SIMULATOR DEVELOPMENT OF INDUSTRIAL PROCESS OF NORMAL ALKANES C_9-C_{14} DEHYDROGENATION USING METHODS OF QUANTUM CHEMISTRY

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Abstract

Based on mathematical approach method, computer modeling system was applied to higher alkanes dehydrogenation process optimization. Use of the system allows determination of the optimal technological characteristics; calculation of process characteristics taking into account feed composition, technological conditions and type of catalyst.

Key words: alkanes dehydrogenation; process model; quantum-chemical calculations; kinetic characteristic.

1. Introduction

Optimization of processes, search for new ways of effective stuff use are possible on models, having high reliability and forecasting ability in broad diapason of technological conditions changes [1]. Such models are formed on the basis of reactants transformation chemical system that takes into account formalized mechanism of most probable reactions and their thermodynamic probability.

The best of all mathematical modeling methods are developed for mixtures consisting of some components [2,3]. In this case there are no fundamental problems with development of mathematical model reactions and determination of their characteristics. This task is complicated for oil treatment reactor processes of broad hydrocarbons stuff fractions. On the one hand adequacy of model increases taking into account detailed mechanism, on the other hand it results in complexity of mathematical description and embarrasses practical application over inaccuracy of characteristics determination. At the same time hydrocarbons transformation mechanism formalization must be conducted taking into account reactivity of mixture components that depends on entropy and enthalpy characteristics determining character of molecular bonds and their energies [4].

Thus the main difficulty in industrial processes and manufactures modelling lies in choice of necessary level of mechanism refinement and description of complicated hydrocarbon mixtures transformation kinetics taking into account peculiarity of used catalysts.

At the department of chemical technology of fuels and cybernetics the approach to composition of oil chemistry processes models, based on use of components of multipartite mixture bulk aggregation method was developed and successfully applied [5]. For integration of hydrocarbons in groups proximity of their reactivity was used. It determines product quality, detonation characteristic, biochemical decomposition and other. Application of higher hydrocarbons dehydrogenation process mathematical model to «KINEF» allows optimizing technological routine of work of higher alkanes dehydrogenation industrial installation on the base of hydrocarbon reactivity [6]. However for creation of the system monitoring dehydrogenation catalyst work and coke formation decrease development of this approach for mathematical modeling with use of quantum-chemistry methods was needed.

The purpose of present work is creation of alkanes C_9-C_{14} dehydrogenation process mathematical model sensitive to stuff composition and technological characteristics with refinement of substances transformation scheme on basis of quantum-chemical calculations and conceptions of reactions mechanism, kinetic characteristics estimation for all reactions occurring during the process.

2. Experimental

2.1 Hydrocarbons transformation on surface of platinum catalysts scheme formalization

Literary data analysis of alkanes catalytic dehydrocyclization [7] shows that alkanes aromatization behavior on oxide and metal catalysts occurs through alkenes and alkadienes formation by moving away two or more hydrogen atoms. Dehydrocyclization passes through consistent stages of dehydrogenation product desorption and these products adsorption in another form.

Dehydrogenation scheme can be presented as chain of solid and surface intermediate compounds:

$$\underset{n>6}{C_nH_{2n}} \rightarrow \underset{0<r<2}{(C_nH_{2n-r})} \rightarrow C_nH_{2n-2} \rightarrow \underset{0<r_1<2}{(C_nH_{2n-2-r_1})} \rightarrow C_nH_{2n-4} \rightarrow \underset{0<r_2<2}{(C_nH_{2n-4-r_2})} \rightarrow C_nH_{2n-6}$$

(surface compounds in parenthesis). Every stage of scheme can consist of a number of steps. And vice versa not all specified stages are imperative. Under definite conditions synchronous removal of a number of hydrogen atoms from dehydrogenate molecule is possible or transformation on some stages can occur step by step but without intermediate compounds isolation in gaseous phase.

As during all stages of industrial process mathematical model composition surface mechanism can't be taken into account therefore it is formalized to shorten model characteristics list. However that model must be sensible to stuff composition. Only in this case forecasting ability will be achieved.

On basis of foresaid dehydrogenation mechanism conceptions presumable transformation scheme of present process was formed. With usage of Gaussian program package containing PM3 procedure of NDDO method [8], based on quantum-chemistry modeling, electron molecule structures were calculated and reaction thermodynamic characteristics estimation ((ΔG_r, ΔH_r, ΔS) was conducted under 753 K and 0,2 MPa. Results are illustrated in table 1. Method under consideration takes into account oscillatory and rotator movements of atoms, electron orbit pattern, effects of double bonds conjugation and reproduces the structure and energy hyper valence compounds with high accuracy, providing adequate accuracy for high-quality reproduction of molecule physiochemical characteristics [9].

