

## Mathematical model of straight run diesel catalytic hydroisomerization

N Belinskaya<sup>a</sup>, E Ivanchina<sup>b</sup>, E Ivashkina<sup>c</sup>, E Frantsina<sup>d</sup> and G Silko<sup>e</sup>  
Tomsk Polytechnic University, Tomsk, Russia

E-mail: <sup>a</sup>belinskaya@tpu.ru, <sup>b</sup>ied@tpu.ru, <sup>c</sup>ivashkinaen@tpu.ru, <sup>d</sup>evf@tpu.ru,  
<sup>e</sup>silko\_gy@mail.ru

**Abstract.** Straight run diesel catalytic hydroisomerization mathematical model has been developed. There are the following steps for sequential accomplishment: assessment of thermodynamic possibility of spontaneous reactions under the existing technological conditions, development and formalization of hydrocarbon reaction network scheme, kinetic parameters evaluation, industrial verification of the model. The temperature impact within 345-405 °C, the pressure impact in the range of 5-8 MPa and hydrogen bearing gas consumption impact within 3000-51000 m<sup>3</sup>/h on higher molecular n-alkanes conversion and i-alkanes yield as the basic components which determine diesel fuels low-temperature characteristics to the fullest extent, have been investigated using the developed model. It has been revealed that hydroisomerization process ought to be carried out under such temperature and pressure which do not lead to catalyst exploitation properties come-down in order to receive the product with the required low temperature characteristics. They are 355 °C and 6,7 MPa. The optimal hydrogen bearing gas consumption has been adopted as 39000 m<sup>3</sup>/h when the feed flow rate is 301 m<sup>3</sup>/h.

### 1. Introduction

At present the most important problems of petroleum refining industry development are the following:

1. Involvement in processing “heavy” oil feedstock, which is characterized by high-boiling oil fractions, sulfur residuals, resins and high metal content
2. Increase of oil conversion ratio
3. Toughening of ecological requirements for fuels quality
4. Growing demand for high quality motor fuel.

In addition, the climatic conditions of northern regions in the Russian Federation stipulate the demand for fuels with improved low temperature characteristics.

One of the latest technologies which are used in producing high quality diesel fuels is straight run diesel hydroisomerization. The hydroisomerization unit allows the processing of atmospheric gas oil into straight run diesel in order to produce ecologically friendly summer and winter diesel fuel components with ultra-low sulfur and polyaromatic compounds, as well as improved low temperature characteristics, which, in its turn, correspond to the European Standards for motor fuels [1,2].

During the technological process, sulfur-, nitrogen- and oxygen containing compounds and aromatic hydrocarbon hydrogenation reaction occurs based on modern Co-Mo and Ni-Mo catalysts, as well as alkanes hydroisomerization, in order to improve the low temperature properties of diesel fuels.



The purpose of this research is to improve hydroisomerization unit work efficiency by technological schedule optimization using mathematical modeling method.

## 2. Materials and methods

The full-scale experimental data for different days, which have been obtained from the industrial unit working in the regular technological schedule, are initial data for model development. Namely, they are material balances, technological conditions, and raw material and product compositions.

Mathematical modeling method as an effective tool for solving complex multifactorial problems within petroleum refining and petrochemical industries has been used in the current research. The reactor model which is based on physical-chemical laws provides a means of industrial process prognosis in dynamics without any interference in unit operation [3-7].

The main stages of mathematical model development include estimation of spontaneous reactions under the existing technological conditions, hydrocarbon reactions network scheme development and formalization, kinetic parameters evaluation, industrial verification of the model.

## 3. Model formulation of catalytic hydroisomerization

### 3.1. Thermodynamic analysis and reaction network scheme of hydroisomerization

The experimental data analysis has showed that the product composition most significantly changes due to the decrease in high molecular n-alkanes concentration and increase in i-alkanes and cycloalkanes concentration. The alkenes content in raw material differs from that in the product negligible, because of n-alkanes isomerization reaction mechanism, which includes the intermediate stage of alkenes formation. The monoaromatic compounds (MAC) and polyaromatic compounds (PAC) concentrations practically do not change during the process.

