UDC 66.011/66.012:662.765

GLOBAL FLOWSHEET OF CONTROL ETHYLEN REGION OF A CHEMICAL-TECHNOLOGICAL COMPLEX ON PROCESSING CRACKING AND PYROLYSIS GASES WITH CONSIDERATION FOR NON-STATIONARITY OF THE PROCESSES PROCEEDING IN IT

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Received 10.06.2019

The article presents a course and results of conducting the processes of ethylenic region of chemical technological complex according to the proposed earlier [1] flowsheet of their calculations under non-stationary conditions. The tasks of their optimal conduction have been decided and on the basis of work carried out general flowsheet of conducting ethylenic region of studied complex taking into account non-stationarity of the processes proceeding there, was developed.

Keywords: non-stationarity, conduction functions, production capacity, dynamics, activity, block-flowsheet, general flowsheet of conduction.

doi

The purpose of work consists in maintaining optimal production capacities of the target products in ethylenic region of chemical technological complex (CTC), found out for stationary conditions of their proceeding at optimization of CTC, not depending on reasons at which this stationarity is destroyed.

Fulfillment of work

According to a flowsheet of the basic actions, proposed in [1] to achieve the purpose set there are provided the results of their subsequent fulfillment for the concrete processes of ethylenic region. Regime parameters of the processes and denotions to them are presented references corresponding to each process.

Dealkylation of toluene with water vapor [2]

1. Stoichiometric flowsheet of the process:

2. Stationary kinetic model:

$$\begin{aligned} w_{\text{BENZ}} &= \left[\frac{k_{\text{EFF}}^1 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \frac{k_{\text{EFF}}^2 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \right. \\ &\quad \left. + \frac{k_{\text{EFF}}^3 P_{\text{TOL}} P_{\text{H}_2}}{1 + K_{\text{TOL}} P_{\text{TOL}} + K_{\text{H}_2} P_{\text{H}_2}} \right]; \\ -w_{\text{TOL}}^{\Sigma} &= \frac{k_{\text{EFF}}^1 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \frac{k_{\text{EFF}}^2 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \\ &\quad + \frac{k_{\text{EFF}}^3 P_{\text{TOL}} P_{\text{H}_2}}{1 + K_{\text{TOL}} P_{\text{TOL}} + K_{\text{H}_2} P_{\text{H}_2}} + \frac{k_{\text{EFF}}^4 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}}; \\ W_{\text{H}_2} &= \frac{k_{\text{EFF}}^1 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \frac{k_{\text{EFF}}^2 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} - \\ &\quad - \frac{k_{\text{EFF}}^3 P_{\text{TOL}} P_{\text{H}_2}}{1 + K_{\text{TOL}} P_{\text{TOL}} + K_{\text{H}_2} P_{\text{H}_2}}; \\ w_{\text{XYL}} &= \frac{k_{\text{EFF}}^4 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}}; w_{\text{CO}_2} = \frac{k_{\text{EFF}}^1 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}}; \\ w_{\text{CO}} &= \frac{k_{\text{EFF}}^2 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}}; w_{\text{CH}_4} = \frac{k_{\text{EFF}}^3 P_{\text{TOL}} P_{\text{H}_2}}{1 + K_{\text{TOL}} P_{\text{TOL}} + K_{\text{H}_2} P_{\text{H}_2}}, \\ k_{\text{EFF}}^j &= k_0^j \cdot \exp\left(-\frac{E_{\text{EFF}}^j}{RT}\right), K_i = K_0^i \exp\left(\frac{Q_i}{RT}\right) \end{aligned} \quad (2)$$

3. Equation of heat balance:

$$\frac{dT}{dl} = 0. \quad (3)$$

4. Function of deactivation of a catalyst:

$$\theta = e^{-k_A \alpha \tau}. \quad (4)$$

5. By introducing function of a catalyst's deactivation (3) into equation of benzene formation velocity

$$w_{\text{BENZ}} = \left[\frac{k_{\text{EFF}}^1 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \frac{k_{\text{EFF}}^2 P_{\text{TOL}}}{1 + K_{\text{TOL}} P_{\text{TOL}}} + \frac{k_{\text{EFF}}^3 P_{\text{TOL}} P_{\text{H}_2}}{1 + K_{\text{TOL}} P_{\text{TOL}} + K_{\text{H}_2} P_{\text{H}_2}} \right] \cdot \theta, \quad (5)$$

together with other equations of the system (2) constructed dynamic kinetic model.