Table 1 The mean values of reaction thermodynamic characteristics in dehydrogenation process (under 753 K, P=0,20 MPa)

Reaction	ΔG_r, kJ/mole	ΔH_r, kJ/mole	ΔS, kJ/ (mole·K)
1. Alkan $\rightleftarrows$ Alken-1 + H$_2$	−47,94	49,89	0,13
2. Alkan $\rightleftarrows$ Alken-2(n) + H$_2$	−70,34	33,04	0,14
3. Alken-2(n) $\rightleftarrows$ Alkadiene (cumul) + H$_2$	−5,44	90,37	0,13
4. Alken-2(n) $\rightleftarrows$ Alkadiene (conn) + H$_2$	−69,26	32,49	0,14
5. Alken-2(n) $\rightleftarrows$ Alkadiene (sec) + H$_2$	−47,69	49,89	0,13
6. Alken-1 $\rightleftarrows$ Alkadiene (cumul) + H$_2$	−8,28	78,56	0,13
7. Alken-1 $\rightleftarrows$ Alkadiene (conn) + H$_2$	−67,49	29,59	0,13
8. Alken-1 $\rightleftarrows$ Alkadiene (sec) + H$_2$	−47,29	49,92	0,13
9. Isoalkan $\rightarrow$ Isoalken + H$_2$	−81,14	24,50	0,14
10. Isoalken $\rightleftarrows$ Isoalkadiene + H$_2$	−67,91	33,38	0,14
11. Alken $\rightleftarrows$ Isoalken	−2,27	0,94	0,0009
12. Alkan $\rightleftarrows$ Isoalkan	3,06	2,51	0,0009
13. Alkan $\rightleftarrows$ Cycloalkan + H$_2$	−64,21	−33,12	0,04
14. Alkan $\rightarrow$ Aren + 4H$_2$	−331,21	−58,68	0,36
15. Alken $\rightleftarrows$ Cycloalkan	−7,86	−64,51	−0,07
16. Alken $\rightarrow$ Aren + 3H$_2$	−289,29	−90,07	0,27
17. Cycloalkan $\rightarrow$ Aren + 3H$_2$	−333,12	−25,52	0,36
18. Alkadiene $\rightarrow$ Aren + 2H$_2$	−251,07	−137,45	0,15
19. Isoalkan $\rightarrow$ Cycloalkan + H$_2$	−76,48	−37,15	0,05

Reaction	ΔG_r, kJ/mole	ΔH_r, kJ/mole	ΔS, kJ/(mole·K)
20. Isoalkan → Aren + 4H$_2$	−353,6	−49,66	0,40
21. Isoalken → Aren + 3H$_2$	−289,56	−67,64	0,30
22. Isoalken → Cycloalkan	−12,44	−55,13	−2,04
23. Alkan → Cracking product	−137,77	84,03	1,05
24. Alken → Cracking product	−137,76	84,05	0,14
25. Alkadiene → Cracking product	−137,22	83,26	0,17
26. Isoalkan → Cracking product	−138,74	84,39	0,16
27. Isoalken → Cracking product	−140,03	81,69	0,16
28. Isoalkadien → Cracking product	−137,75	98,31	0,16
29. Aren → Coke formation product	−510,66	−425,15	0,56
30. Alken → Coke formation product	−508,64	−423,12	0,56
31. Alkadiene → Coke formation product	−509,35	−424,17	0,56

Thus the results of calculation show that aromatization reaction appears to be the most thermodynamically probable ($\Delta G^0_r \approx -300$ kJ/mol). Paraffins and olefines isomerization reactions do not run in the present process. Also the reactions of dienes formation with cumulative double bonds are not thermodynamically allowed ($\Delta G^0_r \approx -5$ kJ/mole). The presence of isomeric paraffins in product is determined by iso-paraffins dehydrogenation processes which are present in raw materials. All other possible reactions are thermodynamically probable and have approximately the same value of isobaric-isothermal potential ($\Delta G^0_r \approx -70$ kJ/mol). In the process the dienes with conjugate and secured double bonds are produced, whereas formation of dienes with cumulative double bonds is not thermodynamically allowed under these conditions. Cracking ($\Delta G^0_r \approx -140$ kJ/mol) and coke formation ($\Delta G^0_r \approx -510$ kJ/mol) are the main by-reactions.

