Research of Diesel Fuels Dewaxing Process via Mathematical Model

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Abstract. The aim of the work is to carry out the research of diesel fuels dewaxing process. The study is based on fundamental mathematical model of the process, which takes into account poisoning of the metal centers and acid sites due to coking. Formed mathematical model was implemented for monitoring calculation with the aim of improving the efficiency of dewaxing catalyst loaded to the industrial reactor. Three operational modes were recorded for dewaxing unit. Optimization calculation of temperature at summer mode revealed that temperature in the dewaxing reactor could be decreased to 325°C without fuel quality loss.

INTRODUCTION

Catalytic dewaxing unit is used to produce winter, summer, and arctic diesel fuels [1,2] (Fig. 1). Main production stages involve hydrotreating and dewaxing of the feedstock (mixture of atmospheric gas oil, straight-run diesel fractions, and visbreaking gasoline), stabilization of the product, and distillation with diesel fractions and stable naphtha production [3,4].

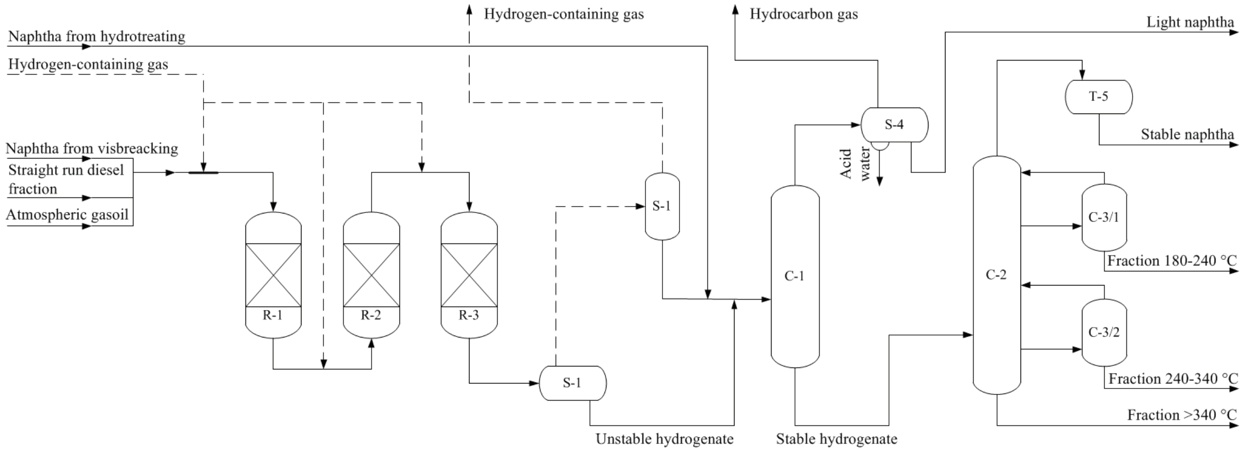

FIGURE 1. Industrial diesel fuels catalytic dewaxing unit

Catalytic dewaxing is a complex process of cracking, alkylation, isomerization and hydrogenation reactions taking place on Ni-containing catalyst [5–7]. Besides, there are many possible side reactions, such as cyclization of isoparaffins, hydrogenation of monoaromatic and polyaromatic hydrocarbons, coke and mercaptanes formation.

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Also, a catalytic dewaxing reactor has the desulphurization section, which is the layer of Co-Mo catalyst located at the bottom of the reactor, for the hydrogenation of unsaturated sulfur-containing compounds (mercaptanes).

The main reactions of the process, as authors of [8] show, are hydrocracking of normal and slightly branched chain paraffins along with degradation of naphthenes and formation of low boiling liquid and gaseous products, as well as partial cyclization isoparaffinic hydrocarbon feedstock and the products of reactions.

Low-temperature properties of diesel fuels strongly depend on the content of n-paraffins in the feed, because these hydrocarbons have the highest values of pour and cloud points [9–11]. Therefore, the concentration of long-chain paraffins is to be reduced.

METHODS AND MATERIALS

The considered hydrodewaxing industrial plant uses the pentasil zeolite ZSM-5 based catalyst impregnated with nickel.

The main reactions occurring on the catalyst are selective cracking and isomerization of n-paraffins, at the same time there is not a significant effect on other compounds, such as isoparaffins, naphthenes and aromatics.

