

REACTOR BLOCK OPERATION ANALYSIS AND EFFICIENCY PREDICTION IN PARAFFINS DEHYDROGENATION PROCESS WITH USE OF TECHNOLOGICAL MODELING SYSTEM

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Abstract

An application of technological modeling system for n-alkanes dehydrogenation process on Pt-catalyst has been examined. Using of the developed system allows catalyst lifetime prolongation as a result of operation conditions optimization and calculation of different variants of plant reconstruction. After preliminary research it was revealed that one of possible variants is switching into two-reactor scheme.

Keywords: linear alkylbenzenes (LAB); linear alkylbenzene sulfonates (LAS), mathematical modeling; dehydrogenation; process efficiency.

1. Introduction

Last years development of the consumer market actively stimulates development of the industry, including petrochemical one. In particular, manufactures of synthetic detergents and their raw-material base - linear alkylbenzenes (LAB), linear alkylbenzene sulfonates (LAS) are rapidly developing.

LAB manufacturing complex (UOP technology) includes three technological stages: dehydrogenation of higher paraffins, hydrogenation of by-products and benzene alkylation with obtained monoolefines. Production of maximum quantity of desired product is possible only at maintenance of optimum conditions of the process carrying out.

Earlier for taking influence of raw material composition on efficiency of all stages into account and for optimum technological mode maintaining it was necessary to carry out numerous experiments and that was not favorable from the economic point of view.

Nowadays there are modern methods of production efficiency increase which are based on innovative mathematical models that can be used for optimization of catalysts composition and, at the same time, reactors construction ^[1].

The present work includes a number of innovative characteristics:

- For the first time, with use of the system approach it is shown, that methodical bases of the description of kinetic laws of transformation of hydrocarbons C₉-C₁₄ on a surface of Pt-catalysts are based on association of hydrocarbons with close reactionary ability on number of atoms of carbon in a molecule in groups of pseudo-components.
- It is established, that the reaction network of higher paraffins dehydrogenation process provides universality and adequacy of the kinetic description of proceeding reactions at wide change of technological conditions and raw material composition
- It is established, that the mathematical model of typical petrochemical higher paraffins dehydrogenation process allows to model technology of monoolefins obtaining, suitable for alkylbenzenes manufacture in conditions of various technological modes, for various types of the loaded catalysts.

Application of the developed mathematical model to dehydrogenation process monitoring and forecasting is the purpose of the present work.

2. Experimental

2.1. Model development

Main concepts of mathematical modeling are completely realized for the process of gasoline catalytic reforming. Computer modelling systems of this process allow choosing

an optimum design of reactor devices [2], supporting the most effective technological mode of the process carrying out [3, 4], catalysts testing [5]. In spite of the fact that modeling of multicomponent processes is extremely challenging, the developed technique can be successfully applied for higher paraffins dehydrogenation process of LAB manufacture.

The developed methodology of mathematical modeling for multicomponent catalytic processes of oil processing is based on the following concepts of the system analysis of chemical-technological processes:

- 1) Availability and reliability of the experimental data put in a basis of research (raw material, products and conditions of the process);
- 2) Formalization of the mechanism of hydrocarbons transformation on the catalyst surface, based on aggregation of components according to their reactivity; drawing up the transformation scheme of the incorporated components, finding out the dependence of hydrocarbons reactivity on their physical and chemical properties;
- 3) An establishment of catalyst deactivation kinetic laws, based on the calculation of simultaneously proceeding reactions of coke formation, aging and poisoning of an active contact surface, and also influence of process conditions and hydrocarbon composition of processed raw material on speed of catalyst deactivation;
- 4) Construction of technological modeling systems for units monitoring and operation prediction, computer support and revealing of "narrow" places in production process.

At the first stage of drawing up of model research of the aprioristic information on dehydrogenation processes has been carried out, in particular, the thermodynamic analysis of the prospective reactions proceeding during given process is in table 1.