On the basis of these results formalized scheme of higher alkanes C$_9$-C$_{14}$ dehydrogenation process was formed (fig. 1) and substances were combined into groups of pseudo components according to their reactionary ability that is evaluated according to isobaric-isothermal potential ΔG_r. Thus 11 groups of pseudo components take part in 22 types of chemical reactions.
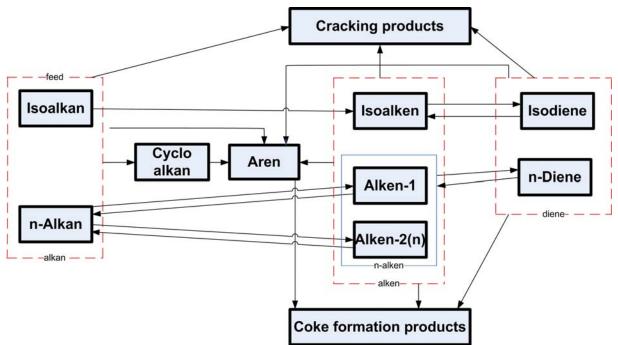

Figure 1 Formalized scheme of dehydrogenation process mechanism

This level of mechanism formalization permits to cut down mathematical description of passing reactions and time solution of material and thermal balance equations, as well as keep the sensitivity concerning stuff components and the self-descriptiveness concerning products of passing reactions.

Dehydrogenation process kinetic model according to the law of active mass is written down in the following way (table 2).

Table 2 Normal paraffines dehydrogenation process kinetic model on basis of formalized scheme of hydrocarbons transformation

Group of compounds	Compounds concentration depending on time
Paraffin	$$\frac{dC_{C_nH_{2n+2}}}{dt} = -k_1 C_{C_nH_{2n+2}(n-paraffin)} + k_{17} C_{C_nH_{2n}(olefin-1)} C_{H_2} - k_2 C_{C_nH_{2n+2}(n-paraffin)} + k_{18} C_{C_nH_{2n}(olefin-2(n))} C_{H_2}$$ $$- k_6 C_{C_nH_{2n+2}(\sum paraffin)} - k_7 C_{C_nH_{2n+2}(\sum paraffin)} - k_{11} C_{C_nH_{2n+2}(\sum paraffin)}$$
Isoparaffin	$$\frac{dC_{C_nH_{2n+2}}}{dt} = -k_4 C_{C_nH_{2n+2}(isoparaffin)} - k_6 C_{C_nH_{2n+2}(\sum paraffin)} - k_7 C_{C_nH_{2n+2}(\sum paraffin)} - k_{11} C_{C_nH_{2n+2}(\sum paraffin)}$$
Olefin-1	$$\frac{dC_{C_nH_{2n}}}{dt} = k_1 C_{C_nH_{2n+2}(n-paraffin)} - k_{17} C_{C_nH_{2n}(olefin-1)} C_{H_2} - k_3 C_{C_nH_{2n}(n-olefin)} + k_{19} C_{C_nH_{2n-2}(n-dien)} C_{H_2}$$ $$- k_9 C_{C_nH_{2n}(\sum olefin)} - k_{12} C_{C_nH_{2n}(\sum olefin)} - k_{15} C_{C_nH_{2n}(\sum olefin)}$$
Olefins-2(n)	$$\frac{dC_{C_nH_{2n}}}{dt} = k_2 C_{C_nH_{2n+2}(n-paraffin)} - k_{18} C_{C_nH_{2n}(olefin-2(n))} C_{H_2} - k_{21} C_{C_nH_{2n}(olefin-2(n))} - k_9 C_{C_nH_{2n}(\sum olefin)}$$ $$- k_{15} C_{C_nH_{2n}(\sum olefin)} - k_{12} C_{C_nH_{2n}(\sum olefin)} + k_{22} C_{C_nH_{2n-2}(n-dien)} C_{H_2}$$
Isoolefin	$$\frac{dC_{C_nH_{2n}}}{dt} = k_4 C_{C_nH_{2n+2}(isoparaffin)} - k_5 C_{C_nH_{2n}(isoolefin)} + k_{20} C_{C_nH_{2n-2}(isodien)} C_{H_2} - k_9 C_{C_nH_{2n}(\sum olefin)}$$ $$- k_{12} C_{C_nH_{2n}(\sum olefin)} - k_{15} C_{C_nH_{2n}(\sum olefin)}$$
Diene	$$\frac{dC_{C_nH_{2n-2}}}{dt} = k_3 C_{C_nH_{2n}(olefin-1)} - k_{19} C_{C_nH_{2n-2}(n-dien)} C_{H_2} + k_{21} C_{C_nH_{2n}(olefin-2(n))} - k_{13} C_{C_nH_{2n-2}(\sum dien)}$$ $$- k_{22} C_{C_nH_{2n-2}(n-dien)} C_{H_2} - k_{10} C_{C_nH_{2n-2}(\sum dien)} - k_{16} C_{C_nH_{2n-2}(\sum dien)}$$
Isodiene	$$\frac{dC_{C_nH_{2n-2}}}{dt} = k_5 C_{C_nH_{2n}(isoolefin)} - k_{20} C_{C_nH_{2n-2}(isodien)} C_{H_2} - k_{13} C_{C_nH_{2n-2}(\sum dien)}$$ $$- k_{10} C_{C_nH_{2n-2}(\sum dien)} - k_{16} C_{C_nH_{2n-2}(\sum dien)}$$
Cyclohadrocarbon	$$\frac{dC_{C_nH_{2n}}}{dt} = k_6 C_{C_nH_{2n+2}(\sum paraffin)} - k_8 C_{C_nH_{2n}(Cycloparaffin)}$$
Aren	$$\frac{dC_{C_nH_{2n-6}}}{dt} = k_8 C_{C_nH_{2n}(cycloparaffin)} + k_7 C_{C_nH_{2n+2}(\sum paraffin)} + k_9 C_{C_nH_{2n}(\sum olefin)} + k_{10} C_{C_nH_{2n-2}(\sum dien)}$$ $$- k_{14} C_{C_nH_{2n-6}(aren)}$$
Cracking gases	$$\frac{dC_{Cracking\ products}}{dt} = k_{11} C_{C_nH_{2n+2}(\sum paraffin)} + k_{12} C_{C_nH_{2n}(\sum olefin)} + k_{13} C_{C_nH_{2n-2}(\sum dien)}$$
Coke	$$\frac{dC_{CokeFormation\ products}}{dt} = k_{14} C_{C_nH_{2n-6}(aren)} + k_{15} C_{C_nH_{2n}(\sum olefin)} + k_{16} C_{C_nH_{2n-2}(\sum dien)}$$
Hydrogen	$$\frac{dC_{H_2}}{dt} = k_1 C_{C_nH_{2n+2}(n-paraffin)} - k_{17} C_{C_nH_{2n}(olefin-1)} C_{H_2} + k_2 C_{C_nH_{2n+2}(n-paraffin)} - k_{18} C_{C_nH_{2n}(olefin-2(n))} C_{H_2}$$ $$+ k_3 C_{C_nH_{2n}(olefin-1)} - k_{19} C_{C_nH_{2n-2}(n-dien)} C_{H_2} + k_{21} C_{C_nH_{2n}(olefin-2(n))} + k_4 C_{C_nH_{2n+2}(isoparaffin)}$$ $$- k_{22} C_{C_nH_{2n-2}(n-dien)} C_{H_2} + k_5 C_{C_nH_{2n}(isoolefin)} - k_{20} C_{C_nH_{2n-2}(isodien)} C_{H_2}$$ $$+ k_6 C_{C_nH_{2n+2}(\sum paraffin)} + 3k_9 C_{C_nH_{2n}(\sum olefin)} + 4k_7 C_{C_nH_{2n+2}(\sum paraffin)} + 3k_8 C_{C_nH_{2n}(cycloparaffin)}$$ $$+ 2k_{10} C_{C_nH_{2n-2}(\sum dien)}$$

