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Optimal technological parameters of diesel fuel hydroisomerization unit work investigation by means of mathematical modelling method

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Abstract

Mathematical model of diesel fuel hydroisomerization has been developed on the base of the system analysis strategy, which consists of the sequence of the following stages: thermodynamic analysis of chemical reactions possibility, the hydrocarbons conversion scheme drafting, kinetic model development, kinetic parameters estimation by means of inverse kinetic problem solution and large massive of full-scale experimental data and model verification to the real process. Using the developed model, the hydroisomerization process kinetic regularities have been investigated, the temperature influence in the range of 350–410 °C, pressure influence within 4.3-9.3 MPa, hydrogen containing gas flow rate influence in the range of 5000–53000 m³/h while the feed flow rate is 301 m³/h on the product composition have been studied. An optimal technological regime has been determined.

1. Introduction

For winter grades of diesel fuel the specific requirements for low-temperature properties, namely for the cloud point, the maximum filtration temperature and the pour point, have been developed. To ensure these requirements some special technologies are needed[1-10].

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There are different variants for diesel fuel pour point reducing. For example, blending with kerosene cut, pour-point depressants introduction[11,12], the catalytic hydroisomerization process, which finds increasing application. Different technologies for this process carrying out exist. The first is the combined hydrotreating and dewaxing process, occurred in one reactor. Another one consists of connected hydrotreating and dewaxing reactors in a different sequence. Also various catalytic systems combinations are used[13].

The problem of diesel fuel manufacture optimization is multifactorial, because the product yield and quality significantly depend on the feed composition, technological conditions, catalyst activity and other factors. To solve this problem it is necessary to apply the system analysis strategy and the mathematical modelling method. Using the industrial reactor model, it is possible to accurately predict the studied system behavior when the raw materials composition and the technological regime change. Moreover, the mathematical model allows to carry out the required amount of research without the intervention in the unit work[14-27].

The aim of the present study is diesel fuel catalytic hydroisomerization industrial plant optimization by means of the mathematical modelling method.

Nomenclature	
ΔH	enthalpy change during a chemical reaction, kJ/mol
ΔS	entropy change during a chemical reaction, kJ/mol·K
ΔG	Gibbs energy change during a chemical reaction, kJ/mol
C_{i0}	concentration of ith group of hydrocarbons at the initial time, mol/l
C_i	concentration of ith group of hydrocarbons, mol/l
τ	residence time, s
W_j	direct chemical reaction rate
W_{-j}	reverse chemical reaction rate
V_{cat}	catalyst volume, m^3
G_f	feed volume flow rate, m^3/h
G_{HG}	hydrogen containing gas volume flow rate, m^3/h
k_i	direct chemical reaction rate constant
k_{-i}	reverse chemical reaction rate constant
k_e	equilibrium constant
R	universal gas constant, J/kg·K
T	temperature, K
P	pressure, MPa

2. Catalytic hydroisomerization technology

The straight run diesel with atmospheric gas oil mixture hydroisomerization unit main streams scheme is shown in Fig. 1.
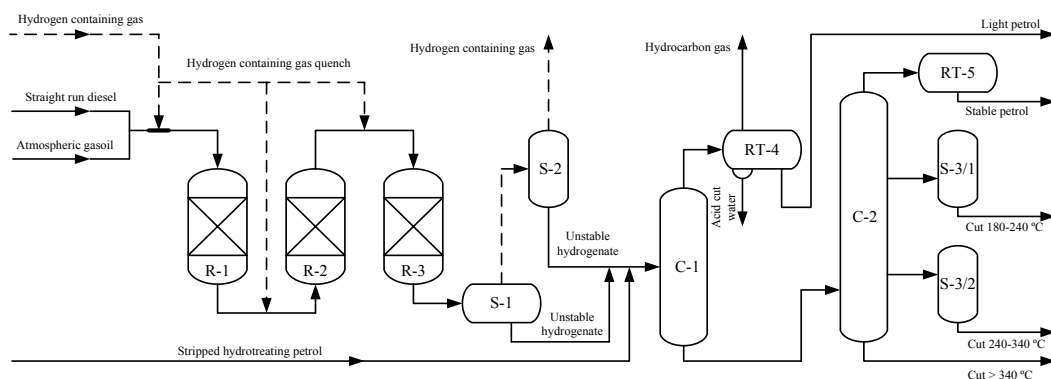