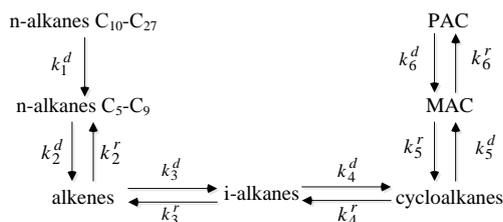
Thermodynamic possibility of spontaneous reaction has been proved by changing Gibbs free energy values which have been calculated under an average technological conditions (temperature 353 °C and pressure 6,9 MPa) using quantum-chemical methods and Gaussian-98 software, (table 1).

**Table 1.** Change in free Gibbs energy during the hydroisomerization process reactions.

No	Reaction	$\Delta G$ , [kJ/mol]
1	Hydrocracking of n-alkanes C <sub>10</sub> -C <sub>27</sub>	-85,16
2	Dehydrogenation of n-alkanes C <sub>5</sub> -C <sub>9</sub>	-52,22
3	Hydrogenation of alkenes with i-alkanes formation	-67,75
4	Cyclization of i-alkanes	-4,98
5	Hydrogenation of MAC	32,52
6	Hydrogenation of PAC	-65,14

According to the reaction reversibility condition ( $-70 \leq \Delta G \leq +70$  kJ/mol [8]), low molecular n-alkanes isomerization, i-alkanes cyclization and alkenes, MAC, PAC hydrogenation are reversible reactions, while high molecular n-alkanes hydrocracking is irreversible one.

According to thermodynamic analysis results, the hydroisomerization process reaction network scheme has been drafted (figure 1).



**Figure 1.** The hydroisomerization process reaction network scheme

where,  $k_j^d$  is rate constant of  $j^{\text{th}}$  direct reaction,  $k_j^r$  is rate constant of  $j^{\text{th}}$  reverse reaction.

### 3.2. Hydroisomerization process kinetic model

On the basis of drafted reaction network scheme the hydroisomerization process kinetic model has been developed. It can be written as

$$\frac{dC_i}{d\tau} = \sum_{j=1}^6 W_{fj} - \sum_{j=1}^6 W_{ej} . \quad (1)$$

Initial conditions are the following:  $\tau=0$ ,  $C_i=C_{i0}$ .

here,  $C_i$  is  $i^{\text{th}}$  components group concentration (alkanes  $C_{10}$ – $C_{27}$ , alkanes  $C_5$ – $C_9$ , etc.), mol/l

$C_{i0}$  is  $i^{\text{th}}$  components group concentration at the initial time, mol/l

$\tau$  is residence time, s

$W_{fj}$  is  $i^{\text{th}}$  components group formation reaction rate

$W_e$  is  $i^{\text{th}}$  components group consumption reaction rate

Reactions rates have been written according to the law of mass action.

The residence time is calculated as

$$\tau = \frac{V_{cat}}{G_f + G_{HG}} . \quad (2)$$

where,  $V_{cat}$  is the volume of the catalyst,  $m^3$

$G_f$  is flow rate of the feed,  $m^3/h$

$G_{HG}$  is flow rate of the hydrogen bearing gas,  $m^3/h$

### 3.3. Kinetic parameters evaluation

Preexponential factors in the Arrhenius equation for all reactions have been determined by calculated and experimental values divergence minimization. Direct reactions rate constants have been calculated by the Arrhenius equation. Reverse reactions rate constants have been calculated through equilibrium constants.

