UDC 66.011/66.012:662.765

SOLUTION OF THE PROBLEMS OF NON-STATIONARITY PROCESSES IN ETHYLENE REGION OF A CHEMICAL TECHNOLOGICAL COMPLEX ON PROCESSING THE CRACKING AND PYROLYSIS GASES

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Received 14.03.2019

Dynamics of the processes in the greatest – ethylene region of chemical-technological complex has been studied, the functions taking into account non-stationarity of the processes has been chosen, their dynamic kinetic model were constructed, and on the basis of entire mathematical descriptions there have been decided the tasks of their optimal control. This in result enabled to fulfill the goal to be achieved – to maintain the optimum production capacity of the target products found out at optimization of chemical-technological complex for stationary conditions of their proceeding.

Keywords: *non-stationarity, functions of deactivation, of control, productivity capacity, dynamics, catalyst, activity, block-flowsheet, cracking and pyrolysis gases.*

<https://doi.org/10.32737/0005-2531-2019-3-75-83>

Introduction

To answer the Republics demands olefins obtained from cracking and pyrolysis gases from BNZ named after H.Aliyev and equipment EP-300 of Sumgait plant Ethylene-Polyethylene and their rational using in the Institute of Catalysis and Inorganic Chemistry, named after M.Nagiev, Azerbaijan National Academy of Sciences there have been developed the chemical-technological complex (CTC) on co-processing of these gases. Functioning of such CTC will permit to achieve the needed productivity capacity of the target products, the Republic demands, will minimum expenditures Calculation of the processes entering CTC has been made by mathematical models constructed for stationary conditions of their proceeding. However, the processes considered in CTC, both catalytic and non-catalytical, often take place in conditions of non-stationarity caused by various reasons [7]. Depending on conclusions of running the processes, change in their activity in time occurs differently decreasing reactors production activity, term of catalysts operation, selectivity of the process.

Our task consists in that data on optimal productivities capacity of the target products obtained at optimization of an entire CTC and meeting the Republics need in them, would be destroyed because of possible non-stationarity of the processes. This can be provided by introducing into the kinetic models of stationary processes the

corresponding functions of non-stationarity, and on their basis to operate them by the entire mathematical models of the processes, each taken separately.

Fulfillment of work

Based on work done the article offers the flow sheet of these basic actions which were implemented for each process of the region for obtaining demanded results, namely:

1. design of a stoichiometric flowsheet of the process on the basis of experimental data;
2. working out the kinetic models of the process on the basis of stoichiometric flow sheet;
3. making up complete mathematical model of the process for stationary conditions on the basis of kinetic model and studying heat and hydrodynamic conditions in a reactor;
4. choice of the functions of process non-stationarity based on studying its reasons;
5. receiving dynamic mathematical model of the process;
6. working out algorithm of operating the process using non-stationary mathematical description;
7. obtaining results of operating the process in non-stationary conditions.

Below there are cited the results of the successive fulfillment of suggested scheme for the concrete processes of ethylene region in CTC. The regime parameters of the process and designations to them are offered in references corresponding to each process.

Pyrolysis of ethane [1, 2]