Table 1 Basic thermodynamic and kinetic parameters of the process

Reaction	Gibbs energy, kJ/mole	Enthalpy, kJ/mole	Reaction rate constant* (T=753 K)
paraffins dehydrogenation	-71,58	173	2,19 sec ⁻¹
olefins dehydrogenation	-6,59	84,77	4,19 sec ⁻¹
paraffins isomerization	-77,75	-9,68	0,0009 sec ⁻¹
diolefins dehydrocyclization	-49,96	-17,76	0,0043 sec ⁻¹
iso-paraffins dehydrocyclization	-50,38	237	2,43 sec ⁻¹
paraffins hydrocracking	-139,23	-35,0	1,87 · 10 ⁻⁸ l mole ⁻¹ sec ⁻¹

Considering, that the basic reactions proceeding in the process are: paraffins dehydrogenation up to n-olefins (target reaction); formation of diolefins from n-olefins; formation of aromatic hydrocarbons from formed diolefins; cracking of hydrocarbons with formation of products of condensation and easy hydrocarbons; reaction of coke formation, following reaction network was chosen (table 2., fig. 1).

Table 2 Gross reactions in paraffin dehydrogenation process

Type of reaction	Equation
paraffins dehydrogenation	$C_n H_{2n+2} \xrightleftharpoons[k_{-1}]{k_1} C_n H_{2n} + H_2$
olefins dehydrogenation	$C_n H_{2n} \xrightleftharpoons[k_{-2}]{k_2} C_n H_{2n-2} + H_2$
Coke formation from olefins	$C_n H_{2n-2} \xrightarrow{k_3} KOKC$
paraffins isomerization	$C_n H_{2n} \xrightarrow{k_4} C_6 H_5 - C_{n-6} H_{2n-9} + 2H_2$
diolefins dehydrocyclization	$C_n H_{2n+2} \xrightleftharpoons[k_{-5}]{k_5} i-C_n H_{2n+2}$
iso-paraffins dehydrocyclization	$i-C_n H_{2n+2} \xrightarrow{k_6} C_6 H_5 - C_{n-6} H_{2n-9} + 3H_2$
coke formation from aromatic hydrocarbons	$C_6 H_5 - C_{n-6} H_{2n-9} \xrightarrow{k_7} KOKC$
paraffins hydrocracking	$C_n H_{2n+2} + H_2 \xrightarrow{k_8} C_{n-m} H_{2(n-m)+2} + C_m H_{2m+2}$

Here k_i - reaction rate constants.

Thus, in view of formalization of the basic stages of process on the Pt-catalyst, the following reaction network has been chosen (Figure1) Kinetic model on groups of substances is presented in Table 3.

