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Improving the Efficiency of Dehydrogenation Catalyst Resource while Reducing the H_2 Gas Circulation Rate

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Abstract

In the research the various ways of increasing the selectivity of the dehydrogenation process and reducing the intensity of coke formation have been studied. All results were received by means of the mathematical model of the dehydrogenation process with the calculating technique of optimal water flow. The main conclusion consists in the fact that the decrease in molar ratio H2/feed leads to increasing the catalyst deactivation by coke. It can be partially compensated by increasing the supplied water flow to the reactor to 13-14 l/h instead of 9-10 l/h at the end of cycle. Reducing the life of the catalyst to 270-290 days even at an increased water flow is determined by the intensity of the coking reactions. However, the economic feasibility of operating in such condition causes a considerable increase in production of LAB to 181-186 t/day.

Keywords: dehydrogenation, H_2-containing gas, deactivation, modelling

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1. Introduction

Deactivation of industrial catalysts is the most important problem of modern refining and petrochemical industries. According to the scientists[1], it absorbs more than 90 % of all investments in the field of catalysis and is about 50% of the development.

Technology and hardware design of many processes are completely conditioned by deactivation. These include: cracking, reforming, all dehydrogenation processes, isomerization, hydrotreating, and many others[2-5].

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Many dehydrogenation processes (butylene, isoamylene, ethyl benzene, cumene, etc.) are conducted at a large excess of steam (10-20 mol/mol) not only to shift the equilibrium but also to reduce coke formation.

In some cases deactivation determines the cyclic mode of the process, often alternating the periods of work and recovery catalysts. In the processes of dehydrogenation of butane, isobutane, isopentane and catalytic cracking in a fluidized bed operating period is every 6-15 minutes, but at upstream cracking with zeolite catalysts it is 5-10 seconds[6-7].

One of the most important parameters of the paraffins dehydrogenation process as well as one of the main stages of linear alkyl benzenes production is the molar ratio of hydrogen/feed or related circulation rate ratio of hydrogen-containing gas (HCG). It is known that increase in the molar ratio of hydrogen/feedstock reduces coke formation on platinum-containing catalysts and increases its lifetime. At the same time an increase in the circulating gas volume slows down the target reaction and causes an increase in energy costs.

Obviously, such an important parameter as the molar ratio of hydrogen/feed during operation of existing plants should be selected on the basis of the feasibility analysis performed by considering the influence of the hydrogen-containing gas circulation rate on the yield and quality of the products in the changing composition of the feedstock and catalyst activity.

The aim of this work is to improve the resource efficiency while reducing the dehydrogenation catalyst circulation rate of hydrogen-containing gas using a mathematical model.

2. Theoretical base

The literature discusses the various ways of increasing the selectivity of the dehydrogenation process and reducing the intensity of coke formation.

It has been known that the industrial process of paraffins dehydrogenation comprises adding an amount of hydrogen in the initial feed mixture to achieve the active state of the catalyst. Specifically, hydrogen plays an suppressing role in the formation of coke on the catalyst surface and brings platinum in the desired active state[8].

The amount of added hydrogen varies within a wide range and the ratio of hydrogen/hydrocarbons may remain constant or vary during the reaction cycle. Among the advantages of using a low ratio are small-sized equipment, low power cost and the ability to carry out the process at low temperatures. Low temperatures are particularly desirable in the early feed cycle at high catalyst activity.

A change of hydrogen-containing gas circulation in the industrial environment is connected with a change in the total pressure in the system.

Thus, in the book[9] a graphical representation of the pressure effect on the selectivity of olefins is presented at constant temperature and the molar ratio of hydrogen to feedstock. At low pressure, high normal paraffin conversion and selectivity is achieved due to the favorable equilibrium of the dehydrogenation process.

The same effect is achieved by decreasing the molar ratio of hydrogen to feedstock.

In addition to the technological methods described in the literature, there are data from various sources confirming the effect of water in the oxidation coke structures, thereby increasing the stability of the catalyst[10].

In patent[11] the invention consisting in increase of the activity of the dehydrogenation catalyst by increasing the concentration of water in the reaction zone is described, which is accompanied by the tendency to increase toward the end of the feed cycle. Optimization process performance is achieved in the case when the concentration of water was gradually increased with temperature growth in the reactor.