Initial conditions $t=0$, $C_i=C_{0i}$, where i-corresponding hydrocarbon (paraffin, olefin, alkadien and other.).

Developed kinetic model is formalized and quasi homogeneous, therefore rate constants are effective, i.e. they are constant combination of all intermediate stages.

2.2 Development of algorithm for kinetic characteristics estimation of paraffin C_9-C_{14} dehydrogenation process model and its software support

Higher hydrocarbons C_9-C_{14} dehydrogenation process modeling represents a difficult task. Fair quantities of passing reactions bring to high dimensionality of mathematical model and demands determination of a great number of kinetic parameters (pre-exponential factors k_0 and activation energies E_a) for all chemical reaction types. Kinetic experiment realization on industrial installation is not possible. Therefore a more effective variant of k_0 and E_a determination is decision of reverse kinetic task [10]. Theoretically, when we know compounds concentration values at the entry of reactor and at the exit of it under different contact times and temperatures reaction kinetic characteristics from transformation scheme can be estimated by force of design and experimental data deviation minimization. This is the task of multivariate optimum search that needs on the one hand much experimental data under different installation route of work, and on the other hand narrow interval search of parameters. Desired parameters are values of activation energies and pre-exponential factors for all chemical reaction types and optimization function is square difference sum of experimental and calculating indexes.