1. Stoichiometric scheme of the process

2. Stationary kinetic model

$$\begin{aligned}
 \frac{dn_{\text{C}_2\text{H}_6}}{dl} &= -u^{-1} \left[k_1 n_{\text{C}_2\text{H}_6} + k_7 n_{\text{C}_2\text{H}_6} n_{\text{C}_2\text{H}_4} P / RT \sum_i n_i - (k_1 / K_{p1}) n_{\text{C}_2\text{H}_4} n_{\text{H}_2} P / RT \sum_i n_i \right], \\
 \frac{dn_{\text{C}_2\text{H}_4}}{dl} &= u^{-1} n_{\text{C}_2\text{H}_4} \left\{ k_1 n_{\text{C}_2\text{H}_6} / n_{\text{C}_2\text{H}_4} - (k_1 / K_{p1}) n_{\text{H}_2} P / RT \sum_i n_i - k_2 \left[n_{\text{H}_2} P / RT \sum_i n_i \right]^2 + (k_1 / K_{p2}) \times \right. \\
 &\quad \left. \times (n_{\text{C}_2\text{H}_4}^2 / n_{\text{C}_2\text{H}_4}) P / RT \sum_i n_i - k_3 - k_4 - k_5 - k_6 - k_7 n_{\text{C}_2\text{H}_6} P / RT \sum_i n_i \right\}, \\
 \frac{dn_{\text{H}_2}}{dl} &= u^{-1} \left[k_1 n_{\text{C}_2\text{H}_6} + (k_2 / K_{p2}) n_{\text{C}_2\text{H}_4}^2 P / RT \sum_i n_i + n_{\text{C}_2\text{H}_4} \left[- (k_1 / K_{p1}) n_{\text{H}_2} P / RT \sum_i n_i - \right. \right. \\
 &\quad \left. \left. - 2k_2 \left(n_{\text{H}_2} P / RT \sum_i n_i \right)^2 + 1/8 k_3 + k_4 + k_5 + 2k_6 + (93/150) k_7 n_{\text{C}_2\text{H}_6} P / RT \sum_i n_i \right] + \right. \\
 &\quad \left. + n_{\text{H}_2\text{O}} P (k_8 n_{\text{C}} + k_9 n_{\text{CO}}) / RT \sum_i n_i \right], \\
 \frac{dn_{\text{CH}_4}}{dl} &= 2k_2 u^{-1} \left[n_{\text{C}_2\text{H}_4} \left(n_{\text{H}_2} P / RT \sum_i n_i \right)^2 - (1/K_{p2}) \left(n_{\text{CH}_4} P / RT \sum_i n_i \right)^2 \right], \\
 \frac{dn_{\text{C}_4\text{H}_6}}{dl} &= (1/4) u^{-1} k_3 n_{\text{C}_2\text{H}_4}, \quad \frac{dn_{\text{C}_4\text{H}_8}}{dl} = (1/8) u^{-1} k_3 n_{\text{C}_2\text{H}_4}, \quad \frac{dn_{\text{C}_4\text{H}_{10}}}{dl} = (1/8) u^{-1} k_3 n_{\text{C}_2\text{H}_4}, \quad \frac{dn_{\text{C}_6\text{H}_6}}{dl} = (1/3) u^{-1} k_4 n_{\text{C}_2\text{H}_4},
 \end{aligned} \tag{2}$$

$$\begin{aligned}
dn_{C_2H_2}/dl &= u^{-1}k_5n_{C_2H_4}, \quad dn_C/dl = u^{-1}\left(2k_6n_{C_2H_4} - k_8n_Cn_{H_2O}P/RT \sum_i n_i\right), \\
dn_{C_3H_6}/dl &= (143/150)u^{-1}k_7n_{C_2H_4}n_{C_2H_6}P/RT \sum_i n_i, \\
dn_{C_3H_8}/dl &= (57/150)u^{-1}k_7n_{C_2H_4}n_{C_2H_6}P/RT \sum_i n_i, \\
dn_{CO}/dl &= u^{-1}n_{H_2O}P(k_8n_C - k_9n_{CO})/RT \sum_i n_i, \\
dn_{CO_2}/dl &= u^{-1}k_9n_{CO}n_{H_2O}P/RT \sum_i n_i.
\end{aligned}$$

3. Equation of heat balance and hydrodynamics $g_{C_2H_4}^{nonst} \sim g_{C_2H_4}^{nonst}$

$$\frac{dT}{dL} = \frac{\pi d_H q - \sum_j r_j \Delta H_{Rj}}{\sum_i \left(\frac{g_{C_2H_6}^0}{\bar{M}} \sum_i \alpha_i' + \sum_i \Delta n_i \right) C_{pi}}; \quad (3)$$

$$\frac{dP}{dL} = -2160.4 \cdot 10^{-13} \left(1 + \frac{30d_B}{L_0} \right) \frac{g_{C_2H_6}^0}{P_0 d_{ins}^5}. \quad (4)$$