Similar results are given in[12], where there is a recommendation to regulate the water flow when the temperature of the dehydrogenation process is increasing.

The literature review showed that such technological methods as hydrogen or diluting raw water supply to the reactor are efficient ways of using the dehydrogenation catalyst. However, excessive moisture leads to enhancement of the cracking reactions, the shortage of water enhanced the coking reaction, which also results in shortage of hydrogen in the system. At the same time, increasing the HCG circulation ratio causes a decrease in desired products yield - olefins. Therefore, it is important to match the optimum conditions for the industrial process to ensure long-term stability of the catalyst at the desired output of olefins. The method of mathematical modeling helps to solve these problems.

Based on the proposed scheme of hydrocarbon transformations (Figure 1), the authors developed the mathematical model of the dehydrogenation process presented by the system of equations for material and heat balance of each component of the selected formalized transformation scheme with the assumption for the applicability of the model of plug flow reactor as a hydrodynamic reactor model[13].

$$\begin{cases} G\dfrac{\partial C_i}{\partial z} + G\dfrac{\partial C_i}{\partial V} = (1-\varepsilon)\sum\limits_{j=1}^{n} a_j r_j \\ G\dfrac{\partial T}{\partial z} + G\dfrac{\partial T}{\partial V} = -(1-\varepsilon)\dfrac{\sum\limits_{j=1}^{n}(\Delta H_j a_j r_j)}{C_p \cdot \rho} \end{cases} \qquad (1)$$

The initial and boundary conditions are:

$z = 0;\ C_i = 0;\ T = T_{initial};$
$V = 0;\ C_i = C_{inlet};\ T = T_{inlet};$

C_i– is the i-th hydrocarbon concentration, mol/m^3; V – is the catalyst volume, m^3; a – deactivation coefficient (0..1); r_j – is the j-th reaction rate, mol/(m^3·h); G – is the raw material flow rate, m^3/h; Z– is the total volume of processed feed after catalyst regeneration, m^3, $z = G \cdot t$; t – is the time, h; M – is the number of components; N – is the number of reactions; T – is the process temperature, K; ΔH_j– is the reaction heat, J/mol; C_p – is the heat capacity of the mixture, J/(kg K); ρ – is the raw material density, kg/m^3; ε– is the catalyst layer porosity (0.19–0.58);

Kinetic parameters of the model were determined by solving the inverse kinetic problem. In this case an error in model calculation did not exceed 5.10 %. Accounting for the changes in the model catalyst activity under the coke influence provided its predictive capacity and the opportunity to be used for optimization. Along with the equations of material and heat balances of dehydrogenation reactor the mathematical model includes description of Pt- catalyst deactivation with coke[14].

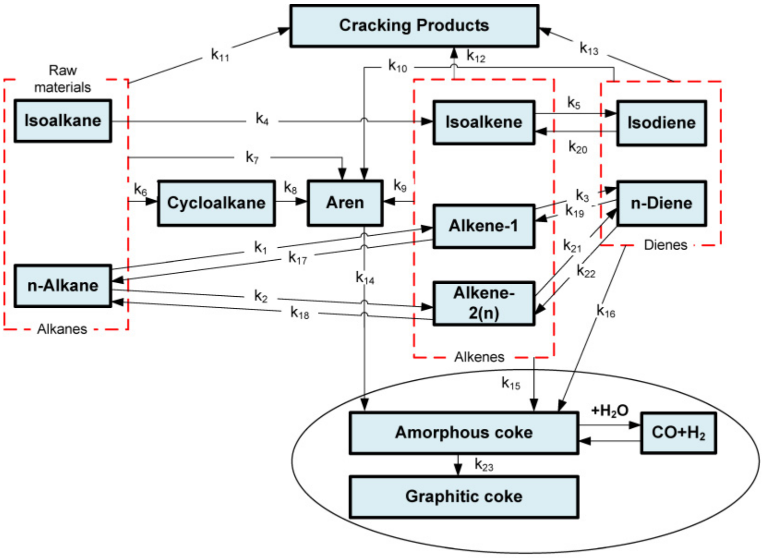


Fig. 1. The formalized reaction network of the dehydrogenation process with reversible oxidation of amorphous coke by water

The coke concentration on the catalyst is calculated according to developed transformation formalized scheme as a reaction product of the aromatic and diene hydrocarbons (Figure 1)[12].