Fig. 1. Hydroisomerization technological scheme

R-1 and R-2 – hydrotreating reactors; R-3 – hydroisomerization reactor; S-1 – high-pressure separator; S-2 – low-pressure separator; C-1 – stabilization column; C-2 – rectification column; S-3/1, 3/2 – strippers; RT-4, RT-5 – reflux tanks

During the process sulfur-, nitrogen- and oxygen containing compounds and aromatic hydrocarbons hydrogenation occurs over modern Co-Mo and Ni-Mo catalysts, as well as paraffins hydroisomerization in order to improve diesel fuel low-temperature properties.

3. Hydroisomerization process hydrocarbons conversion scheme

Petroleum cuts, entering the raw hydrocarbon deep conversion, are the large number of individual hydrocarbons mixture. All individual substances consideration in the conversion scheme is not appropriate, since it leads to considerable complication of mathematical description as well as calculated and experimental data comparison impossibility[20,24,25]. Therefore, in the present study, individual components have been integrated into some groups according chemical characteristics and reactions mechanisms, which occur over hydroisomerization catalyst.

High-molecular paraffins hydroisomerization is performed by hydrocracking with low-molecular paraffins formation and followed by their isomerization via n-paraffins dehydrogenation and i-olefins formation stages[28-32]. Also, monoaromatic and polyaromatic hydrocarbons hydrogenation and i-paraffins cyclization occur over the catalyst. The hydroisomerization process reactions thermodynamic possibility has been confirmed by the Gibbs energy change value calculation using the ab initio quantum-chemical method DFT (Density Functional Theory)[34], which is realized in the Gaussian software. The B3LYP model has been adopted as the theoretical approximation. The basis 3-21G has been taken.

Table 1. Hydroisomerization process reactions thermodynamic characteristics (at T=353 °C, P=6.9 MPa)

№	Reaction	ΔH, kJ/mol	ΔS, J/mol·K	ΔG, kJ/mol	Reaction reversibility
1	N-paraffins C_{10}–C_{27} hydrocracking	−62.71	34.64	−85.16	irreversible
2	Olefins hydrogenation	−145.11	−143.36	−52.22	reversible
3	I-paraffins isomerization	−9.68	89.61	−67.75	reversible
4	I-paraffins cyclization	53.18	100.08	−11.68	reversible
5	Monoaromatic compounds hydrogenation	−242.83	−424.92	−32.52	reversible
6	Polyaromatic compounds hydrogenation	−48.31	25.98	−65.14	reversible

The reaction reversibility condition is −70≤ΔG≤+70 kJ/mol [33].

The obtained Gibbs energy change values confirm that n-paraffins C_{10}–C_{27} hydrocracking and n-paraffins C_5–C_9 isomerization through the i-olefins formation stage target reactions occurrence is the most probable.

Thus, according to the reactions mechanisms over hydroisomerization catalyst as well as thermodynamic analysis and reactive components grouping the hydrocarbons by chemical principals conversion scheme in the hydroisomerization process has been drafted (Fig. 2).
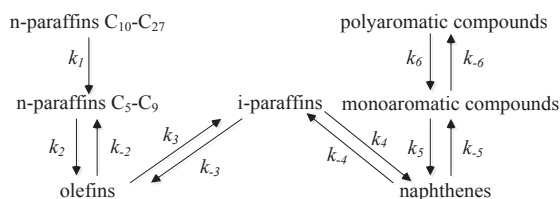

Fig. 2. Formalized hydrocarbons conversion scheme in the hydroisomerization process