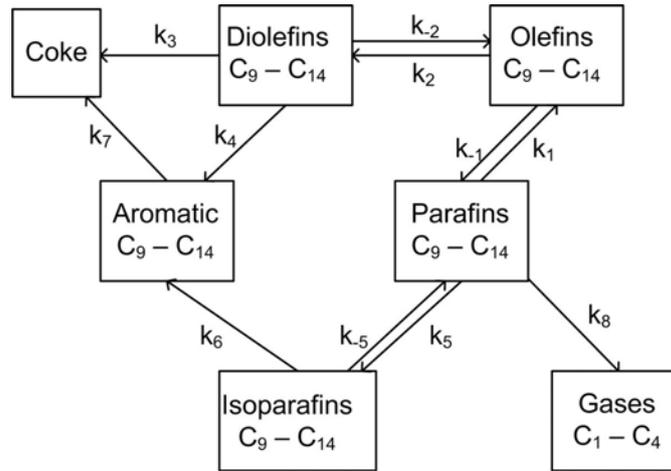


Figure 1. – Formalized reaction network of dehydrogenation process

Table 3 Kinetic model of dehydrogenation process

group of substances	Dependence of substances concentration on time
paraffins	$\frac{dC_P}{dt} = -k_1 C_P + k_{-1} C_O C_{H_2} - k_5 C_P + k_{-5} C_{IP} - k_8 C_P C_{H_2}$
isoparaffins	$\frac{dC_{IP}}{dt} = k_5 C_P - k_{-5} C_{IP} - k_6 C_{IP}$
olefins	$\frac{dC_O}{dt} = k_1 C_P - k_{-1} C_O C_{H_2} - k_2 C_O + k_{-2} C_{DO} C_{H_2}$
diolefins	$\frac{dC_{DO}}{dt} = k_2 C_O - k_{-2} C_{DO} C_{H_2} - k_3 C_{DO} - k_4 C_{DO}$
aromatic hydrocarbons	$\frac{dC_A}{dt} = k_6 C_{IP} + k_4 C_{DO} - k_7 C_A$
gaseous hydrocarbons	$\frac{dC_G}{dt} = k_8 C_P C_{H_2}$
coke	$\frac{dC_K}{dt} = k_7 C_A + k_3 C_{DO}$

For example, the kinetic model of $C_{10}H_{22}$ transformation can be presented by the ordinary 1 order differential equation:

$$\frac{dC_{C_{10}H_{22}}}{dt} = -k_1 C_{C_{10}H_{22}} + k_{-1} C_{C_{10}H_{20}} C_{H_2} - k_5 C_{C_{10}H_{22}} + k_{-5} C_{i-C_{10}H_{22}} - k_8 C_{C_{10}H_{22}} C_{H_2}$$

After drawing up of kinetic model of the process the inverse kinetic problem was solved and for all reactions with participation of hydrocarbons C9-C14 kinetic parameters were evaluated.

We assume that diffusion complications in a reactor for reactions of paraffins isomerization, diolefins hydrocracking and dehydrocyclization are absent, and they proceed in kinetic area. This assumption is checked up by calculation of module Tile and an estimation of the factor of efficiency of catalyst grain internal surface use, eq. 1.

$$\varphi = l \cdot \sqrt{\frac{k}{D_{\rightarrow\phi\phi}}} \tag{1}$$

The choice of plug flow reactor model is proved on the basis of criteria analysis and calculation of Péclet criterion ($Pe > 200$). For the account of characteristics of catalyst layer, porosity value ε was included into model. For industrial catalysts it is equal to 0,19-0,58.

As a result of reaction network analysis and hydrodynamic regime evaluation mathematical model of the process was built. The generalized mathematical description of process is represented by system of the following differential equations of material and thermal balances eq. (1) - (2).:

$$G \frac{\partial C_i}{\partial z} + G \frac{\partial C_i}{\partial V} = (1 - \varepsilon) \sum_j w_j \quad (2)$$

s. c. $z=0$: $C_i=0$, b. c. $V=0$: $C_i=C_{in}$

$$G \frac{\partial T}{\partial z} + G \frac{\partial T}{\partial V} = (1 - \varepsilon) \frac{\sum_j \Delta H_j r_j}{C_p \rho} \quad (3)$$

s. c. $z=0$: $T=T_0$, b. c. $V=0$: $T=T_{in}$, Here $z=Gt$.

2.2. Research of double-reactor scheme efficiency

One of possible ways of plant productivity increase is switching of a reserve dehydrogenation reactor in parallel work with the operating one. The basic purpose of research is development of technological parameters recommendations for carrying out of industrial dehydrogenation process with simultaneous work of two dehydrogenation reactors for various flow rates of processed raw material. Switching to parallel work of dehydrogenation reactors means decrease in raw material volume rate for one reactor from $75 \text{ m}^3 \text{ h}^{-1}$ to $37.5 \text{ m}^3 \text{ h}^{-1}$, that will be reflected both on kinetic and on a hydrodynamic operating conditions of the reactor. While experimental researches allow only estimating influence of change of volume speed of raw materials supply on process parameters, double-reactor scheme operation forecasting can be effectively fulfilled with application of the developed model which sufficiently describes real industrial paraffins dehydrogenation process. The developed mathematical model is sensitive to a chemical composition of raw material processed [6].