The performed numerical and experimental-industrial research in cooperation with technologists of LLC "KINEF" allowed developing a method for calculating optimal water flow on the basis of experimental and literature data on the structure of amorphous coke deposited on the surface of Pt-catalyst, the thermodynamic analysis of the coking process as well as using the mathematical model of the dehydrogenation process[14]. This methodology is based on the need to maintain the constant conversion of the amorphous coke by water over the entire process temperature range.

Thermodynamic analysis of the process showed that the reaction of coke formation from aromatic and diene hydrocarbons occurs in both forward and reverse directions, and it is important to determine the conditions under which the equilibrium is shifted towards lower molecular weight products.

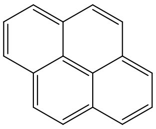
One needed to evaluate the thermodynamic probability of reactions at a working temperature 743-763 K and pressure 0.2 MPa.

The main problem in these calculations was the need to determine the thermodynamic parameters of the reactions involving various polyaromatic structures formed during the coking and the lack of experimental data in this area. However, in the research[15] the basic thermodynamic properties of these substances were defined by Benson for various structures of pyrene, naftalino-pyrene and coronen series.

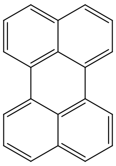
For the calculation of each series the following structure were chosen (Figure 2):

Pyrene series:

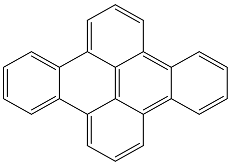
$C_{16}H_{10}$



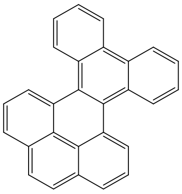
$C_{20}H_{12}$



$C_{24}H_{14}$



$C_{28}H_{16}$



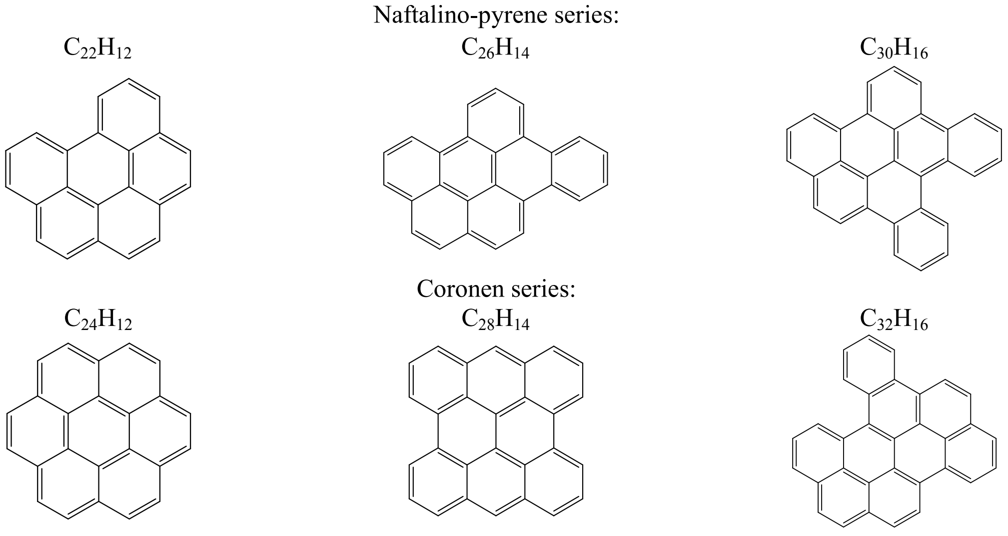


Fig. 2. The structure of coke compounds

Then, calculation of the thermodynamic parameters of the reactions of hydrogenation and oxidation was performed for each structure at operating temperature 755 K. The results of calculations for the thermodynamically possible reactions are listed in Tables 1, 2.

Tables 1 and 2 provide the hydrogenation reaction and the oxidation of 1 mole of coke submitted the relevant structure (Initial Structure), to the products listed in the first column (Product) of these tables.