4. Hydroisomerization process kinetic model

According to the developed hydrocarbons conversion scheme, the hydroisomerization process kinetic model is written as follows:

$$
\begin{cases}
\dfrac{dC_{N-paraffins\ C_{10}-C_{27}}}{d\tau} = -W_1 \\[2mm]
\dfrac{dC_{N-paraffins\ C_5-C_9}}{d\tau} = 2\cdot W_1 + W_2 - W_{-2} \\[2mm]
\dfrac{dC_{i-paraffins}}{d\tau} = W_3 - W_{-3} - W_4 + W_{-4} \\[2mm]
\dfrac{dC_{Olefins}}{d\tau} = W_2 - W_{-2} - W_3 + W_{-3} \\[2mm]
\dfrac{dC_{Naphthenes}}{d\tau} = W_4 - W_{-4} + W_5 - W_{-5} \\[2mm]
\dfrac{dC_{Monoaromatic\ compounds}}{d\tau} = -W_5 + W_{-5} + 2\cdot W_6 - 2\cdot W_{-6} \\[2mm]
\dfrac{dC_{Polyaromatic\ compounds}}{d\tau} = -W_6 + W_{-6} \\[2mm]
\dfrac{dC_{Hydrogen}}{d\tau} = -W_1 - W_3 + W_{-3} + W_4 - W_{-4} - 3\cdot W_5 + 3\cdot W_{-5} - W_6 + W_{-6}
\end{cases}
$$

initial conditions are following: $\tau=0$, $C_i = C_{i0}$,

The residence time is determined by the formula:

$$\tau = \frac{V_{cat}}{G_f + G_{HG}} \cdot$$

The model kinetic parameters include preexponential factor in the Arrhenius equation and reactions rate constants. In the present work the preexponential factors value has been estimated by the inverse kinetic problem solution using large massive of full-scale experimental data, obtained from existing hydroisomerization industrial unit, which is operated in a regular mode. The direct reactions rate constants have been calculated according to the Arrhenius equation. The reverse reactions rate constants have been calculated by the following formulas:

$$k_{-i} = \frac{ki}{k_e}, \ \ k_e = e^{\frac{-\Delta G}{RT}} \cdot$$

Table 2. Hydroisomerization process reactions kinetic parameters (at T=353 °C)

№	Реакция	k_i	k_{-i}
1	N-paraffins C_{10}–C_{27} hydrocracking	1.090	–
2	N-paraffins C_5–C_9 dehydrogenation	1.666	$3.833\cdot10^{-6}$
3	Olefins hydrogenation to i-paraffins	2.920	$1.317\cdot10^{-4}$
4	I-paraffins cyclization	0.013	$5.006\cdot10^{-3}$
5	Monoaromatic compounds hydrogenation	0.120	$2.360\cdot10^{-4}$
6	Polyaromatic compounds hydrogenation	0.119	$4.515\cdot10^{-7}$

As it can be seen in table 2, a target n-paraffins C_{10}–C_{27} hydrocracking, n-paraffins C_5–C_9 dehydrogenation and olefins hydrogenation to i-paraffins reactions proceeds with the highest rate, which is consistent with previously studied theoretical and thermodynamic laws.

5. Calculated and experimental data comparison

Calculated and experimental components mass concentrations comparison is shown in Fig. 3.
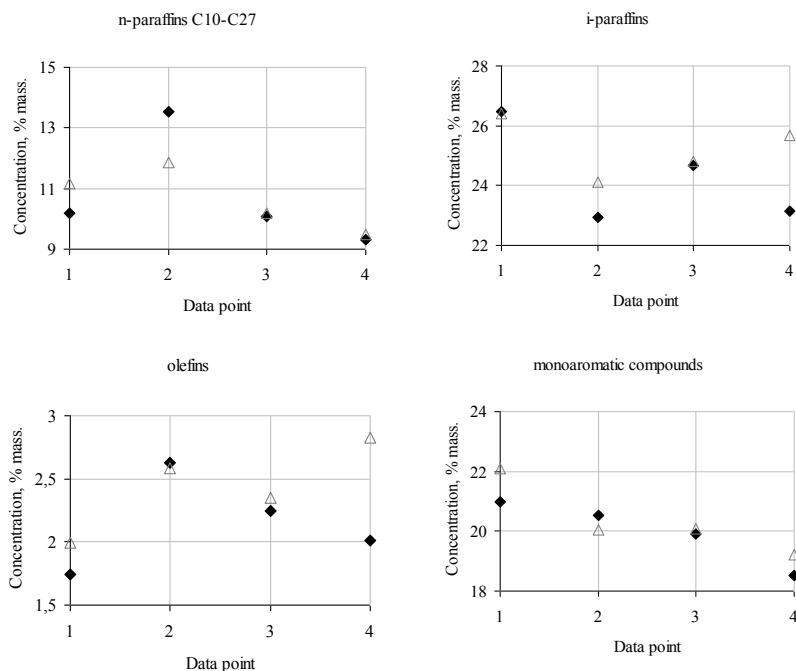
Fig. 3. Calculated and experimental components mass concentrations comparison. (♦) – experiment values, (Λ) – calculated values