The kinetic description put in a basis of technological modeling system is developed taking different reactivity of paraffins with carbon number from 9 to 14 into account in dehydrogenation reactions. The hydrodynamic component of the model allows calculation of influence of the raw material rate on parameters of the process. With decrease in volume rate of raw material (from 75 to $37.5 \text{ m}^3 \text{ h}^{-1}$) the input temperature in a dehydrogenation reactor can be decreased on the average in 20°C in view of equally set concentration of a target product (at carrying out forecast calculations on model - 9.89 % mass.), Figure 2.

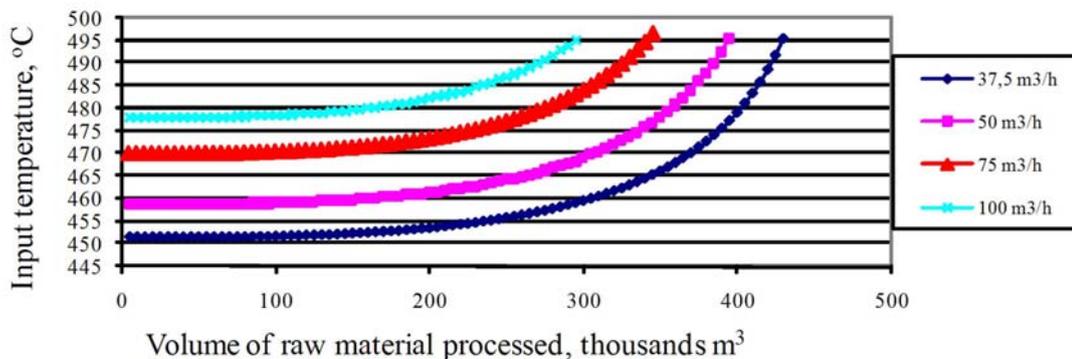


Figure 2. – Change of input temperature at the various raw material volume rates

Possible variant of decrease in rate of coke accumulation and also growth of by-products concentration is the increase of molar ratio "hydrogen: raw material". Results of modeling researches are presented in Tables 4-5.

Table 4 Concentration of target and by-products

Products (% mass.)	Temperature (°C)	
	470	490
	Raw material volume rate = 37.5 m ³ h ⁻¹	
Olefines	12.67	16.58
Diolefines	1.24	2.59
Aromatic hydrocarbons	0.57	0.70
	Raw material volume rate = 50 m ³ h ⁻¹	
Olefines	11.15	15.28
Diolefines	0.89	1.97
Aromatic hydrocarbons	0.54	0.68
	Raw material volume rate = 75 m ³ h ⁻¹	
Olefines	8.96	13.06
Diolefines	0.53	1.28
Aromatic hydrocarbons	0.47	0.63
	Raw material volume rate = 100 m ³ h ⁻¹	
Olefines	7.47	11.35
Diolefines	0.36	0.91
Aromatic hydrocarbons	0.41	0.58

**(without taking into account a stage of hydrogenation) at various temperature and raw material volume rate (molar ratio "hydrogen: hydrocarbons" = 8: 1, volume of the raw material processed 184000 m³)*

Table 5 Concentration of target and by-products

Products (% mass.)	Temperature (°C)	
	470	490
	Raw material volume rate = 37.5 m ³ h ⁻¹	
Olefines	13.46	18.28
Diolefines	0.19	0.55
Aromatic hydrocarbons	0.49	0.61
	Raw material volume rate = 50 m ³ h ⁻¹	
Olefines	11.69	16.58
Diolefines	0.12	0.36
Aromatic hydrocarbons	0.46	0.60
	Raw material volume rate = 75 m ³ h ⁻¹	
Olefines	9.24	13.88
Diolefines	0.07	0.20
Aromatic hydrocarbons	0.39	0.55
	Raw material volume rate = 100 m ³ h ⁻¹	
Olefines	7.63	11.91
Diolefines	0.04	0.13
Aromatic hydrocarbons	0.34	0.50

**(with taking into account a stage of hydrogenation) at various temperature and raw material volume rate (molar ratio "hydrogen: hydrocarbons" = 8: 1, volume of the raw material processed 184000 m³)*

Calculations on the model show, that the thermodynamics of target reaction will not allow raising essentially an output of a target product with decrease in raw material volume rate. Undoubtedly, the variant of simultaneous increase of raw material volume rate is economically justified and more effective.