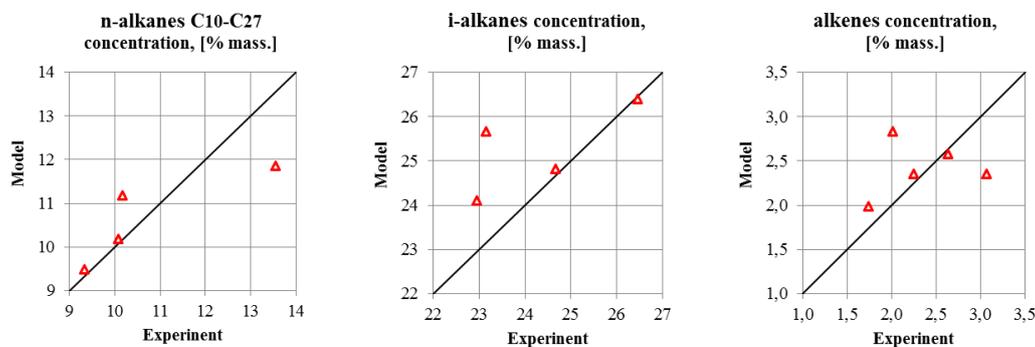
**Table 2.** Reactions kinetic parameters (under temperature 355 °C).

No	Reaction	$k_j^d$	$k_j^r$
1	Hydrocracking of n-alkanes $C_{10}$ – $C_{27}$	1,410	–
2	Dehydrogenation of n-alkanes $C_5$ – $C_9$	1,933	$4,448 \cdot 10^{-6}$
3	Hydrogenation of alkenes with i-alkanes formation	3,305	$1,491 \cdot 10^{-4}$
4	Cyclization of i-alkanes	0,016	$6,162 \cdot 10^{-3}$
5	Hydrogenation of MAC	0,141	$2,773 \cdot 10^{-4}$
6	Hydrogenation of PAC	0,139	$5,274 \cdot 10^{-7}$

The determined kinetic parameters values correlate to the theoretical and thermodynamic regularities. Namely, primary reactions, which are high molecular n-alkanes hydrocracking, low molecular n-alkanes dehydrogenation and alkenes hydrogenation with i-alkanes formation pass with top speed.

### 3.4. Model verification

The model verification to the real industrial process has been carried out by means of calculated and experimental components group concentrations in the product comparison (figure 2).



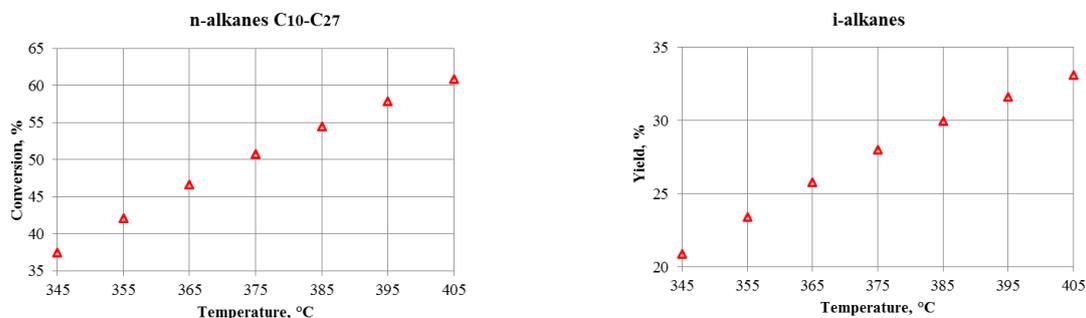
**Figure 2.** Model verification.

## 4. Results and discussion

### 4.1. The temperature impact on high molecular n-alkanes conversion and i-alkanes yield

High molecular n-alkanes and i-alkanes are of the most importance for diesel fuels low temperature characteristics values [9,10].

The temperature in the hydroisomerization reactor impact on high molecular n-alkanes conversion and i-alkanes yield has been studied within the temperature range of 345-405 °C.