Table 1. Gibbs energy of hydrogenation, kJ/mol

Initial Structure Product	$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$
CH_4	-696.6	-828.5	-681.8	-975.3	-843.7	-1047	-488.5	-887.3	-998.6	-1295.0
C_2H_4	-14.6	23.8	340.9	217.9	93.8	60.5	789.9	135.4	194.7	68.8
C_3H_4	-77.8	-55.2	246.2	107.4	6.9	-42.1	671.5	40.6	84.0	-57.5
C_6H_6	-205.0	-214.2	55.3	-115.2	-167.9	-248.9	432.9	-150.2	-138.6	-312.0
C_7H_8 (toluene)	-76.8	-53.9	247.7	109.2	8.4	-40.5	673.4	42.2	85.9	-55.5
$C_{10}H_8$ (naphthalene)	-207.9	-217.7	51.1	-120.2	-171.9	-253.5	427.6	-154.4	-143.5	-317.6
$C_{14}H_{10}$ (phenanthrene)	-61.6	-34.9	270.5	135.8	29.3	-15.8	701.9	64.9	112.5	-25.1
$C_{14}H_{10}$ (anthracene)	-38.2	-5.7	305.5	176.7	61.4	22.2	745.7	100.0	153.3	21.6
$C_{16}H_{34}$ (hexadecane)	-82.2	-60.6	239.6	99.7	0.9	-49.2	663.3	34.1	76.5	-66.3

Table 2. Gibbs energy of oxidation, kJ/mol

Initial Structure Product	$C_{16}H_{10}$	$C_{20}H_{12}$	$C_{24}H_{14}$	$C_{28}H_{16}$	$C_{22}H_{12}$	$C_{26}H_{14}$	$C_{30}H_{16}$	$C_{24}H_{12}$	$C_{28}H_{14}$	$C_{32}H_{16}$
CO	-526.6	-616.1	-426.9	-677.9	-610.0	-771.4	-169.9	-632.5	-701.2	-955.1
CO_2	-1933.0	-2375.0	-2537.0	-3140.0	-2544.0	-2954.0	-2808.0	-2743.0	-3163.0	-3769.0

As the calculations of the Gibbs energy have shown: 1) hydrogenation of polyaromatic structures at operating temperature are thermodynamically possible; 2) hydrogen saturation of polyaromatic structures leads to the formation of less saturated structure; 3) process for the hydrogenation and oxidation of methane to CO or to CO_2 is thermodynamically most probable.

As shown in Tables 1, 2, many types of reactions are characterized by small absolute value of the Gibbs energy, which indicates the possibility of their occurrence in both the forward and reverse directions. Of particular interest are the reactions involving hexagonal structures that are most relevant to the amorphous coke (because they have C:H relations in the range from 0.67 to 0.78). This suggests the possibility of achieving a balance between the formation of intermediate cokes structures and their hydrogenation.

In this paper, we have made the assumption that the surface of the dehydrogenation catalyst is covered by deposited coke, the structure of which is similar to the coronene structure.

The next stage of the study was to consider the possibility of the oxidation reaction of amorphous coke with water taking into account that the amorphous coke has empirical formula $C_{28}H_{14}$ and a structure similar to the structure of coronene[14].

For the reaction $C_{28}H_{14} + 28H_2O = 28CO + 35H_2$, the thermodynamic parameters of the process at temperature 480°C (753K) were calculated (ΔG_r = -50.84 kJ/mol, ΔH_r = 145 kJ/mol, ΔS_r = 0.26 kJ/(mol K). The value obtained for the free energy (ΔG_r =-50.84 kJ/mol) suggests that this reaction is thermodynamically feasible under the given operating conditions of the dehydrogenation process.

These features of change in the conversion of amorphous coke in its oxidation reaction with water formed the basis for an applied procedure that makes it possible to calculate the optimal rate of water supply to the reactor depending on the temperature and degree of catalyst deactivation.

The essence of the procedure is as follows. First of all the concentrations of the products were calculated according to the scheme of transformations proposed above using the software implemented kinetic model of the dehydrogenation process. Coke with the amorphous structure is formed from aromatic and diene hydrocarbons. Taken as initial data in this case the composition of the feedstock hydrocarbon mixture was supplied to the dehydrogenation reactor. Then, depending on the coke concentration, the number of moles of water needed to maintain the equilibrium of the oxidation reaction according to Eq. (1) was calculated. The equilibrium constant was calculated from the thermodynamic parameters of the reaction by Eq. (1).

