twins of the reactor processes in order to solve the tasks of process optimization depending on the feedstock composition and technological parameters, prognostic calculations of catalyst deactivation and recommendation of the ways to prolong their service life [13-15].

2. Object and method of research

The object of research is the process of atmospheric oil distillates catalytic dewaxing, a part of the industrial unit for diesel fuel hydrotreating and dewaxing. The process flow diagram of this process is illustrated in Fig. 1 [16].

The unit is aimed at hydrotreating for sulphur-containing compounds removal and for dewaxing of diesel fuels. The feedstocks for the unit are straight-run diesel fraction and heavy diesel fraction. The products of the unit are: stable gasoline; hydrotreated diesel fraction, a component of low-freezing diesel fuel of winter and arctic grades; hydrocarbon gas. The process uses a zeolite catalyst for dewaxing.

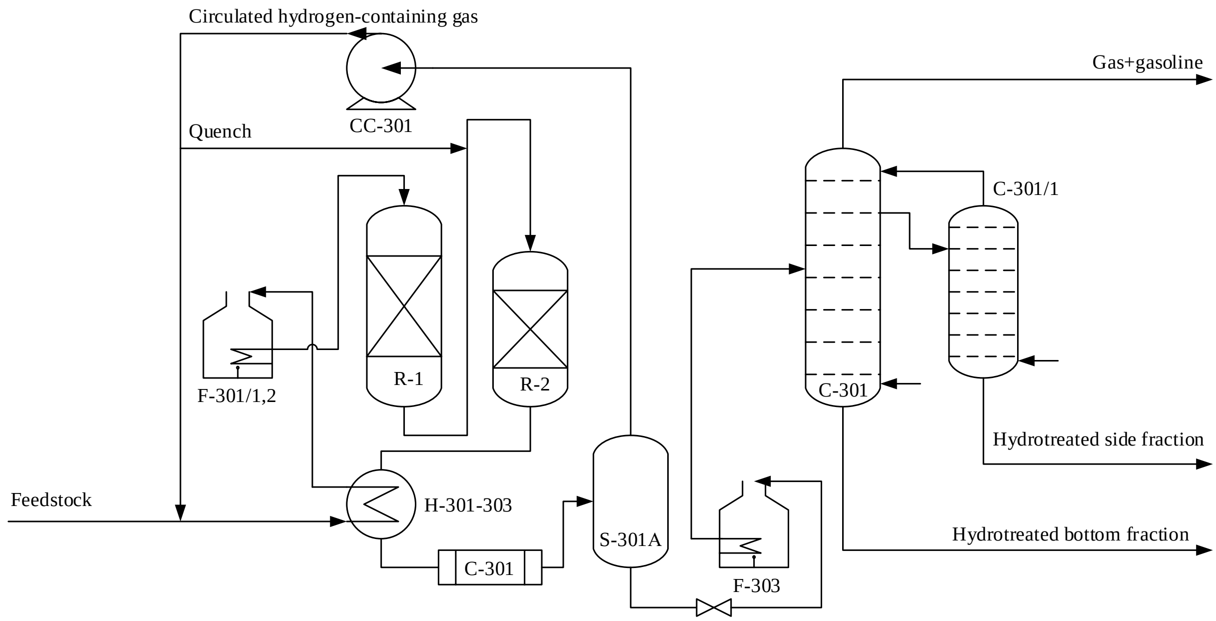

Figure 1. Process flow diagram of the industrial unit for hydrotreating and catalytic dewaxing of atmospheric oil distillates
R-1 – hydrotreating reactor; R-2 – catalytic dewaxing reactor; F-301/1,2 – furnace; CC – circulation compressor for hydrogen-containing gas; H-301-303 – heat exchangers; C-301 – air cooler; S-301A – high pressure separator; C-301 – stabilization column; C-301/1 – the column for stabilization of side fraction from the column C-301

In this work, the method of mathematical modelling was applied. The model of diesel fuel catalytic dewaxing process was created by the following steps: analysis of experimental data from the industrial unit; studying the mechanism of reactions occurring on the catalyst surface; creation of the reactions list; estimation of the reactions thermodynamic parameters; creation of the formalized chemical conversion scheme; selection and validation of the hydrodynamic model; development of the system of differential equations of the model; estimation of the model kinetic parameters using experimental data; validation of the model.