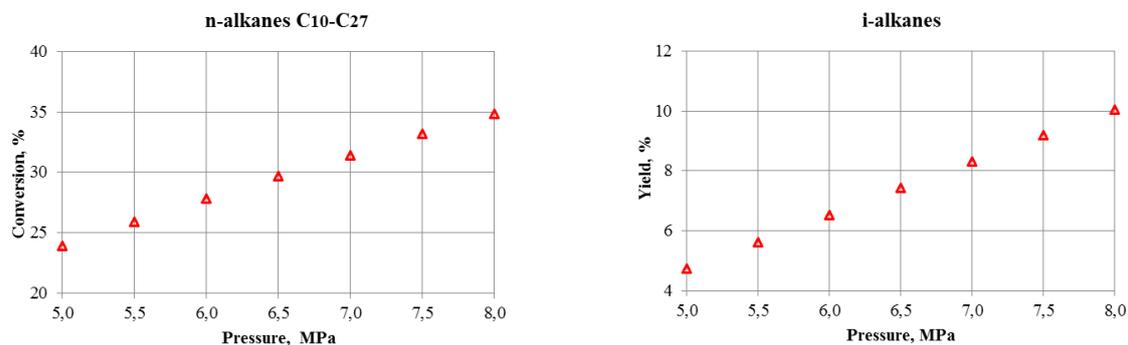


**Figure 3.** The temperature in the hydroisomerization reactor impact on high molecular n-alkanes conversion and i-alkanes yield

Figure 3 shows, that when the temperature in the hydroisomerization reactor raises from 345 to 405 °C n-alkanes C<sub>10</sub>–C<sub>27</sub> conversion increases by 23 % from 37 % to 60 %. I-alkanes yield goes up by 12 % from 21 % to 33 %.

### 4.2. The pressure impact on high molecular n-alkanes conversion and i-alkanes yield

The pressure in the hydroisomerization reactor impact on high molecular n-alkanes conversion and i-alkanes yield has been studied in the range of 5-8 MPa (figure 4).



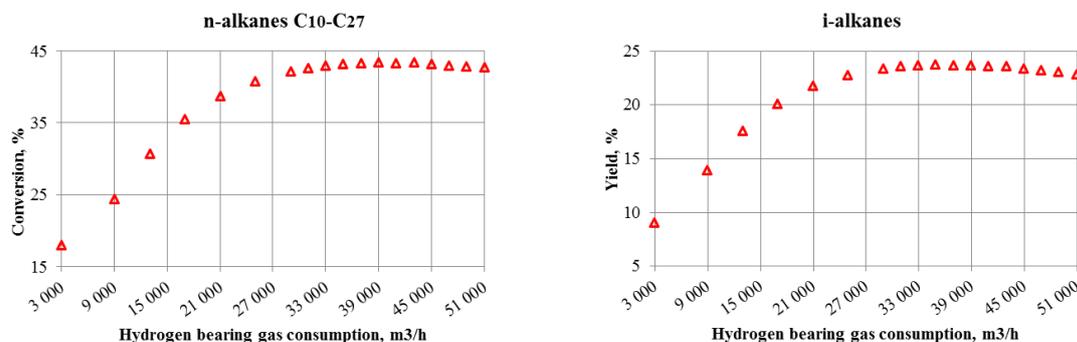
**Figure 4.** The pressure in the hydroisomerization reactor impact on high molecular n-alkanes conversion and i-alkanes yield.

Figure 4 shows that if the pressure is from 5 to 8 MPa n-alkanes C<sub>10</sub>-C<sub>27</sub> conversion increases up to 10 %, i.e. from 24 % to 34 %. I-alkanes yield rises up to 5 %, i.e. from 5 % to 10 %.

Thus, increase in temperature and pressure in the hydroisomerization reactor furthers the production of diesel fuels with lower pour point, maximum filtration temperature and cloud point due to an increase in alkanes C<sub>10</sub>-C<sub>27</sub> conversion, as well as i-alkanes yield.

#### 4.3. The hydrogen bearing gas consumption impact on high molecular n-alkanes conversion and i-alkanes yield

The hydrogen bearing gas consumption impact on high molecular n-alkanes conversion and i-alkanes yield has been studied within the limits of 3000-51000 m<sup>3</sup>/h (figure 5). The feed flow rate has been adopted as 301 m<sup>3</sup>/h.