Fig. 3 shows good agreement between calculated and experimental components mass concentrations values. The absolute accuracy does not exceed 3 %.

6. Calculations carried out on the developed model

6.1. Temperature change influence on the product composition study

The temperature in the reactor is one of the key factors influencing on the reaction rate in deep oil refining processes. Fig. 4 shows the temperature influence in range of 350-410 °C on the concentrations of components in the product, the content of which foremost determines the obtained diesel fuel low-temperature properties[35,36].
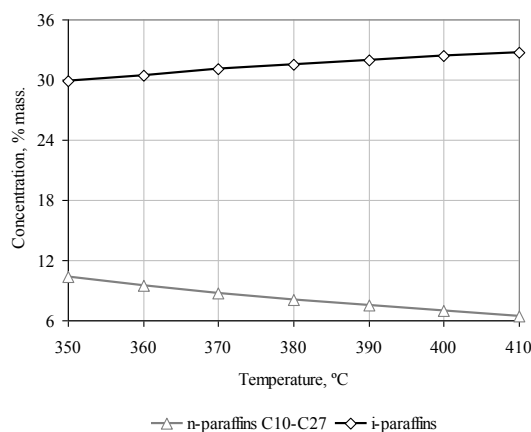
Fig. 4. The temperature change influence on the n-paraffins C_{10}-C_{27} and i-paraffins concentrations in the product

As it can be seen in Fig. 4, when increasing the temperature in the hydroisomerization reactor of 60 °C the n-paraffins C_{10}-C_{27} concentration goes down on 4 % mass. from 10.7 % mass. to 6.7 % mass. (by 37 %). At the same time, i-paraffins concentration rises on 3.0 % mass. from 29.5 % mass. to 32.5 % mass. (by 10 %). Higher process temperature promotes n-paraffins dehydrogenation endothermic reaction, which is hydroisomerization reaction intermediate stage.

6.2. Pressure change influence on the product composition study

The pressure change in the hydroisomerization reactor influence on the n-paraffins C_{10}–C_{27} and i-paraffins mass concentrations in the product has been studied in range of 4.3–9.3 MPa (see Fig. 5).
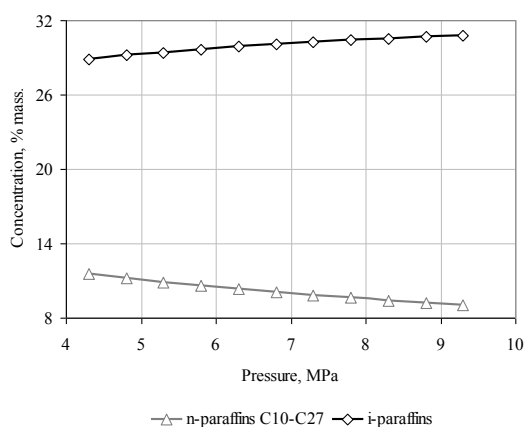

Fig. 5. The pressure change influence on the n-paraffins C_{10}-C_{27} and i-paraffins concentrations in the product

Fig. 5 shows that when the pressure rises of 5 MPa the n-paraffins C_{10}–C_{27} concentration goes up on 2.48 %mass. from 11.56 % mass. to 9.08 % mass. (by 21 %). The i-paraffins concentration increase on 1.91 % mass. from 28.91 % mass. to 30.82 % mass. (by 6.61 %). So, the pressure increasing leads to more complete high-molecular n-paraffins conversion in hydrocracking reaction as well as more complete low-molecular n-paraffins conversion to i-paraffins on the i-olefins hydrogenation stage due to hydrogen partial pressure rising.