The developed model, which is a system of differential equations of material and heat balance, is written as follows:

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

Initial conditions: $z = 0$: $C_i = C_{i,0}$; $T = T_0$; $V=0$; $C_i = C_{i,0}$; $T = T_0$, where z – the volume of processed feedstock from the moment of fresh catalyst load, m^3; G – feedstock flow rate, m^3/h; $z = G\cdot t$ (t – amount of time from the moment of fresh catalyst load, h); C_i – the content of i^{th} component, mol/l; V – the volume of catalyst bed, m^3; a_j – catalyst activity in j^{th} reaction; ρ – density of the mixture, kg/m^3; C_p^{mix} – specific heat capacity of the mixture, J/(kg·K); Q_j – heat effect of j^{th} reaction, J/mol; T – temperature, K; W_j – the rate of j^{th} reaction, mol/(l·s), m – number of reactions.

Catalyst activity: $a_i = A_j\cdot e^{-\alpha_j C_D}$,

where A_j, α_j – deactivation coefficients; C_D – content of compounds deposited on the catalyst surface, %wt.

Kinetic parameters of the model, such as preexponential factor in the Arrhenius equation (k_0) and activation energy (E_a) were estimated by solving the reverse kinetic task. The calculation error using the model does not exceed the error of the experimental methods used for determination of the same parameters.

Using the developed model, the studies were carried out on the influence of the feedstock composition, flow rate, and the process temperature on the yields of products and cold filter plugging point (CFPP) of the obtained diesel product. Prognostic calculation was performed for catalyst activity depending on the feedstock composition.

3. Results and discussion

3.1. Studying the influence of feedstock composition on the yields of products and CFPP of the obtained diesel fuel

Studying the influence of feedstock composition on the yields of products and CFPP of diesel fuel obtained in the process of atmospheric oil distillates catalytic dewaxing was carried out for two fraction compositions, which differ by boiling temperatures of the distilled fractions and density. The fractional composition is recalculated into group composition by the method, developed by the authors. The method is based on the calculation of hydrocarbon group content via the boiling temperature of 50% fraction and the density of feedstock.

Initial data on the feedstock composition and density is illustrated in Table 1. Initial data on the technological parameters is illustrated in Table 2. The results of calculations are illustrated in Fig. 2 and Fig. 3.

Table 1. Initial data on the feedstock composition and density

	Feedstock-1	Feedstock-2
Boiling temperature of 10 % fraction, °C	238	263
Boiling temperature of 50 % fraction, °C	275	317
Boiling temperature of 90 % fraction, °C	340	365
Density, kg/m^3	847	858

Table 2. Initial data on the technological parameter

Technological parameter	Value
Feedstock flow rate, m^3/h	280
Flow rate of hydrogen-containing gas, m^3/h	25000
Temperature, °C	360
Pressure, MPa	7.5

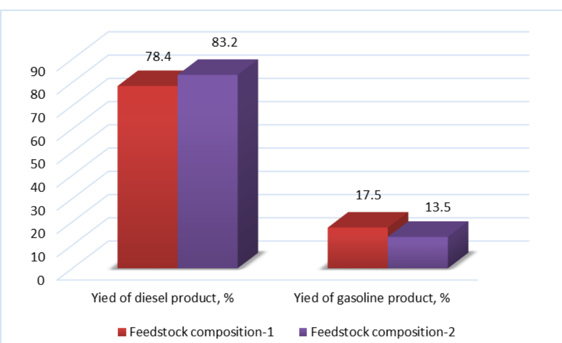

Figure 2. The influence of feedstock composition on the product yields in the process of atmospheric oil distillates catalytic dewaxing

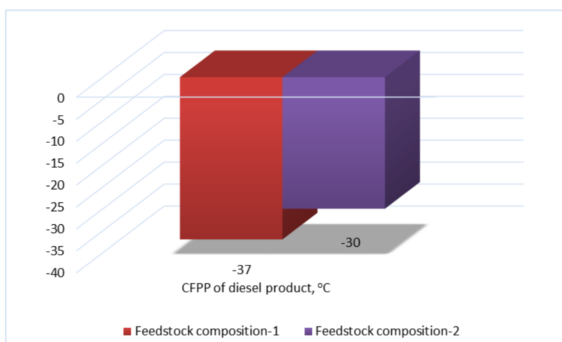

Figure 3. The influence of feedstock composition on the CFPP of diesel product, obtained in the process of atmospheric oil distillates catalytic dewaxing

With the change in the feedstock composition, the yield of diesel product changes by 4.8%, while the yield of gasoline product changes by 4.0 %. With the change is the feedstock composition, the CFPP of diesel product, obtained in the process of atmospheric oil distillates catalytic dewaxing, changes by 7°C.