The equation relating the equilibrium degree of conversion to the equilibrium constant of the reaction is as follows[10-15]:

$$K_p = \frac{P_{CO}^{28} P_{H_2}^{35}}{P_{H_2O}^{28}} = \frac{P_{tot}^{35} x_{CO}^{28} x_{H_2}^{35}}{x_{H_2O}^{28}} = \frac{P_{tot}^{35} n_{CO}^{28} n_{H_2}^{35}}{n_{H_2O}^{28}} \frac{1}{n_{tot}^{35}}.$$

x is the mole fraction of a component in the mixture

$$K_p = \frac{P_{tot}^{35} n_{CO}^{28} n_{H_2}^{35}}{n_{H_2O}^{28}} \frac{1}{n_{tot}^{35}} = \frac{P_{tot}^{35} (n'_{H_2O} a)^{28} (1.25 n'_{H_2O} a)^{35}}{n'_{H_2O}(1-a))^{28}}.$$

$$\frac{1}{(n'_{H_2O} a + 1.25 n_{H_2O} a + n'_{H_2O}(1-a))^{35}} = \frac{a^{63} 1.25^{35}}{(1-a)^{28}} \cdot \frac{P_{tot}^{35}}{(1.25a+1)^{35}},$$

a is the conversion of the process or the degree of conversion in fractions of unity, n_{H2O} is the initial number of moles of water.

In developing techniques were assumed constant concentrations of CO and H2 in the exhaust gases of the reactor due to their low concentrations and the inability to measure.

Equating the equilibrium constant expressed in terms of ΔG with the equilibrium ratio of the mole fractions of the components, we get:

$$K_{ip} = \frac{P_{tot}^{35} \cdot n_{1H_2O}^{63} \cdot x_1^{63} \cdot 1.25^{35}}{(n_{iH_2O} \cdot (1 - x_i))^{28}} \times \frac{1}{(2.25 n_{1H_2O} \cdot x_1 + n_{iH_2O}(1 - x_i))^{35}}$$

$$K_{ip} = \exp(-\frac{\Delta G}{RT_i})$$

$$\frac{P_{tot}^{35} \cdot n_{1H_2O}^{63} \cdot x_1^{63} \cdot 1.25^{35}}{(n_{iH_2O} \cdot (1 - x_i))^{28}} \times \frac{1}{(2.25 n_{1H_2O} \cdot x_1 + n_{iH_2O}(1 - x_i))^{35}} = \exp(-\frac{\Delta G}{RT_i})$$

n1 - the initial number of moles of water, mol (when i=1);

x1 - the initial coke conversion (when i=1).

The equilibrium constant of the coke conversion reaction were calculated for the operating temperature range of 723 to 773 K. The calculation results show that as the temperature increases, the conversion of the amorphous coke-generating entity by water increases, the relation is due to the endothermic nature of this reaction. Thus, the conversion is 20.70% at temperature 723 K and 21.45% at 773 K. The conversion is obviously limited by thermodynamic equilibrium at certain pressure and temperature. The optimal feed flow rate of water in the dehydrogenation reactor maintains stable equilibrium of the oxidation reaction of coke-generating compounds with water. When the process temperature is elevated, it is necessary to increase the water flow rate to ensure a constant conversion of the reaction at the level of about 20%.

$$\begin{cases} \dfrac{K_{i+1}}{K_i} = \left(\dfrac{n^*_{\mathrm{CO}(i+1)}}{n^*_{\mathrm{CO}(i)}} \right)^{63} \cdot \left(\dfrac{n_{i\mathrm{H_2O}} - n^*_{\mathrm{CO}(i)}}{n_{\mathrm{H_2O}(i+1)} - n^*_{\mathrm{CO}(i+1)}} \right)^{28} \cdot \left(\dfrac{n_{i\mathrm{H_2O}} + 1,25 n^*_{\mathrm{CO}(i)}}{n_{\mathrm{H_2O}(i+1)} + 1,25 n^*_{\mathrm{CO}(i+1)}} \right)^{35} = 1 \\ K_p = -\dfrac{(\Delta H_r - T \cdot \Delta S)}{RT} \end{cases} \quad (2)$$