Mathematical Model of Dewaxing Process

The initial step in mathematical model development is formulation of the formalized hydrocarbon conversions scheme in the process. Thus the problem which arises when creating dewaxing model is that the process is a multi-component: a mixture of raw materials is a large fraction of diesel hydrocarbons and atmospheric gas oil, rather than an individual substance. Ways of reactions with hydrocarbons having different numbers of carbon atoms in the molecule and the degree of branching are diverse and numerous. Therefore, the process simulation requires formalization of hydrocarbons conversions scheme: the individual substances are united in the groups of substances and reactions - in the types of reactions. Besides, when aggregating substances it is necessary to take into account their different reactivity, which depends on the entropy and enthalpy characteristics. The characteristics of entropy and enthalpy are determined by the nature of bonds in molecules and their energies.

Only this condition provides predictive ability of the formalized model, as well as its sensitivity to changes in the feed composition.

Based on the analysis of experimental data and thermodynamic analysis the formalized scheme of catalytic dewaxing chemical conversions was created, taking into account reactivity of the hydrocarbons (Fig. 2). To reduce the number of components the reacting and produced substances were grouped according to the value of Free Gibbs Energy change ΔG in the reactions of their formation and consumption along with grouping according to the belonging to a particular homologous series.

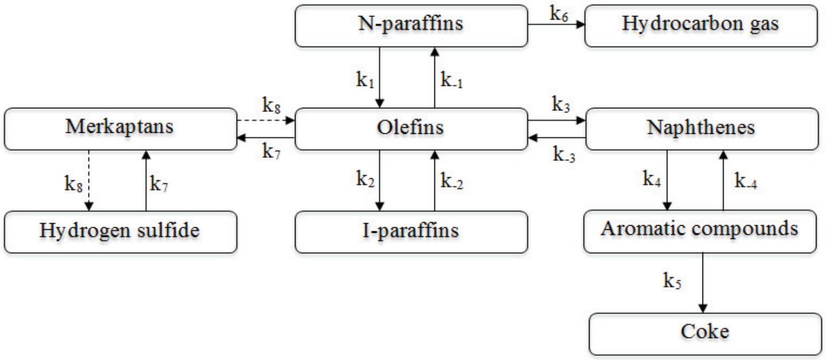

FIGURE 2. Formalized scheme of catalytic dewaxing chemical conversions. k – reaction rate constant. The solid line shows reactions on the dewaxing catalyst, dashed line - on the hydrotreating catalyst

In the proposed conversion scheme n-paraffins include unbranched paraffins having chain length from 5 to 27 carbon atoms, the group “hydrocarbon gas” consists of methane, ethane, propane and butane, and the structure of coronen was taken as a structure of coke as the formation of this structure is the most thermodynamically probable. The criterion for reaction reversibility is the value of Free Gibbs Energy change. According to the literature data [12] the reaction is reversible if the value of Free Gibbs Energy change lies within the range from –70 to +70 kJ/mol.

On the basis of the created scheme the kinetic model of catalytic dewaxing process was designed, which comprises grouped components concentration changes in time as a system of ordinary differential equations with the initial conditions.

Hydrocarbon groups	Kinetic model equation
Normal paraffins	$\frac{dC_1}{d\tau} = -W_1 + W_{-1} - W_6$
Iso-paraffins	$\frac{dC_2}{d\tau} = W_2 + W_{-2}$
Naphthenes	$\frac{dC_3}{d\tau} = W_3 + W_{-3} - W_4 + W_{-4}$
Aromatic compounds	$\frac{dC_4}{d\tau} = W_4 - W_{-4} - W_5$
Olefins	$\frac{dC_5}{d\tau} = W_1 - W_{-1} - W_2 + W_{-2} - W_3 + W_{-3}$
Coke	$\frac{dC_6}{d\tau} = W_5$
Hydrocarbon gas	$\frac{dC_7}{d\tau} = W_6$
Hydrogen	$\frac{dC_8}{d\tau} = W_1 - W_{-1} - W_2 + W_{-2} + 3 \cdot W_4 - 3 \cdot W_{-4} + W_5$

Initial conditions are as follows: t=0, $C_i=C_{i0}$.

$W_{c.r.}$ – chemical reaction rate, s^{-1}; C_i – concentration of i^{th} component (i=1-8), mol/l; C_{i0} – initial concentration of i^{th} component (i=1-8), mol/l; τ – contact time, s.

The feature of hydrocarbons transformations in the hydroprocessing processes is that they occur in the presence of hydrogen-containing gas. Therefore it is necessary to take into account the dilution of the feedstock by hydrogen-containing gas in hydrodewaxing process mathematical model, which was done by the authors in [13,14]. The values of the pre-exponential factors in the Arrhenius equation were estimated by solving the inverse kinetic problem, which lies in the selection of the values of the kinetic parameters which ensuring minimum deviations between the calculated and experimental parameters.

An adequate model of the catalytic dewaxing process should describe not only the kinetics of reactions between hydrocarbons, but also a hydrodynamic mode of a reactor in which the process takes place. Industrial dewaxing reactor is vertical unit with axial input of the feedstock.