6.3. Hydrogen containing gas flow rate change influence on the product composition study

Hydrogen plays an important role in the hydroisomerization process. Hydrogen containing gas flow rate influence on the product composition research has been carried out in range of 5000-53000 m^3/h (see Fig. 6). The raw materials flow rate has been adopted as 301 m^3/h.
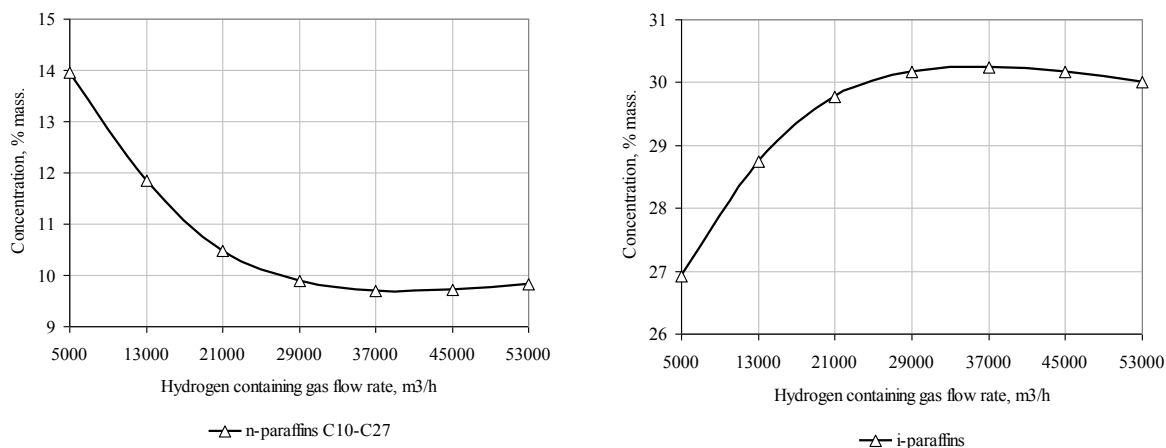

Fig. 6. The hydrogen containing flow rate change influence on the n-paraffins C_{10}-C_{27} and i-paraffins concentrations in the product

According to the Fig. 6, increase in hydrogen containing gas on 32000 m^3/h from 5000 to 37000 m^3/h allows to decrease in n-paraffins C_{10}–C_{27} content in the product on 4.26 % mass. (by 30 %), increase in i-paraffins concentration on 3.32 % mass. (by 12 %). Further hydrogen containing gas flow rate rising is not desirable, as it leads to isomerization rate falling because of n-paraffins dehydrogenation suppression at the olefins formation stage.

7. Conclusions

Mathematical model of diesel fuel hydroisomerization has been developed on the base of the system analysis strategy, which consists of the sequence of the following stages: thermodynamic analysis of chemical reactions possibility, the hydrocarbons conversion scheme drafting, kinetic model development, kinetic parameters estimation by means of inverse kinetic problem solution and large massive of full-scale experimental data and model verification to the real process. Using the developed model, the process kinetic regularities have been investigated, the temperature influence in range of 350–410 °C, pressure influence in range of 4.3-9.3 MPa, hydrogen containing gas flow rate in range of 5000–53000 m^3/h on the product composition have been studied.

- Revealed that the temperature and the pressure have a significant impact on the product composition, namely, when temperature and pressure increase, the content of n-paraffins C_{10}–C_{27} decreases and the content of i-paraffins rises, which is advantageous from the viewpoint of diesel fuels low-temperature properties values reducing.
- Identified that hydrogen insufficiency leads to the adverse reactions increase, olefins formation and does not allow obtaining the specified quality product. The hydrogen excess reduces isomerization rate because of n-paraffins dehydrogenation suppression at the olefins formation stage

Thus, to obtain the required low-temperature properties product, the hydroisomerization process should be carried out at a temperature and a pressure, which do not adversely effect on the catalyst properties (355 °C, 6.7 MPa). The temperature and pressure should be adjusted depending on the catalyst activity. The process must be carried out at a flow rate of hydrogen containing gas not exceeding 37.000 m^3/h.

Acknowledgements

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