From the position of system analysis every chemical process mathematical model can be represented by nonlinear algebraic or differential equation system in total and partial derivatives that represent stuff components transformation to product, heat and mass transfer in reactor, catalyst deactivation and others [11]. Models structure of this process is difficult and has nonlinear dependence between parameters that bring to difficulties by decision of parametritic identification tasks.

When deciding the differential equations system that describes real chemical process numerical method of calculation is to be used, in this case we used net method. All hydrocarbon physiochemical parameters (heat effect of reactions, heat and other) that were needed for equation system decision entered in the data basis, created in Microsoft® Office Access 2007. Program reads off these parameters from basis and writes the results in the form of Microsoft® Office Excel 2007 document.

Hereby differential equations system decision was provided kinetic parameters were calculated. As only finite compounds concentration and temperature are known, so kinetic parameters of the model must be estimated. Under algorithm offered by authors kinetic parameters process estimation was realized by force of pre-exponential factors and activation energies updating taking into account calculated concentration value. At comparison of findings and experimental concentration values corresponding pre-exponential factors and activation energies are automatically corrected. It says about intellectuality of that method realizing directional research and parameters updating.

The first assortment of activation energies for all reactions is assigned based on literary data about dehydrogenation process and last investigations conducted by our department [2, 5]. For creation of the first pre-exponents assortment a position is used that preexponential factor is a function of entropy change in the intermediate compounds formation [12]:

$$k_{0,i} = \chi \cdot \frac{k_B \cdot T}{\hbar} \cdot (e^{\frac{\Delta S_i^{\neq}}{R}}),$$

where χ – transmission coefficient, k_B – Boltzmann constant, T – temperature, $\hbar$ – Planck constant, R – absolute gas constant, $\Delta S_i^{\neq}$ – entropy change in the intermediate compounds formation.

For evaluation of rate reaction constants influence on hydrocarbon concentration in product coefficients A matrix is introduced:

$$A = \begin{bmatrix} a_{1,1} & a_{2,1} & \cdots & a_{M,1} \\ a_{1,2} & a_{2,2} & \cdots & a_{M,2} \\ \vdots & \vdots & \cdots & \vdots \\ a_{1,N} & a_{2,N} & \cdots & a_{M,N} \end{bmatrix},$$

where $a_{i,j}$ – stoichiometric coefficient in the presence of reaction rate in the right part of material balance differential equations.

I-hydrocarbon, formed in *j*-reaction, concentration influence function of this reaction rate constant can be presented in the following way:

$$k_{0i} = k'_{0i} \cdot (1 + a_{i,j} \cdot r_j),$$

where k_{0i} и k'_{0i} – preexponent of *i*-chemical reaction on the next or last step of iteration, dimension depends on kind of kinetic equation; r_j – corrective coefficient that is calculated in the following way:

$$r_j = b_{i,j} \cdot \frac{C_j^{\text{exp.}} - C_j^{\text{calc.}}}{C_j^{\text{exp.}} + C_j^{\text{calc.}}},$$

where $C_j^{\text{calc.}}$ и $C_j^{\text{exp.}}$ – calculating and experimental value of *j*-component concentration, mole/litre; $b_{i,j}$ – weighting coefficient that defines pre-exponent sensitiveness to all hydrocarbons concentration (taking influence of this reaction on process as a whole into account).

Coefficients $b_{i,j}$ value is defined depending on strength influence of *i* component concentration on *j* reaction. Overview of coefficients matrix is presented in the following way:

$$B = \begin{bmatrix} b_{1,1} & b_{2,1} & \cdots & b_{M,1} \\ b_{1,2} & b_{2,2} & \cdots & b_{M,2} \\ \vdots & \vdots & \cdots & \vdots \\ b_{1,N} & b_{2,N} & \cdots & b_{M,n} \end{bmatrix}.$$

Temperature influence on pre-exponential factors for every reaction is taken into account similarly.

Functional of mistake is presented in the following way:

$$\frac{1}{N+1} \sqrt{\sum_{j=1}^{N} \left(\frac{C_j^{\text{exp.}} - C_j^{\text{calc.}}}{C_j^{\text{exp.}}} \right)^2 + \left(\frac{T^{\text{exp.}} - T^{\text{calc.}}}{T^{\text{exp.}}} \right)^2} < \varepsilon,$$

where N – a number of components taking part in process; ε – value of allowable mistake that is determined from apparatus mistake that measure technological parameters; $T^{\text{calc.}}$ и $T^{\text{exp.}}$ – calculating and experimental value of temperature, К.

Further pre-exponential factors with use of iteration method and offered policy are picked up automatically.

The next stage of parametric identification task decision is reactions activation energy assortment with use of already defined pre-exponential factors values.