4. Account of the process non-stationarity

Equation of cokeformation rate:

$$r_C = \frac{dC}{d\tau} = k_1 \cdot C_4^+ = k_{01} \exp\left(-\frac{E_1}{RT}\right) \cdot C_4^+ \quad (5)$$

increase in coke thickness for time break $\Delta\tau$:

$$\Delta t_c = \frac{r_C \Delta\tau}{\rho_C}; \quad (6)$$

change of pipe diameter as a result of coke deposit:

$$\Delta d_{ins} = d_{ins}^0 - d_{ins}^f = 2 \cdot \Delta t_C \quad (7)$$

5. Equation of pressure loss in dynamic conditions:

$$\frac{dP}{dL} = -2160.4 \cdot 10^{-13} \left(1 + \frac{30d_{ins}^f(\tau)}{L_0} \right) \frac{g_{C_2H_6}^0}{P_0 (d_{ins}^f(\tau))^5}. \quad (8)$$

6. Function of control:

– regressive dependences of ethylene yield on time of stove work $\tau(X_1)$, reactor leading $g_{C_2H_6}^0(X_2)$ and change of pressure in it $\Delta P(X_3)$:

$$Y_{cal} = 0.1094X_1 + 0.4853X_2 - 316.1281X_3 \quad (9)$$

$$\bar{Y}_{cal} = -5646 + 21.24Y_{cal} - 0.02295Y_{cal}^2 + 8.256 \cdot 10^{-6}Y_{cal}^3. \quad (10)$$

The system of equations (2), (3), (8) with account of (9), (10) is a complete mathematical model of the process for non-stationary conditions.

Block-scheme of process operation in non-stationary conditions:

7. Results of calculation:

Table 1. The course and results of calculation of non-stationary process of ethane pyrolysis

Time τ , h, X_1	Load of reactor $g_{C_2H_6}^0$, kg/h, X_2	Change of pressure ΔP , atm, X_3	Decreasing of inner diameter Δd_{ins} , m	Final diameter, d_{ins}^f , m	Thickness of coke deposit, Δt_c , mm	Pressure at inlet to reactor, P_0 , atm	Pressure at outlet from reactor, P_f , atm	Yield of ethylene $g_{C_2H_4}^{exs}$, Y_{exs}	Yield of ethylene $g_{C_2H_4}^{cal}$, $Y_{cal}^{(5)}$	Relative error $\frac{(Y_{exs} - Y_{cal}^{(5)})}{Y_{exs}} \cdot 100\%$	Yield of ethylene $g_{C_2H_4}^{cal}$, $\bar{Y}_{cal}^{(6)}$	Relative error $\frac{(Y_{exs} - \bar{Y}_{cal}^{(6)})}{Y_{exs}} \cdot 100\%$
100	2504	0.904	0.00424	0.1280	2.12	3.245	2.341	900.14	940.35	-4.46	898.3	0.2073
200	2510	1.088	0.00898	0.1232	4.50	3.253	2.165	901.1	896.04	0.56	899.1	0.217
300	2526.8	1.252	0.01274	0.1195	6.40	3.274	2.022	899.5	863.28	4.02	898.1	0.1536
400	2619.3	1.438	0.01605	0.1162	8.02	3.395	1.958	900	860.31	4.41	897.9	0.235
500	2993.8	1.922	0.02030	0.1119	10.20	3.878	1.956	901.13	899.99	0.12	899.1	0.2226
600	3057.6	2.018	0.02410	0.1081	12.05	3.970	1.952	900.46	911.55	-1.23	899	0.1669
700	3086.4	2.05	0.02950	0.1027	14.75	4.000	1.950	900.61	926.35	-2.86	898.6	0.2222

Yield of ethylene is maintained at demanded stationary level (≈ 900 kg/h) and limit for end pressure is not destroyed.

Ethylene polymerization [3]

1. Stoichiometric scheme of the process

2. Stationary kinetic model:

$$\frac{dx}{dt} = \left[-A_R [M]_0 \exp\left(-\frac{b_1}{T}\right) \cdot Ty^{1/2} \right], \quad (12)$$

$$\frac{dy}{dt} = -A_I [M]_0 \exp\left(-\frac{b_2}{T}\right) y. \quad (13)$$

3. Equation of heat balance

$$\frac{dT}{dt} = -a_3 \exp\left(-\frac{b_1}{T}\right) xy^{1/2} + a_4 (T - T_0), \quad (14)$$

$$x = [M]/[M]_0,$$

$$y = [I]/[M]_0,$$

$$b_1 = -(E_R + \Delta V \Delta p)/R,$$

$$b_2 = E_I/R;$$

$$a_3 = A_R [M]_0 Q_R;$$

$$a_4 = -4K/\pi d_{ins}^2 C_p \rho$$

4. Function of non-stationarity

$$\theta = e^{-\left(Ae^{\frac{E_{in}}{RT}}\right) t_R \cdot b \cdot F_{C_2H_4}}, \quad (15)$$