3.2. Studying the influence of feedstock flow rate on the yields of products and CFPP of the obtained diesel fuel

Studying the influence of feedstock flow rate on the yields of products and CFPP of the diesel fuel obtained in the process of atmospheric oil distillates catalytic dewaxing was carried out for two feedstock flow rates: 250 m^3/h ("Feedstock flow rate-1") and 310 m^3/h ("Feedstock flow rate-2"). Feedstock composition was taken from Table 1 ("Feedstock-1"). The remaining technological parameters were taken from Table 2. The results of calculations are illustrated in Fig. 4 and Fig. 5.

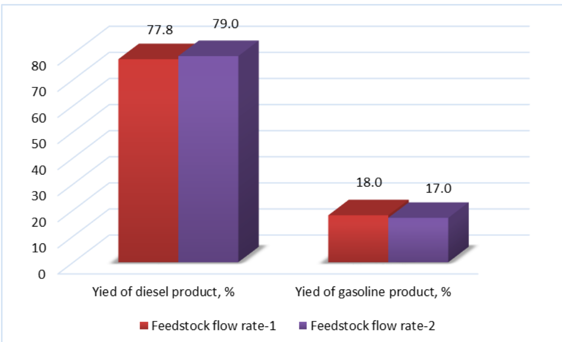

Figure 4. The influence of feedstock flow rate on the product yields in the process of atmospheric oil distillates catalytic dewaxing

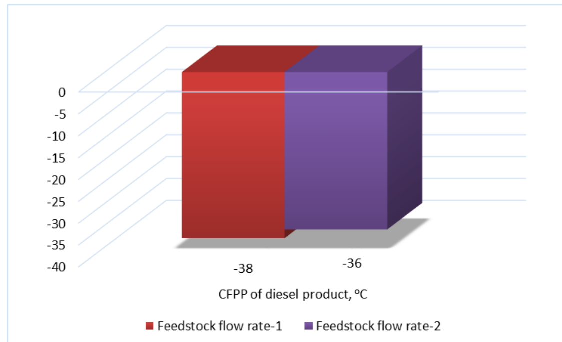

Figure 5. The influence of feedstock flow rate on the CFPP of diesel product, obtained in the process of atmospheric oil distillates catalytic dewaxing

With increase in the feedstock flow rate by 60 m^3/h, the yield of diesel and gasoline product changes insignificantly – by 1.2% and 1.0% respectively. With increase in the feedstock flow rate by 60 m^3/h, the CFPP of obtained diesel fuel changes insignificantly by 2°C.

3.3. Studying the influence of process temperature on the yields of products and CFPP of the obtained diesel fuel

Studying the influence of the process temperature on the yields of products and CFPP of the diesel fuel obtained in the process of atmospheric oil distillates catalytic dewaxing was carried out for two process temperatures: 340 °C ("Temperature-1") and 370°C ("Temperature-2"). Feedstock composition was taken from Table 1 ("Feedstock-1"). The remaining technological parameters were taken from Table 2. The results of calculations are illustrated in Fig. 6 and Fig. 7.

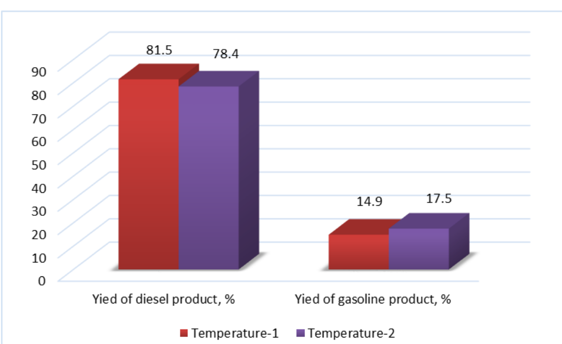

Figure 6. The influence of temperature on the product yields in the process of atmospheric oil distillates catalytic dewaxing