6. Function of conducting – regression dependences of selectivity of benzene and xylene on additions of hydrogen and time of a catalysts work:

$$S_{\text{BENZ}} = 73.0071 + 0.5068M + 0.003\tau, \quad (6)$$

$$S_{\text{XYL}} = -0.2770 - 0.1354M + 0.0082\tau. \quad (7)$$

The system of equations (2, 3) with consideration (4–7) is a complete mathematical model of the process for non-stationary conditions.

Suggested method of hydrogen additive to the reactionary mixture (TOL+H₂O) in found out interval of their change (0.2–1.5) permits preserve production capacity of benzene at needed optima level (76.6%).

7. Results of calculation:

Table 1. Results of a catalysts work within 1000 hours (without additions of hydrogen)

Time of catalysts work, h	200	400	600	800	1000
Selectivity for benzene, %	76.6	75.8	75.0	74.4	73.2
Selectivity for xylenes, %	1.2	2.3	8.4	9.9	11.2

Table 2. The best yields of benzene at indicated additions of hydrogen to reactionary mixture at inlet into reactor

Volumetric velocity of feeding TOL+H ₂ O+H ₂ , h ⁻¹	Ratios			Selectivity by benzene, %	Selectivity by xylenes, %
	TOL	H ₂ O	H ₂		
1800 ^{opt}	1	4	–	76.6 ^{opt}	7.5 ^{opt}
1835	1	4	0.1	75.6	7.5
1872	1	4	0.2	76.0	7.4
1980	1	4	0.5	76.2	7.1
2070	1	4	0.75	76.5	6.9
2160	1	4	1	77.0	6.6
2250	1	4	1.25	77.1	6.5
2340	1	4	1.50	77.3	6.3
2430	1	4	1.75	75.5	8.4

Alkylation of benzene by ethylene [3]

1. Stoichiometric flowsheet of process:

(8)

2. Stationary kinetic model:

$$\frac{dX_{\text{EB}}}{dl} = \left[\frac{(\gamma P - A)(K_1 C_c X_B - K_2 C_c X_{\text{EB}})}{w_l (1 + B)} + \frac{K_3 C_c C_B X_{\text{PAB}} - K_4 C_c C_B X_{\text{EB}}^2}{w_l} \right] \quad (9)$$

$$\frac{dX_{\text{PAB}}}{dl} = \frac{K_D G_g^2 T (\gamma P - A) K_2 C_c X_{\text{EB}}}{273 M_g \gamma_g F P w_l} + \frac{K_4 C_c X_B X_{\text{EB}}^2 - K_3 C_c C_B X_{\text{PAB}}}{w_l},$$

where

$$A = \frac{(K_3 X_B X_{PAB} - K_4 X_{EB}^2) C_k n_B^2 \gamma_1}{K_D W_g},$$

$$B = \frac{(K_1 X_B + K_2 X_{EB}) C_k n_B}{K_D W_g} \quad (10)$$

$$3. \frac{dT}{dl} = 0 \text{ (isothermic reactor).} \quad (11)$$

$$4. \text{Conducting function } \theta = G_{ET}/G_B:$$

$$\bar{\theta} = 0.3e^{-0.2\tau} \text{ (design value)} \quad (12)$$

5. By introducing θ into equation (9)

$$\frac{dX_{EB}}{dl} = \left[\frac{(\gamma P - A)(K_1 C_k X_B - K_2 C_k X_{EB})}{W_l (1+B)} + \frac{K_3 C_k C_b X_{PAB} - K_4 C_k C_b X_B^2}{W_l} \right] \theta \quad (13)$$

dynamic kinetic model of the process jointly with equation (10) was received. The system of equations (10), (11), (13) taking an account for (12) is a complete mathematical one of the process with consideration for non-stationarity of its proceeding.