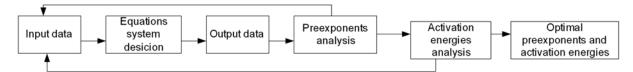Flow block of offered by authors algorithm is represented in the figure 2.

Figure 2 Flow block of algorithm according to optimal kinetic parameters of hydrocarbons C$_9$-C$_{14}$ dehydrogenation process calculation.

Program of model was realized in integrated environmental Delphi 7. Input data for calculation are physic-chemical properties of hydrocarbons, composition of component stuff and product mixture, technological conditions that are read off from generated in Microsoft® Office Access 2007 data basis.

With use of the present program estimation of all chemical reaction types was realized. Calculation results are represented in the third table.

Table 3 Values of the main kinetic parameters of higher paraffines C_9–C_{14} dehydrogenation process

Reaction	Kinetic parameter of reaction			
	$k_{0icalc.}$, s^{-1}	$k_{0idefinite.}$, s^{-1}	X	E_a, kJ/mole
N-paraffin $\rightarrow$ Olefin-1+H$_2$	$9,76 \cdot 10^{20}$	$6,01 \cdot 10^7$	$6,16 \cdot 10^{-14}$	150
N-paraffin $\rightarrow$ Olefin -2(n)+H$_2$	$3,25 \cdot 10^{21}$	$7,91 \cdot 10^7$	$2,43 \cdot 10^{-14}$	150
Olefin -1 $\rightarrow$ N-dien+H$_2$	$9,76 \cdot 10^{20}$	$5,09 \cdot 10^{10}$	$5,21 \cdot 10^{-11}$	180
Isoparaffin $\rightarrow$ Isoolefin+H$_2$	$3,25 \cdot 10^{21}$	$1,73 \cdot 10^9$	$5,32 \cdot 10^{-13}$	185
Isoolefin $\rightarrow$ Isodien+H$_2$	$3,25 \cdot 10^{21}$	$8,15 \cdot 10^8$	$2,51 \cdot 10^{-13}$	170
Paraffin $\rightarrow$ Cycloparaffin+H$_2$	$3,44 \cdot 10^{10}$	$2,98 \cdot 10^9$	$8,65 \cdot 10^{-2}$	185
Paraffin $\rightarrow$ Aren+4H$_2$	$1,02 \cdot 10^{33}$	$8,27 \cdot 10^{10}$	$8,09 \cdot 10^{-23}$	240
Olefin $\rightarrow$ Aren+3H$_2$	$2,02 \cdot 10^{28}$	$3,59 \cdot 10^{10}$	$1,77 \cdot 10^{-18}$	200
Cycloparaffin $\rightarrow$ Aren+3H$_2$	$1,02 \cdot 10^{33}$	$8,60 \cdot 10^{11}$	$8,41 \cdot 10^{-22}$	200
Dien $\rightarrow$ Aren+2H$_2$	$1,08 \cdot 10^{22}$	$1,00 \cdot 10^{10}$	$9,23 \cdot 10^{-13}$	180
Paraffin $\rightarrow$ Cracking product	$1,18 \cdot 10^{69}$	$4,26 \cdot 10^8$	$3,62 \cdot 10^{-61}$	200
Olefin $\rightarrow$ Cracking product	$3,25 \cdot 10^{21}$	$1,51 \cdot 10^6$	$4,64 \cdot 10^{-16}$	165
Dien $\rightarrow$ Cracking product	$1,20 \cdot 10^{23}$	$1,00 \cdot 10^{10}$	$8,32 \cdot 10^{-14}$	200
Aren $\rightarrow$ Coke formation product	$2,90 \cdot 10^{43}$	$2,37 \cdot 10^6$	$8,18 \cdot 10^{-38}$	200
Olefin $\rightarrow$ Coke formation product	$9,65 \cdot 10^{43}$	$2,41 \cdot 10$	$2,50 \cdot 10^{-43}$	200
Dien $\rightarrow$ Coke formation product	$3,22 \cdot 10^{44}$	$1,00 \cdot 10^{10}$	$3,11 \cdot 10^{-35}$	180
Olefin -1+H$_2$ $\rightarrow$ N-paraffin	$2,52 \cdot 10^7$	$1,50 \cdot 10^3$	$5,95 \cdot 10^{-5}$	60
Olefin -2(n)+H$_2$ $\rightarrow$ N-paraffin	$7,57 \cdot 10^6$	$1,50 \cdot 10^3$	$1,98 \cdot 10^{-4}$	60
N-dien+H$_2$ $\rightarrow$ Olefin -1	$2,52 \cdot 10^7$	$6,52 \cdot 10$	$2,59 \cdot 10^{-6}$	155
Isodien+H$_2$ $\rightarrow$ Isoolefin	$7,57 \cdot 10^6$	$1,27 \cdot 10^2$	$1,68 \cdot 10^{-5}$	150
Olefin -2(n) $\rightarrow$ N-dien+H$_2$	$9,76 \cdot 10^{20}$	$4,79 \cdot 10^9$	$4,91 \cdot 10^{-12}$	180
N-dien+H$_2$ $\rightarrow$ Olefin -2(n)	$2,52 \cdot 10^7$	$4,00 \cdot 10^{-1}$	$1,59 \cdot 10^{-8}$	155