5. Dynamic kinetic model (equations (16) and (13))

$$\frac{dx}{dt} = \left[-A_R [M]_0 \exp\left(-\frac{b_1}{T}\right) \cdot Ty^{1/2} \right] \cdot \theta. \quad (16)$$

The system of equation (16), (13), (14) with account of (15) is a complete kinetic model of the process for non-stationary conditions.

6. Block-scheme of process operating in non-stationary conditions:

7. Results of calculation

In case productivities of polyethylene don't agree with its stationary value the process is regulated by change of value θ on the account of change in turn of amount of ethylene $g_{C_2H_4}$ and initiator g_{in} , passed into polymerizator.

Direct hydration of ethylene [4]

1. Scheme of forming ethyl alcohol

2. Stationary kinetic model of the process

$$\frac{dn}{dt} = \frac{k'}{\left(\frac{n_{H_2O}^0 - n}{n_{C_2H_4}^0 + n_{H_2O}^0 - n} P \right)^{\frac{1}{2}}} \cdot \left(\frac{n_{C_2H_4}^0 - n}{n_{C_2H_4}^0 + n_{H_2O}^0 - n} P - K_{eq}^{-1} \frac{n}{n_{H_2O}^0 - n} \right) \cdot \frac{(n_{C_2H_4}^0 + n_{H_2O}^0 - n)^2}{P(n_{C_2H_4}^0 + n_{H_2O}^0 - n)} \quad (18)$$

3. Equation of heat balance and pressure loss:

$$\frac{4}{\rho_{cat} \pi D^2} \frac{dT}{dl} = - \frac{\sum r \Delta H_R}{\sum_{i=1}^3 n_i C_{pi}} - Q_h, \quad (19)$$

$$\frac{dP}{dl} = - \left(\frac{150}{Re} + 1.75 \right) \frac{\rho_{gas} u_0^2 (1 - \epsilon)}{d_p g \epsilon^3} \cdot 0.987 \cdot 10^{-5}. \quad (20)$$

3. Function of operation:

$$1) \theta = \frac{G_{cur}}{G_{init}} \quad (\text{without additions of phosphorus acid}); \quad (21)$$

$$\theta' = \frac{G_{cur} + G_{add}}{G_{init}} = \frac{G'_{cur}}{G'_{init}} \quad (\text{with additions of phosphorus acid}) \quad (22)$$

4. Dynamic kinetic model:

$$\frac{dn}{dt} = \frac{k' \cdot \theta}{\left(\frac{n_{H_2O}^0 - n}{n_{C_2H_4}^0 + n_{H_2O}^0 - n} P \right)^{\frac{1}{2}}} \cdot \left(\frac{n_{C_2H_4}^0 - n}{n_{C_2H_4}^0 + n_{H_2O}^0 - n} P - K_{eq}^{-1} \frac{n}{n_{H_2O}^0 - n} \right) \times \frac{(n_{C_2H_4}^0 + n_{H_2O}^0 - n)^2}{P(n_{C_2H_4}^0 + n_{H_2O}^0 - n)}. \quad (23)$$

6. Regressive dependence of the current value of phosphorus acid on time:

$$y = G_{cur} = f(\tau) = 0.001\tau^2 - 2.328\tau + 6543. \quad (24)$$

The system of equations (23), (17), (20) with account of (21–24) is a complete non-stationary mathematical model.

Output of ethyl alcohol is maintained at stationary level with loss expenditures for consumption of phosphorus acid (291.6 in proposed method against 637.5 – in industrial one).

As the results of operating the processes N 1, 2 and 3, the use of own function of non-stationarity chosen for every process, permitted to preserve productivities of the purpose products at optimum, stationary level found out at optimization of entire CTC.