6. Block-flowsheet of optimal conducting of the process in non-stationary conditions:

7. Results of calculation:

Table 3. Comparison of well-known and proposed methods of proceeding process

№	Industrial method					Proposed method				
	Inlet into alkylator, kg/h			Yield, kg/h		Inlet into alkylator, kg/h			Yield, kg/h	
	G_{cc}^f	G_{ET}	G_B	G_{PAB}	G_{EB}	G_{cc}^f	G_{ET}	G_B	G_{PAB}	G_{EB}
1	420	5348.12	51477.17	4517.20	20976.56	420	5183.20	51134.52	4416	21071.91
2	420	5253.88	51178.45	4452.80	20803.20	420	5183.20	51134.52	4416	21106.58
3	420	5654.40	54473.20	4554.00	21063.24	420	5183.20	51134.52	4416	21063.24
4	420	4829.80	46477.94	4517.20	20629.84	420	5183.20	51134.52	4416	21071.91
5	420	5583.72	53858.18	4259.60	21037.24	420	5183.20	51134.52	4416	21149.92
6	420	5501.26	53067.44	4121.60	20993.90	420	5183.20	51134.52	4416	21167.26
7	420	5030.06	46978.74	4664.40	20673.18	420	4924.04	48577.79	4195.2	20954.89
8	420	5124.30	48481.15	4728.80	20716.52	420	3592.90	35495.44	3054.4	20868.21
9	420	5242.10	50677.65	4084.80	20794.53	420	3592.90	35495.44	3054.4	20846.54

By ratio of the concentrations of not reacted ethylene and benzene corrected are their amounts at inlet of alkylator to obtain at outlet from it demanded by project amount of ethyl benzene got for stationary conditions. Application of the proposed method of conducting makes it possible to increase by 1% of ethylbenzene yields and decrease by 8–10% amounts of polyalkylbenzenes.

Dehydration of ethylbenzene to styrene [4].

1. Stoichiometric flowsheet of the process:

2. Stationary kinetic model:

$$\frac{dx_2}{dl} = \lambda_2 \frac{1-x_2-x_5}{1+x_2}; \quad (15)$$

$$\frac{dx_5}{dl} = \lambda_5 \frac{1-x_2-x_5}{(1+x_2)^2} (x_2-x_5), \quad (16)$$

$$x_5 = x_3 + x_4; \lambda_2 = k_2\beta/W_0,$$

$$\lambda_5 = k_5\beta C_0/W_0; \beta = \frac{F}{F_0}.$$

3. Equation of heat balance:

$$\frac{dT}{dl} = \frac{N_0}{C_{p\text{mid}} \cdot N_T} Q_2 \frac{dx_2}{dl}, \quad (17)$$

$$C_{p\text{mid}} = C_{pH_2O} \frac{M}{M+(1+x_2)} + \frac{1}{M+(1+x_2)} \times \\ \times \left[x_2 (C_{p\text{ct.}} + C_{pH_2} - C_{p\text{eb.}}) + C_{p\text{eb.}} \right].$$

4. Deactivation functions:

$$\theta = 1 - \left[(1-n) A e^{-\frac{E_A}{RT}} (N_0 M) (\tau - \tau_0) \right]^{\frac{1}{1-n}} \quad (18)$$

5. By introducing θ into the right part of equation (15):

$$\frac{dx_2}{dl} = \lambda_2 \frac{1-x_2-x_5}{1+x_2} \times \theta \quad (19)$$

dynamic kinetic model with equation (16) of the process was received.

6. Function of conducting – regression equations of dependences of ethylbenzene conversion to styrene X_2 and selectivity of the process S on degree of dilution of feed stock by water vapor M , temperature of vapor feed stock mixture at inlet to reactor t_0 and time of work of work setting τ

$$x_2 = 1.257042166 + 0.002389131 \cdot M - \\ - 0.001472064 \cdot t_0 - 0.00000426802 \cdot \tau \quad (20)$$

$$S = 0.791438979 + 0.003849415 \cdot M - \\ - 0.000108156 \cdot t_0 - 0.00000528188 \cdot \tau \quad (21)$$

The system of equations (16), (17), (19) with consideration for (18–21) is an entire mathematical model of the process for non-stationary conditions.