Ideal spilling model of reactor was used. Present assumption was controlled by force of diffusion criterion Pickle Pe_D estimation. Firstly value of thermal criterion Pickle Pe_T was calculated to be 2494. According to literary sources ratio between thermal and diffusion Pickle criterions is 1,05–1,5. Therefore, Pe_D=2375–1663. Since Pe_D>200 и Pe_T>0 convection currents of heat and substance transfer in catalyst layer predominate over diffusion currents and hypothesis about dynamic-pressure regime of ideal spelling is confirmed. General mathematical model of process taking heat balance into account is presented in the following way:

$$
\begin{cases}
G\dfrac{\partial C_i}{\partial z} + G\dfrac{\partial C_i}{\partial V} = (1-\varepsilon)\sum_{j=1}^{N} w_j, i = 1...M, \; j = 1...N \\[3mm]
G\dfrac{\partial T}{\partial z} + G\dfrac{\partial T}{\partial V} = -(1-\varepsilon)\dfrac{\sum_{j=1}^{N}\left(\Delta H_j w_j\right)}{c_p \cdot \rho},
\end{cases}
$$

where G – hour consumption of stuff, meter^3/hour; C_i – i hydrocarbon concentration, mole/meter^3; V – catalyst volume, meter^3; ε – fractional void volume of catalyst layer, $\varepsilon = 0...1$; w_j – j reaction rate, mole/(meter$^3 \cdot$hour); z – «reduced time» or summary volume of processed stuff after catalyst regeneration, meter^3, $z = Gt$; t – time, hour; M – number of components; N – number of reactions; T — process temperature, K; ΔH_j — reaction thermal effect, Joule/mole; C_p — mixture heat, Joule/(kilogram·K); ρ – mixture density, kilogram/meter^3.

Initial and boundary conditions:

$$z = 0 : C_i = 0, T = T_{first};$$
$$V = 0 : C_i = C_{i,enter}, T = T_{enter}.$$

Mathematical model is formed taking stationary factors of industrial process into account that relate to coke structures sediment on surface of catalyst. Exponential dependence of catalyst activity from coke accumulation:

$$a_j = Ae^{-\alpha_j C_k},$$

where a_j – relative catalyst activity which is equal to ratio of reaction rates passing on coked and fresh catalyst; A – entropy factor of process; α_j – poisoning coefficient that depends on ratio of acid and basis factors in the given type of reaction; C_k – coke concentration on catalyst.

2.3 Model adequacy testing

For model adequacy testing calculating indexes of output stream are compared with analogous experimental indexes corresponding to beginning of catalyst industrial cycle when coke deactivation is minimum.
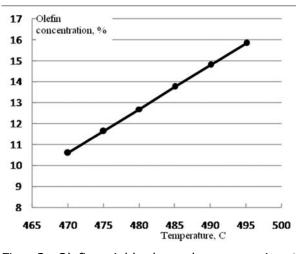
Mistake of primary components concentration calculation does not exceed 4 % (table 4), that confirms high accuracy of process model kinetic parameters determination.

Table 4 Calculating and experimental values of product concentration comparison for dehydrogenation process

Component	Component concentration, mass %		Deviation of calculation, %
	Calculation	Experiment	
Paraffin	86,94	86,93	0,01
Olefin	9,28	9,27	0,11
Dien	0,49	0,5	2,00
Isoparaffin	2,71	2,69	0,74
Isoolefin	0,28	0,29	3,45
Isodien	0,02	0,02	0,00
Aren	0,28	0,29	3,45
Coke formation product	$55,72 \cdot 10^{-3}$	$55,94 \cdot 10^{-3}$	0,40
Cracking product	6,17	5,94	3,77
Hydrogen	93,83	94,06	0,25