The assumption of plug flow reactor was made for the model. The residence time of all the particles in the system is equal and is defined as the ratio of the system volume to the volumetric flow rate of the liquid.

Verification of the model was carried out by comparing calculated components concentrations and concentrations, obtained experimentally from the industrial plant.

The experimental and calculated values of the key components have sufficient convergence, since the absolute error is not greater than 1.16% by weight. That is comparable to the accuracy of the method of chromatographic analysis to determine the concentrations of the components.

Thus, we can conclude that the developed kinetic model adequately describes the real process.

Based on the developed model of dewaxing process a computer modeling system in object-oriented programming environment Delphi 7 was created. The system enables the user to estimate and clarify the kinetic parameters of the reactor model, to carry out the research of the effect of various process parameters on the efficiency of the process, to carry out the operational optimization of the reactor at different feedstock composition.

RESULTS AND DISCUSSION

Monitoring Calculations

The developed dewaxing process mathematical model was applied for monitoring calculations of the industrial unit. The calculation period is 01.01.2015 - 01.01.2016. During this period the plant was operated at three modes of diesel production, which was indentified from dewaxing reactor temperature profile (Fig. 3):

- from 01.01.2015 to 01.03.2015 (winter mode, T=344–352 ^{o}C, feed rate G = 294–365 m^3/h);
- from 01.03.2015 to 13.08.2015 (summer mode, T=336–338 ^{o}C, feed rate G = 298–363 m^3/h);
- from 18.12.2015 to 01.01.2016 (winter mode, T=337–340 ^{o}C, feed rate G = 211–284 m^3/h)

with a planned stop for repairs from 13.08.2015 to 17.12.2015.

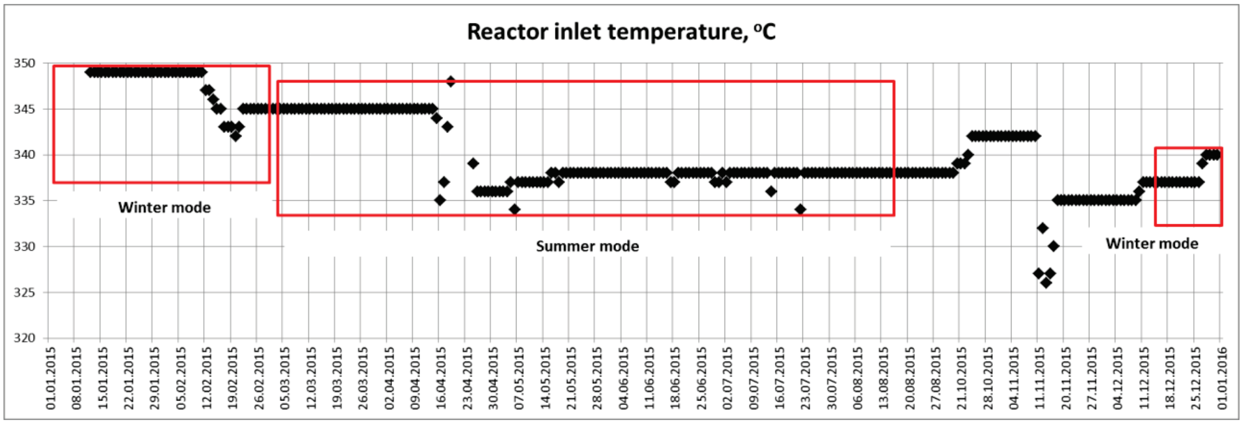

FIGURE 3. Temperature in the dewaxing reactor

Three-mode operation of the unit led to changes of produced diesel fraction hydrocarbon composition. Thus, the content of n-paraffins in the product was an average of 9% by weight when the unit working at winter mode in the period from 01.01.2015 to 03.01.2015; 11.5% by weight when the unit working at summer mode from 03.01.2015 to 13.08.2015 and 9.8% by weight when the unit working at winter mode in the period from 18.12.2015 to 01.01.2016 (Fig. 4).