Quantitatively, the optimum moisture content in the system can be calculated in terms of the displacement condition by the temperature of equilibrium in the oxidation of intermediate amorphous CGCs with water according to the following equations:

where K_p - the equilibrium constant at T, Pa; T - the temperature of the process, K; R = 8.31 J/(mol K) - the gas constant; ΔG - the free energy change of the reaction at a temperature T, J/mol; ΔH_r - the enthalpy change of the reaction at a temperature T, J/mol; ΔS - the entropy change of the reaction at a temperature T, J/(mol K); K_{i+1} - the equilibrium constant at T_{i+1}, Pa^{21}; K_i - the equilibrium constant at T_i, Pa^{21}; $n_{H_2O(i+1)}$ - the initial amount of H_2O at T_{i+1}, mol; n_{iH_2O} - the initial amount of H_2O at T_i, mol; $n^*_{CO(i+1)}$ - the equilibrium amount of CO at T_{i+1}, mol; $n^*_{CO(i)}$ - the equilibrium amount of CO at T_i, mol; ($n_{H_2O(i+1)}$ - $n^*_{CO(i+1)}$) - the equilibrium amount of H_2O at T_{i+1}, mol; (n_{iH_2O} - $n^*_{CO(i)}$) - the equilibrium amount of H_2O at T_i , mol; ($n_{H_2O(i+1)}$ + 1.25$n^*_{CO(i+1)}$) - the equilibrium amount of H_2 at T_{i+1}, mol; (n_{iH_2O} +1.25$n^*_{CO(i)}$) - the equilibrium amount of H_2 at T_i, mol.

This relationship enabled us to develop practical guidance for various schedules of water feed to the dehydrogenation reactor depending on the feedstock composition, the degree of catalyst deactivation, and the process temperature.

However, in case of dehydrogenation catalyst operation under low molar ratio of hydrogen / feedstock it is necessary to adjust water flow chart in the reactor in connection with the increase in the intensity of coke formation reactions. To assess the performance of the dehydrogenation process under reduced molar ratio of hydrogen/feedstock, the industrial experiment was carried out at LLC "KINEF" enterprise.

3. Experimental part

Analyzing the experimental data from the industrial plant during its operation at the end of the cycle 2013-2014, when the molar ratio of hydrogen/feed was reduced from 7/1 to 6/1 (from 11 to 16 April 2014), we can conclude that the reduction of the HCG circulation rate allows for increasing the yield of olefins by shifting the equilibrium of the dehydrogenation reaction of the target in the direction of product formation (Table 3).

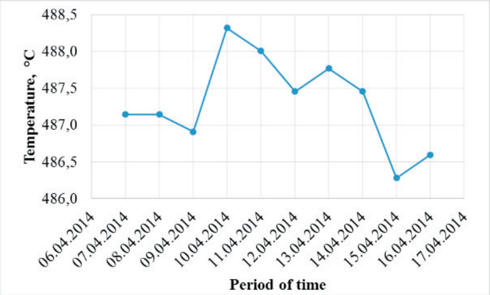


Figure 3. The inlet temperature in the dehydrogenation reactor during operation of the plant in the cycle 2013-2014. (07.04.14-17.04.14)

Table 3. Experimental data on the operation of the plant during the period from March 30 to April 16, 2014

Date	Consumption of LAB, m^3/h	Olefine yeild, wt. %
30.03.14	8.543	8.993
31.03.14	8.569	9.019
01.04.14	8.475	8.92
02.04.14	8.532	8.978
03.04.14	8.696	9.153
04.04.14	8.471	8.916
05.04.14	8.392	8.833
06.04.14	8.669	9.124
07.04.14	8.482	8.929
08.04.14	8.437	8.881
09.04.14	8.486	8.932
10.04.14	8.500	8.947
11.04.14	8.829	9.292
12.04.14	8.299	8.735
13.04.14	8.559	9.009
14.04.14	8.062	8.486
15.04.14	9.002	9.477
16.04.14	8.176	8.606

As is seen from the results, during operation of the dehydrogenation catalyst at molar ratio H_2/feed = 6/1 (HCG Hydrogen concentration decreased to about 84-85 %) at the cycle end (at sufficiently high temperature 760-761 K, Figure 3.) the olefin concentration increased to 9.2-9.5 wt. % (Table 3).