For achievement of the maximal economic benefit raw material volume rate should be kept at level of 50 m³ h⁻¹ (100 m³ h⁻¹ for both reactors).

Thus, realization of the following recommendations is necessary:

1. Temperature of an input in the reactor = 460 - 487 °C.
2. Molar ratio «H₂: hydrocarbons» = 8: 1.

Finally, the choice of any operation variants is determined by compensation of the expenses caused by support of the chosen technological mode with increase in quantity of desired product (LAB), Table 6.

Table 6 Variants of a technological mode at operation of the plant including two dehydrogenation reactors

Raw material volume rate (m ³ h ⁻¹)	Input temperature (°C)	Catalyst lifetime (days)	Average manufacturing of LAB (t/day)	By-products (diolefins) by the end of run (% mass.)
Molar ratio "hydrogen: hydrocarbons" = 7 : 1				
75 (for 1 reactor)	470	263	190	0.84 on the 263 day
50 (100 for 2 reactors)	462	479	256	1 on the 479 day and 0.85 on the 263 day
37.5 (75 for 2 reactors)	456	611	201	1.21 on the 611 day and 1.02 on the 263 day
Molar ratio "hydrogen: hydrocarbons" = 8 : 1				
75 (for 1 reactor)	470	319	178	0.74 on the 319 day and 0.69 on the 263 day
50 (100 for 2 reactors)	462	604	245	0.92 on the 604 day and 0.71 on the 263 day
37.5 (75 for 2 reactors)	456	833	187	1.03 on the 833 day and 0.74 on the 263 day

It is necessary to note, that the quantity of the LAB is estimated without taking into account loss of a target product with polyalkylbenzenes. On average 0.4-0.5 % of LAB are carried away with heavy alkylate (according to results of laboratory analyses).

3. Results and Discussion

Application of intellectual systems similar to that developed by us is known. Such systems are successfully applied to optimization of plants work. The example is a universal mathematical model for catalytic reforming process [7]. The model is derived in a series of three reactors with an intermediate preheated mix. Results are presented for the modeling of reforming processes with a radial axial input of components of the reaction mix; this makes it possible to select the volume of catalyst and inlet temperature, which will ensure a product of the required quality with the reformer operating at a given output. In order to correlate with experimental data, the authors propose to expand the model and to include other important (except reactor) of the reformer: tube heating furnaces, heat exchangers, and separation towers.

Model developed for the process of Liquid-Phase Alkylation of Benzene with Propylene catalysed by HY Zeolites [8] could be instructive in exploratory simulations evaluating the conditions for benzene alkylation in liquid phase. It allows analyzing the performance of two-phase downflow fixed bed reactors used for alkylation of benzene with zeolite catalysts.

Thus, efficiency of modelling systems application is proved. But analogues systems for higher paraffins hydrogenation process are not developed by present time. So, our program is an innovation in the given area.

According to the researches lead with use of model, economic benefit of realization of switching to parallel work of dehydrogenation reactors can be connected with:

- 1) Increase in duration of unit work at one loading of the Pt-catalyst from 263 to 833 days (the maximal possible increase);
- 2) Increase in target product output to 201 ton/day.

Simultaneous achievement of both parameters is obviously possible with increase in volume rate of raw material on 2 reactors to 100 m³ h⁻¹ and increase of molar ratio «H₂: hydrocarbons» up to 8 : 1 (increase in run to 604 day and daily average manufacturing of LAB up to 245 tones).

At the same time, the increase in volume rate in a hydrogenation reactor and, accordingly, in a reactor of hydrogenation, can cause decrease of conversion of diolefins hydrogenation. The rules of the enterprise provide a working temperature interval for this reactor 180-220°C. Calculations on model have shown, that the increase in raw material volume rate

from 75 till 100 m³ h⁻¹ (approximately from 56000 up to 75000 kg h⁻¹) will not essentially affect conversion of diolefins at an intermediate stage of LAB manufacturing - hydrogenation; target concentration of diolefins will not exceed 0.12 % mass. during all the run.