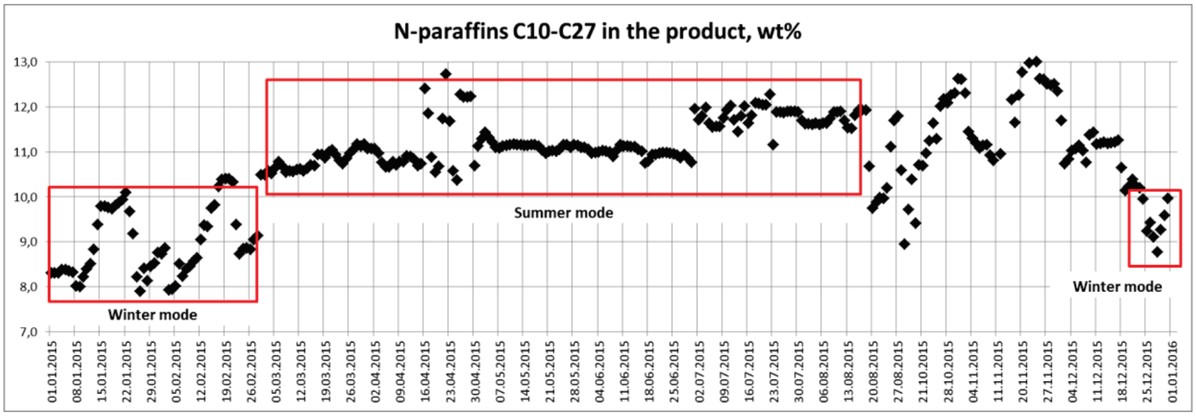

FIGURE 4. Content of n-paraffins C_{10}-C_{27} in the product of dewaxing industrial unit

Such a change in hydrocarbon composition of the product led to changes in the low temperature properties of produced diesel fraction, herewith cloud and freezing points were (Fig. 5):

- –23°C and –33°C (winter mode in the period from 01.01.2015 to 01.03.2015);
- –19°C and –28.5°C (summer mode in the period from 01.03.2015 to 13.08.2015);
- –23°C and –33°C (winter mode in the period from 18.12.2015 to 01.01.2016).

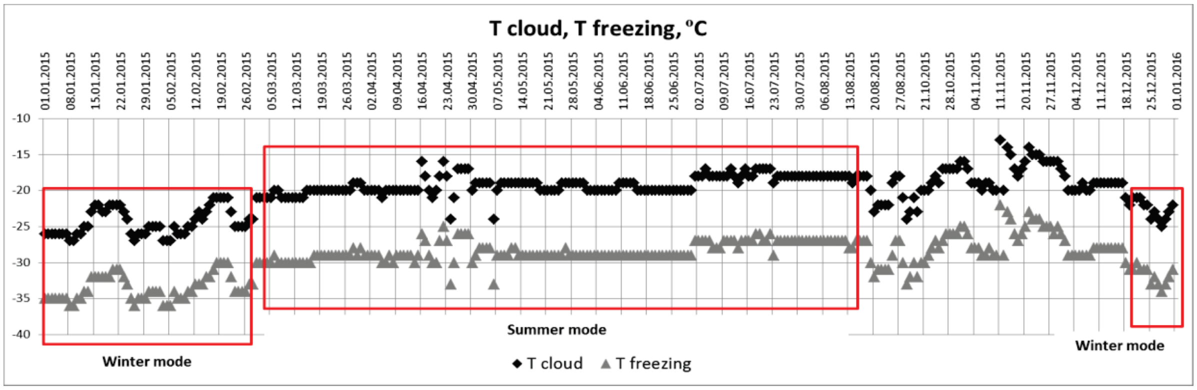

FIGURE 5. The cloud and freezing points of diesel fraction obtained at the dewaxing unit

Optimization calculations of temperature in the dewaxing reactor working at summer mode in the period from 23.04.2015 to 13.08.2015 showed that the temperature in the dewaxing reactor could be reduced to 325°C without loss of diesel fuel quality that would enable to increase the product yield over the summer period to 870 tonnes (Table 1).

TABLE 1. Comparison of the current and optimal operations of the plant

Current operation	Optimal operation
T=336-338°C	T=325°C
T_{cloud}= –21 ÷ –16°C	T_{cloud}= –15 ÷ –11°C
$T_{freezing}$= –30 ÷ –25°C	$T_{freezing}$= –26 ÷ –20°C
Product yield=87%	Product yield=89%
Δyield = 870 tonnes (summer mode period)	

SUMMARY

The developed mathematical model of the catalytic dewaxing process adequately describes the real process, since the absolute error in the calculation of hydrocarbon groups concentration does not exceed 1.16% by weight. The model was applied to the monitoring calculation in order to optimize technological parameters of the dewaxing unit. Model calculations and analysis of the experimental data showed that low-temperature properties of the product were at winter mode T_{cloud}= -23°C and $T_{freezing}$= -33°C. At summer mode, the installation has worked with a large reserve for the low-temperature properties: T_{cloud}= -19°C and $T_{freezing}$= -27.5°C.

Optimization calculations of temperature in the dewaxing reactor working at summer mode showed that the temperature in the dewaxing reactor could be reduced from 336-338 °C to 325°C without loss of low temperature properties and cetane number quality of the diesel fuel that would increase the yield over the summer period to 870 tons.

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