7. Results of calculation:

Table 2. Comparison of results of calculating hydration process in industrial and proposed ways of its implementation

Industrial way					Proposed way		
Time breaks of catalyst work	Rate of removing phos. acid kg/h	Amount of removed phos. acid for every 50 hours, kg	Current amount of phos. acid G_{cur} , kg	Control function (without additions) $\theta = \frac{G_{cur}}{G_{init}}$	Additions of phos. acid G_{add} , kg	Current amount of phos. acid $G_{cur}^1 = G_{cur} + G_{add}$, kg	Control function (with additions) $\theta = G_{cur}^1 / G_{init}^1$
0	0	0	6534	1	–	–	–
0–50	2.00	100	6434	0.9847	–	–	0.985
50–100	1.95	97.5	6336.5	0.9698	66.8	6403.3	0.98
100–150	1.9	95.0	6241.5	0.9552	–	–	0.98
150–200	1.8	90	6151.5	0.9415	58.3	6209.8	0.961
200–250	1.7	85	6066.5	0.9285	–	–	0.98
250–300	1.4	70	5996.5	0.9177	89.1	6085.6	0.966
300–350	1.2	60	5936.5	0.9086	–	–	0.98
350–400	1.0	50	5886.5	0.9009	77.4	5963.9	0.967
400–450	0.8	40	5846.5	0.8947	–	–	0.98
450–500	0.2	10	5836.5	0.8932	–	–	0.98
		$\Sigma 697.5$			$\Sigma 291.6$		

Oxidative conversion of ethyl alcohol into vinegar acid [5]

1. Stoichiometric scheme of the process

2. Stationary kinetic model of the process:

$$\frac{N_1^0}{\rho_{\text{cat}}} \cdot \frac{\pi D^2}{4} \frac{dA_1}{dl} = \frac{k_3 b_1 b_3 P_1 P_4}{N_1^0 (1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5)^2}$$

$$\frac{N_1^0}{\rho_{\text{cat}}} \cdot \frac{\pi D^2}{4} \frac{dA_2}{dl} = \frac{k_2 b_2 \sqrt{P_2} b_4 P - k_3 b_1 b_3 P_1 P_4}{N_1^0 (1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5)^2} \quad (26)$$

$$\frac{N_1^0}{\rho_{\text{cat}}} \cdot \frac{\pi D^2}{4} \frac{dA_3}{dl} = \frac{k_1 b_1 b_2 P_1 \sqrt{P_2} - k_2 b_2 \sqrt{P_2} b_4 P_5 - k_4 b_4 P_5 P_2 (1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5)}{N_1^0 (1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5)^2}$$

$$\frac{N_1^0}{\rho_{\text{cat}}} \cdot \frac{\pi D^2}{4} \frac{dA_4}{dl} = \frac{2k_4 P_2 b_4 P_5}{N_1^0 (1 + b_1 P_1 + b_2 \sqrt{P_2} + b_3 P_4 + b_4 P_5)}$$

3. Equation of heat balance and pressure losses:

$$\frac{N_1^0}{\rho_k} \cdot \frac{\pi D^2}{4} \frac{dT}{dl} = - \frac{\sum_{j=1}^4 r_j \Delta H_{Rj}}{\sum_{i=1}^8 n_i C_{pi}} - \frac{\alpha(T - T_r)}{\sum_{i=1}^8 n_i C_{pi}}, \quad (27)$$

$$\frac{dP}{dl} = - \left(\frac{150}{\text{Re}} + 1.75 \right) \cdot \frac{\rho_{\text{gas}} u_0^2 (1 - \varepsilon)}{d_p g \varepsilon^3} \cdot 0.987 \cdot 10^{-5} \quad (28)$$

Etherification of vinegar acid by ethyl alcohol [5]:

1. Stoichiometric scheme of the process;

2. Stationary kinetic model of the process;

$$\frac{N_1^0}{\rho_{\text{cat}}} \cdot \frac{\pi D^2}{4} \frac{dX}{dl} = \frac{k b_1 b_2 P^2 (1 - X)(\varphi - X)}{N_1^0 (1 + b_1 \frac{1 - X}{1 + \varphi} P + b_2 \frac{\varphi - X}{1 + \varphi} P)^2 (1 + \varphi)^2}$$