2.4 Different factors influencing on process behavior investigation

Investigated models show that output stream indexes are sensible to stuff and technological condition changes: input temperature and mole ration of hydrogen and stuff (figures 3–8).
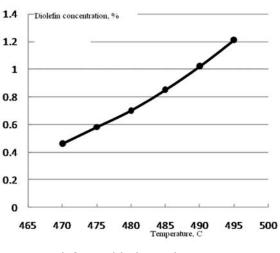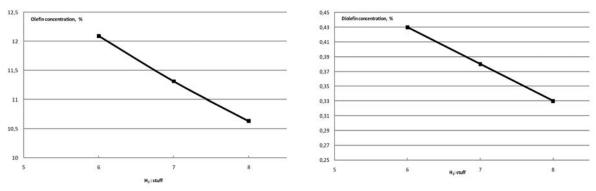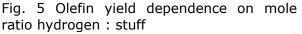

Fig. 3 Olefin yield dependence on input stream temperature

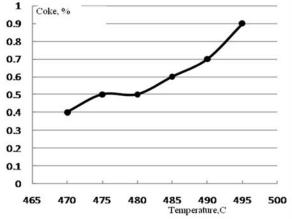Fig. 4 Diolefin yield dependence on stream temperature

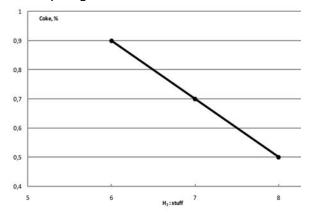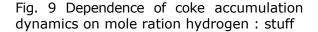Fig. 5 Olefin yield dependence on mole ratio hydrogen : stuff

Fig. 6 Diolefin yield dependence on mole ratio hydrogen : stuff

Fig. 8 Dependence of coke accumulation dynamics on temperature

Fig. 9 Dependence of coke accumulation dynamics on mole ration hydrogen : stuff

Temperature increase results in desired product yield (olefin) increase, however a number of by-products (diolefin) also increase (figures 3, 4). Stuff dilution by hydrogen containing gases makes the reverse influence (figures 5, 6), i.e. ratio hydrogen: stuff increase brings to desired and by-product yield decrease.

Coke quantity on the catalyst is in direct proportion to temperature increase in reactor (figures 7) and inversely to hydrogen quantity in stuff (figures 8). Results of technological parameters and stuff influence are evidence of optimal technological process regimes assortment necessity.

3. Conclusions

Consequently calculations make it clear that isomerization reactions of stuff components and products do not occur in normal paraffin C_9-C_{14} dehydrogenation process as well as olefin cyclization reactions. Dienes with conjugate and secured double bonds are formed, but dienes with cumulative double bonds formation are thermodynamically impossible under present conditions.

Offered mechanism formalization layer lies in hydrocarbons association in reactionary series by ΔG_r index. Reactionary ability of compounds is estimated with quantum-chemical method NDDO usage that contains PM3 procedure. Mechanism layer formalization does not overload mathematical description on the one hand, at the same time it permits to take olefins and dienes with double bonds in different position formation into account, as well as isoparaffines formation as stuff components.

Algorithm of hydrocarbons C_9–C_{14} dehydrogenation process kinetic parameters estimation is offered. Algorithm program realization in Delphi 7.0 environment is realized. Kinetic parameters for all reactions estimation is carried out. Calculation mistake does not exceed 4 % that is compared to chromatographic analysis method mistake usually used for product components concentration determination. Calculation module on the base of present algorithm is placed in common modelling system of synthetic detergents manufacture that includes dehydrogenation paraffines, hydrogen diolefins and alkylation stages.

Program realized model of process permits to calculate material and thermal reactor balances with enough accuracy, as well as investigates the influence of different

technological conditions change on effectiveness of process realization. How much dehydrogenation process is sensible to stuff and technological conditions change is shown with developed model use. Therefore process must be passed under optimal conditions for present type of stuff for requisite product yield maintenance.

Symbols

H	enthalpy, kJ/mole
S	entropy, J/mole·K
C_i	concentration of i-th hydrocarbon, mole/m^3
E	pore volume of catalyst layer
r_i	rate of reaction, mol/m^3·h
w_j	rate of j-th component in i-th reaction transformation, mole/m^3·h
T	temperature of the process, K
ΔH_j	thermal effect of reaction, Joule/mole
C_p	thermal capacity of a mixture, Joule/mole·K
P	density of a mixture, kg/m^3
T_0	start temperature (temperature of an environment), K
T_{in}	temperature of an input in a reactor, K
C_{in}	entrance concentration of hydrocarbon, mole/m^3
V	volume of catalyst, m^3
G	hour expenditure of raw material, m^3/h
T	time, h
Z	total volume of the processed raw material, m^3
Ω	mass concentration of substance in hydrocarbons, % mass
X	molar fraction of substance in hydrocarbons, mole/liter
Mr	molar weight, kg/mole.

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