Contrastive analysis of temperature modes for dehydrogenation reactor at different preset yields of desired product is given at Figure 3.

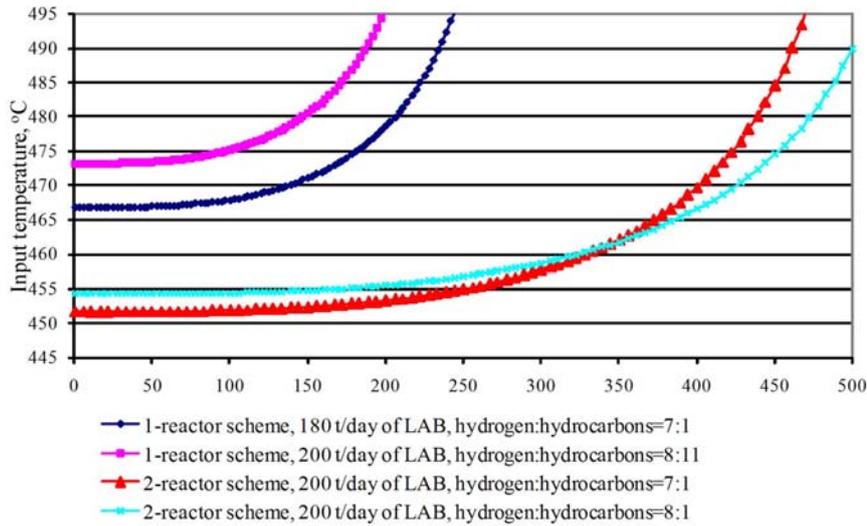


Figure 3. – Influence of dehydrogenation reactor input temperature

Calculation shows that 1-reactor scheme of operation (raw material volume rate 75 m³ h⁻¹, l=7) at LAB yield 180 t/day provides 240 - 250 days of catalyst life with input temperature 470-495°C (diolefins concentration 0.5 - 0.8 % mass., coke concentration 2 % mass.). Monoreactor scheme of operation (raw material volume rate 75 m³ h⁻¹, l=8) at LAB yield 200 t/day provides 200 - 205 days of catalyst life with input temperature 470-495°C (diolefins concentration 0.6 - 0.95 % mass., coke concentration 2.5 % mass.).

Two-reactors scheme of operation (raw material volume rate 37.5 m³ h⁻¹, l=7) at LAB yield 200 t/day provides 470 days of catalyst life with input temperature 450 - 495°C (diolefins concentration 0.64 - 1.1 % mass., coke concentration 2.7 % mass.).

Two-reactors scheme of operation (raw material volume rate 37.5 m³ h⁻¹, l=8) at LAB yield 200 t/day provides 500 days of catalyst life with input temperature 455 - 495°C (diolefins concentration 0.6 - 1.0 % mass., coke concentration 2 % mass.).

As final part of research, we have investigated the influence of technological parameters on dehydrogenation process efficiency with use of mathematical model (Figures 4–6).

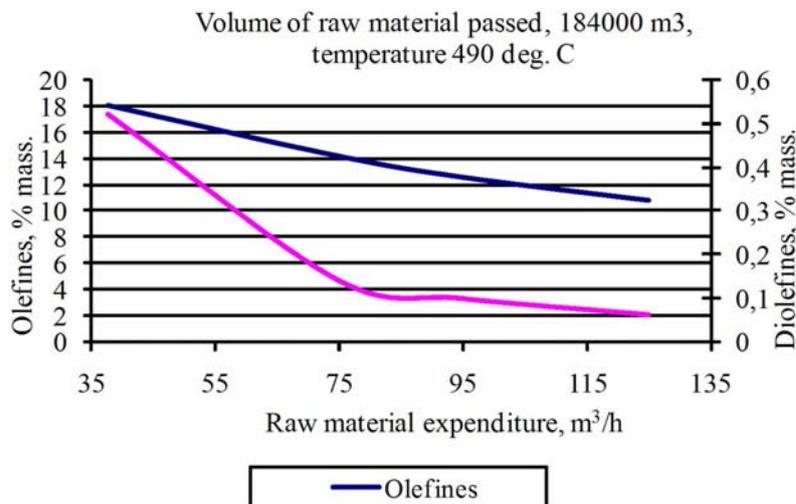


Figure 4. – Change of concentration of olefines and diolefines depending on temperature and the expenditure of raw material at 184 thousand m³ of raw material passed (more than days of plant work)