**Figure 5.** The hydrogen bearing gas consumption impact on high molecular n-alkanes conversion and i-alkanes yield.

It follows from Fig. 5 that the increase in hydrogen bearing gas consumption from 3000 to 39000 m<sup>3</sup>/h leads to n-alkanes C<sub>10</sub>-C<sub>27</sub> conversion raise of 25 %, i.e. from 18 % to 43 %. I-alkanes yield increases up to 14 %, i.e. from 9 % to 23 %. There is no point in further increase in hydrogen bearing gas consumption because it does not lead to the raise in n-alkanes C<sub>10</sub>-C<sub>27</sub> conversion and i-alkanes yield.

## 5. Conclusion

Straight run diesel catalytic hydroisomerization mathematical model has been developed by the following steps for sequential accomplishment: assessment of thermodynamic possibility of spontaneous reactions under the existing technological conditions, development and formalization of

hydrocarbon reaction network scheme, kinetic parameters evaluation, industrial verification of the model.

The temperature impact within the limits of 345-405 °C, the pressure impact in range 5-8 MPa and hydrogen bearing gas consumption impact within range 3000-51000 m<sup>3</sup>/h on higher molecular n-alkanes conversion and i-alkanes yield as the basic components which determine diesel fuels low temperature characteristics to the fullest extent, have been investigated using the developed model.

Thus, hydroisomerization process ought to be carried out under such temperature and pressure which do not lead to catalyst exploitation properties come-down in order to receive the product with the required low temperature characteristics. They are 355 °C and 6,7 MPa. The optimal hydrogen bearing gas consumption has been adopted as 39000 m<sup>3</sup>/h when the feed flow rate is 301 m<sup>3</sup>/h.

### Acknowledgements

The reported study has been carried out in the frame of the State Task “Science” 1.1404.2014.

### References

- [1] Yacine Rezgui and Miloud Guemini 2010 Hydroisomerization of n-decane over Ni-Pt-W supported on amorphous silica–alumina catalysts, *Applied Catalysis A: General.* **374** 31-40
- [2] Konnov S V, Ivanova I I, Ponomareva O A and Zaikovskii V I 2012 Hydroisomerization of n-alkanes over Pt-modified micro/mesoporous materials obtained by mordenite recrystallization *Microporous and Mesoporous Materials* **164** 222–231
- [3] Chekantsev N V, Gyngazova M S and Ivanchina E D 2014 Mathematical modeling of light naphtha (C5, C6) isomerization process *Chemical Engineering Journal* **238** 120-128
- [4] Chsherbakova Y, Dolganova I and Belinskaya N 2012 Benzene alkylation with ethylene process mathematical modeling *7th International Forum on Strategic Technology* **12** 50-53
- [5] Karaba A, Zamostny P, Lederer J and Belohlav Z 2013 Generalized model of hydrocarbons pyrolysis using automated reactions network generation *Industrial and Engineering Chemistry Research* **52** (44) 15407-15416
- [6] Frantsina E V, Ivashkina E N, Ivanchina E D and Romanovskii R V 2014 Developing of the mathematical model for controlling the operation of alkane dehydrogenation catalyst in production of linear alkyl benzene *Chemical Engineering Journal* **238** 129-139
- [7] Luis Pereira de Oliveiraa, Jan J Verstraetea and Max Kolb 2014 Simulating vacuum residue hydroconversion by means of Monte-Carlo techniques *Catalysis Today* **220–222** 208– 220
- [8] Peter Sykes 1986 *A guidebook to mechanisms in organic chemistry* (London: Longman Scientific & Technical)
- [9] Ovchinnikova A V, Boldinov V A, Esipko E A and Prozorova I S 2005 Effect of n-paraffins on the low-temperature properties of aviation diesel fuels *Chemistry and Technology of Fuels and Oils* **41** (6) 462-467
- [10] Siddharth S Ray, Naval K Pandey and Alok K Chatterjee 2009 Effect of aromatics and iso-alkanes on the pour point of different types of lube oils *Fuel* **88** 1629-1633