3. Equation of heat balance and pressure losses:

$$\frac{4}{\rho_{\text{cat}} \pi D^2} \frac{dT}{dl} = - \frac{\Delta H_R N_1^0 \frac{4}{\rho_{\text{cat}} \pi D^2} \frac{dX}{dl} + \alpha(T - T_r)}{(C_{p1} n_1 + C_{p4} n_4 + C_{p3} n_3 + C_{p7} n_7)}; \quad (30)$$

$$\frac{dP}{dl} = - \left(\frac{150}{\text{Re}} + 1.75 \right) \frac{\rho_{\text{gas}} u_0^2 (1 - \varepsilon)}{d_p g \varepsilon^3} \cdot 0.987 \cdot 10^{-5}. \quad (31)$$

Results of calculation the optimum out pus have been found out on the purpose products of two letter processes. As the processes of oxidative conversion of ethyl alcohol into vinegar acid and esterification of vinegar acid by ethyl alcohol within 50 hours of a catalysts work of clinoptilolite and β -zeolite display stable activity, then at calculation of region there were used mathematical models cited for stationary conditions.

Conclusion

The proposed in the work list of main actions which should be fulfilled for preserving stability of work of chemico-technological system, way serve as a guide for calculation of any region of CTC, including the processes with possible non-stationarity of their proceeding.

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РЕШЕНИЕ ВОПРОСОВ НЕСТАЦИОНАРНОСТИ ПРОЦЕССОВ ЭТИЛЕНОВОГО РЕГИОНА ХИМИКО-ТЕХНОЛОГИЧЕСКОГО КОМПЛЕКСА ПО ПЕРЕРАБОТКЕ ГАЗОВ КРЕКИНГА И ПИРОЛИЗА

И.И.Османова

Изучена динамика процессов самого большого – этиленового региона ХТК, выбраны функции, учитывающие нестационарность процессов, составлены их динамические кинетические модели и на основе полных математических описаний решены задачи их оптимального управления, что в итоге позволило выполнить поставленную цель – сохранить оптимальные производительности целевых продуктов, найденных при оптимизации ХТК для стационарных условий их протекания.

Ключевые слова: нестационарность, функция дезактивации, управление, производительность, динамика, активность катализатора, блок-схема.

KREKİŇQ VƏ PİROLİZ QAZLARININ EMALININ KİMYƏVİ TEXNOLOJİ KOMPLEKSİNİN ETİLEN REĞİONUNA DAXİL OLAN PROSESLƏRİNİN QEYRI-STASİONARLIĞI MƏSƏLƏLƏRİNİN HƏLLİ

İ.İ.Osmanova

KTK-in ən böyük – etilen regionu proseslərinin dinamikası öyrənilib, proseslərin qeyri-stasionarlığını nəzərə alan funksiyalar seçilib, onların dinamik kinetik modelləri tərtib və tam riyazi təsvir əsasında onların optimal idarə edilməsi məsələsi həll olunub ki, bu da nəticədə qarşıya qoyulmuş məqsədi – məqsədli məhsulların KTK-in stasionar şəraitdə optimallaşdırılması zamanı alınan məhsuldarlığını sabit saxlamaq məsələsini həll etməyə imkan verdi.

Açar sözləri: qeyri-stasionarlıq, deaktivasiya funksiyası, idarəetmə, məhsuldarlıq, dinamika, katalizatorun aktivliyi, blok-sxem.

Additional remarks for references

1. d_{ins} – inside diameter of tube, m;
2. d_{ins}^f – diameter in the end of time's interval;
3. E_{in} – energy of activation of initiator's decomposition, kJ/mol;
4. $g_{C_2H_4}^{exp}, g_{C_2H_4}^{cal}$ – experimental and calculated yield of ethylene, kg/h;
5. g_{in} – current amount of initiator, kmol/h;
6. $g_{pe}^{nonst}, g_{pe}^{opt}$ – non-stationary and optimal amounts of polyethylene, kmol/h;
7. G_{cur}, G_{init} – current and initial amounts of phosphorus acid, kg;
8. G_{add} – additions of phosphorus acid, kg;
9. P_f – pressure at outlet from reactor, atm;
10. Q_h – warmth of heating of ethylene, kkal/mol;
11. T_r – temperature of refrigerant, K;
12. $Y_{cal}, \bar{Y}_{cal}$ – regressive dependence of ethylene yield;
13. ρ_{cat}, ρ_{gas} – densities of catalizator and gas, kg/m³;
14. K_{eq} – constant of equilibrium.