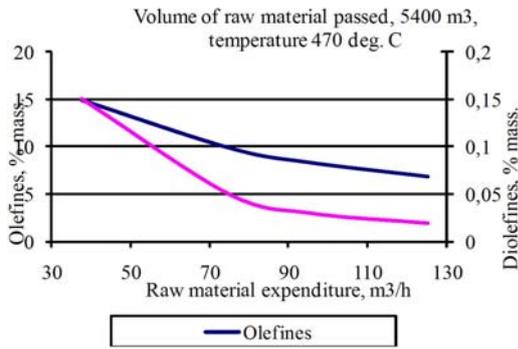


Figure 5. Change of concentration of olefines and diolefines depending on temperature and the expenditure of raw material at 5,4 ths m³ of raw material passed (about 3 days of plant work)

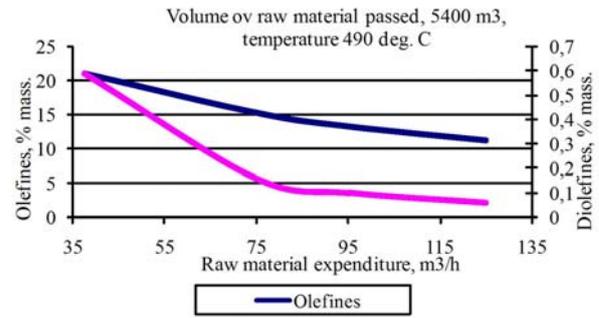


Figure 6. Change of concentration of olefines and diolefines depending on temperature and the expenditure of raw material at 5,4 ths. m³ of raw material passed (about 3 days of plant work)

As it shown in Fig. 4-6, with growth of temperature concentration target and by-products in mixture increases. At the same time it falls with increase of raw material expenditure and volume of raw material passed through dehydrogenation reactor (with strengthening of the catalyst), that does not contradict classical conceptions about heterogeneous catalysis. Inclusion of a reactor of diolefines by-products hydrogenation in the technological scheme allows increasing quantity target olefines, acting on a stage of benzene alkylation with monoolefines.

4. Conclusions

Calculations of influence of dehydrogenation process technological parameters on its efficiency were carried out with the proposed model. It was revealed that increase in production efficiency of dehydrogenation process at 2-reactors operation scheme can be reached by simultaneous increase in raw material volume rate from 75 to 100 m³ h⁻¹ and increase in molar ratio "hydrogen : raw material" from 7: 1 to 8: 1. Under these conditions the maximal effect will be achieved.

It should be mentioned that results of this research work can be interesting both for operating LAS production plants with fixed raw material volume rate – 75 m³ h⁻¹ (also for realization of economical 2-reactors scheme with raw material volume rate 37.5 m³ h⁻¹ and 50 m³ h⁻¹) and for reactor design calculations (with raw material volume rate 80 m³ h⁻¹ and 100 m³ h⁻¹).

Symbols

- L radius of a catalyst grain, m
- K reaction rate constant, sec⁻¹
- $Deff$ effective factor of diffusion, m²/sec
- C_i concentration of i-th hydrocarbon, mole/m³
- E pore volume of catalyst layer
- r_i rate of reaction, mol/m³·h
- w_j rate of j-th component in i-th reaction transformation, mole/m³·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/m³
- 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/m³
- V volume of catalyst, m³
- G hour expenditure of raw material, m³/h
- T time, h
- Z total volume of the processed raw material, m³

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