Analysis of the experimental data on the flow of dehydrogenation gases showed that reducing the molar ratio of hydrogen/hydrocarbon feed at nealy constant water supply (about 12 l/h) led to the enhancement of the cracking reactions (Figure 4) at the beginning of experimental runs (under strict conditions, at high temperature cracking with C_1-C_4 gases formation enhanced, at the end of experiment run with decreasing temperature the rate of cracking reactions decreases, and the production of LAB remains high enough (Table 3), indicating the positive effect of reducing the molar ratio with respect to H_2/feed yield.

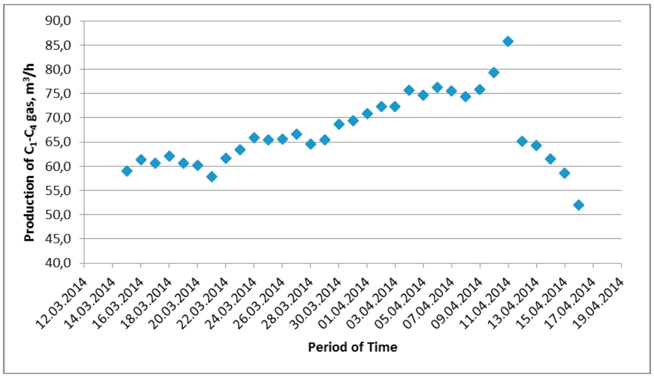


Figure 4. Production of C_1-C_4 gas

4. Modelling Results

The experimental data on the composition of the feedstock and the operating conditions of the dehydrogenation reactor at different ratios of hydrogen/feed were used as a starting material for carrying out calculations by means of the mathematical model.

Results of calculations allowed developing recommendations for optimization water flow in the dehydrogenation reactor during operation of the plant at a reduced molar ratio and performing calculations to determine the life of the Pt- catalyst in the different operation modes (Table 4) for the processing of different composition of the feedstock (Table 5).

Table 4. Expected service life of the dehydrogenation catalyst (olefine concentration 8.5–9.0 %)

	Molar rate H_2/feed = 6:1 (181-186 t LAB/day)	Molar rate H_2/feed = 7:1 (170-174 t LAB/day)
Feed 1	250– 290 days	380 – 400 days
Feed 2	230– 270 days	330– 360 days

Table 5. Raw material composition of the dehydrogenation process

Components (wt. %)	Feed 1	Feed 2
Nonane C_9H_{20}	0.01	0.00
Decane $C_{10}H_{22}$	15.62	16.18
Undecane $C_{11}H_{24}$	28.48	31.10
Dodecane $C_{12}H_{26}$	28.79	30.99
Tridecane $C_{13}H_{28}$	22.68	17.78
Tetradecane $C_{14}H_{30}$	0.48	0.37
Aromatics	1.37	1.30
Isoparaffine	2.57	2.28

The obtained results showed that in processing the same feed type at the decrease in molar H_2/feed ratio the catalyst deactivation by coke considerably increases. One can partially compensate it by increasing the supplied water flow to the reactor to 13-14 l/h instead of 9-10 l/h at the end of cycle.

It should be noted that in the first 80-200 days of catalyst operation the inlet temperature of the dehydrogenation reactor at a molar ratio H_2/feed = 6/1 was lower by 1-2 ºC than at H_2/feed = 7/1, since reduction of HCG circulation rate promotes the shift of dehydrogenation reaction equilibrium towards the products.

Hereafter, at temperature 475 ºC or above catalyst coking reactions predominate that leads to decrease in the yield of olefins that can be compensated by increase in temperature.

Obviously, reducing the life of the catalyst to 270-290 days (Table 4) even at the increased water flow is determined by the intensity of the coking reactions. However, the economic feasibility of catalyst operation in such conditions causes a considerable increase in production of LAB to 181-186 t/day.

Maintaining sufficient concentration of hydrogen in the HCG may be provided by a 'floating' work schedule of installation at low temperatures (up to 475 ºC) - operation at reduced molar, but increasing temperature and water flow - the transition to the molar ratio H_2/feed = 7/1 for hydrogen reconcentration to 90 vol. %.

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