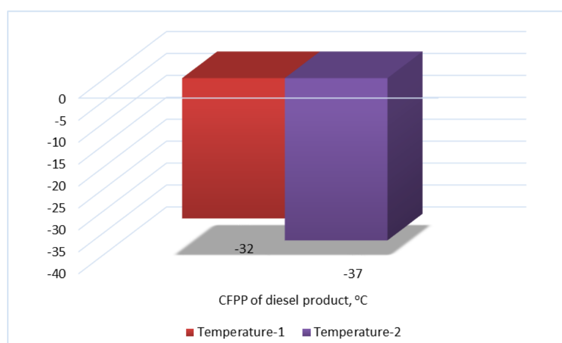

Figure 7. The influence of temperature on the CFPP of diesel product, obtained in the process of atmospheric oil distillates catalytic dewaxing

With increase in the process temperature by 20°C, the yield of diesel product decrease by 3.1%, the yield of gasoline product increases by 2.6%. With increase in the process temperature by 20 °C, the CFPP of the obtained diesel fuel decrease by 5°C.

3.4. Prognosis of the catalyst activity depending on the feedstock composition

Prognostic calculation was carried out on the changing in relative catalyst activity in the process of atmospheric oil distillates dewaxing for two feedstock compositions, presented in Table 1. The calculation results are illustrated in Fig. 8.

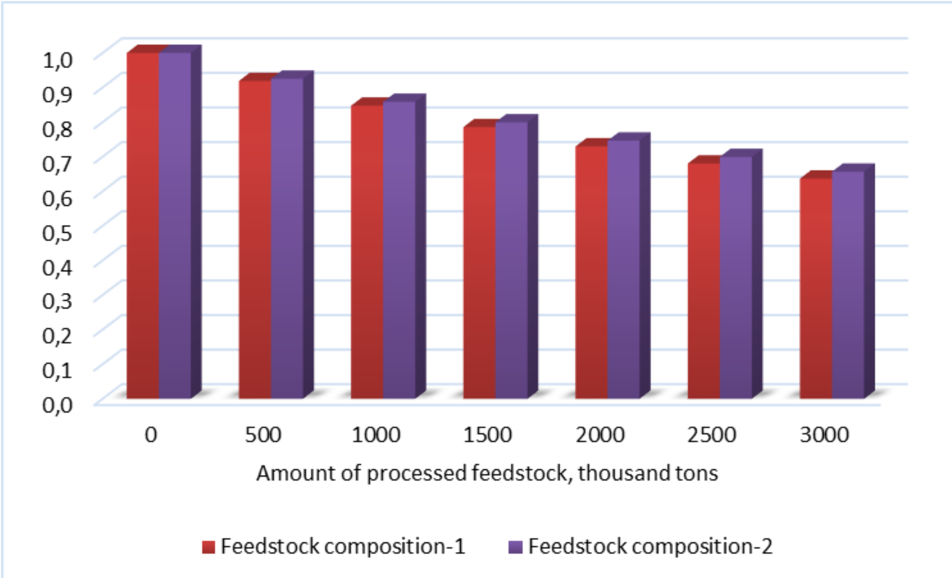

Figure 8. Prognostic calculation on the changing in relative catalyst activity in the process of atmospheric oil distillates dewaxing

As it can be seen from Fig. 8, in case of processing heavier feedstock ("Feedstock-2"), the degree of catalyst deactivation is higher by 2% after treating of 3000 thousand tons of feedstock.

The higher the catalyst activity, the higher feedstock flow rate can be maintained in the process and higher conversion degree is achieved. Due to the passage of time, catalyst activity decreases because of sulphur and coke deposition on its surface. The decrease in the partial pressure in the circulated hydrogen containing gas also promote coke deposition on the catalyst surface. That is why, when catalyst activity decreases, catalyst regeneration is carried out intermittently. As a result, deposited sulphur and coke are burned and the catalyst activity restores. Gradually, the catalyst ages because of recrystallization and changing in the structure, as well as due to adsorption of metal-organic and other compounds, which block active sites of the catalyst. In this case catalytic activity decreases irreversibly and the catalyst is changed by fresh one.

4. Conclusion

With the use of the mathematical model, the study was carried out on the influence of feedstock composition and technological parameters on the process of atmospheric oil distillates catalytic dewaxing. By model calculations in the real time of the industrial unit operation, it is possible to perform process optimization and to prognose the date of catalyst regeneration and the date of full changing by the fresh catalyst.

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