7. Results of calculation:

Table 4. The optimal version of conducting the process

Conversion of ethyl benzene to styrene, X_2 ; selectivity S , mol %	Parameters	Time of a catalyst's work, hours										An average value of water vapor consumption for 5000 hours of a catalysts work
		500	1000	1500	2000	2500	3000	3500	4000	45000	5000	
$X_2=41$ $S=92$	M	16.7	16.9	17.1	17.4	17.7	18.2	18.7	19.4	20.2	21.3	$\bar{N}_{w.v.}=3826.62$ kmol/h $\bar{G}_{w.v.}=68879.16$ kq/h
	t_0	597.6	597.3	597.1	596.4	595.7	594.9	594.1	593.3	592.6	592.1	
	$N_{w.v.}$	3483.62	3525.34	3567.06	3629.64	3692.22	3763.76	3900.82	4046.84	4213.72	4443.18	

Table 5. Results of a catalyst's work after 5000 hours

Time of a catalyst's work, τ , h	Temperature of vapor feedstock mixture at inlet to a reactor, t_0 , °C	Degree of dilution of feedstock by water vapor, M , mol/mol	Conversion of ethylbenzene to styrene X_2 , %, mol	Selectivity of the process, S %, mol
5000	592.1	21.3	41.0	92
5500	593.0	21.3	41.2	91.9
6000	594.0	21.3	41.3	91.85
6500	595.0	21.3	41.35	91.70
7000	596.0	21.3	41.3	91.60
7500	597.0	21.3	41.28	91.40

As we see, to keep up constant for whole period of work the optimal values of styrene yield at 41% and selectivity of the process at 92%, it is expedient to decrease mixture temperature at inlet to reactor from 597.6 at the beginning to 592.1°C in the end of a catalyst's work and degree of delution of feedstock by water vapor to increase simultaneously from 16.7 to 21.3.

It is radically differed from industrial way of carrying out the process, where to maintain activity of a catalyst they resort to increasing temperature of vapor feedstock mixture at inlet to a reactor, at the same time not changing delution degree of feedstock by water vapor that leads to sooner blocking of catalyst's surface by toxicants.

It is seen in the table that a rise temperature about by 4°C for subsequent 2000 hours permits to increase a little yield, keeping up it within a frame of optimal, and though selectivity of the process with increase in temperature will decrease a little, however till 7000 hours the results of a catalyst's work may be considered satisfactory.

The proposed way of optimal conducting process will enable not decreasing styrene yield

not only to reduce expenditures for the process because of lesser consumption of water vapor in comparison with industrial by 25%, but also to prolong service term for 2000 hours work of a catalyst (7000 hours against 5000 hours at the plant). Result-is a tangible economic advantage.

Polymerization of styrene [5]

1. Stoichiometric flowsheet of the process:

2. Stationary kinetic model:

$$\frac{dx_m}{dt} = \left[k_{\text{EFF}} (1-x_m) \sqrt{\frac{I_0 (1-x_1)}{(1+\varepsilon x_m) F(x_m)}} \right]; \quad (23)$$

$$dx_1/dt = k_d (1-x_1), \quad (24)$$

$$x_1 = \frac{(I_0 - I)}{I_0}; \quad I_0 = \frac{M_{\text{inic}}}{M_{0\text{inic}} V_{\text{st}}^0}; \quad k_{\text{EFF}} = k_p \sqrt{\frac{2k_d f}{k_{t_0}}};$$

$$k_t = k_{t_0} F(x_m); \quad \varepsilon = \frac{\rho_{\text{st}}}{\rho_{\text{ps}}} - 1;$$

3. Equation of heat balance:

$$\rho V C_p \frac{dT}{dt} = M_{st} \Delta H \frac{dx_m}{dt} - q_{pot} \quad (25)$$

4. Function of non-stationarity:

$$\theta = e^{-k \alpha N_{st} t} \quad (26)$$

5. Introducing θ into the right part of the equation (23)

$$\frac{dx_m}{dt} = \left[k_{EFF} (1 - x_m) \sqrt{\frac{I_0 (1 - x_1)}{(1 + \varepsilon x_m) F(x_m)}} \right] \cdot \theta, \quad (27)$$

jointly with (24) and (25) dynamic kinetic model of the process is received.

System of equations (24), (25), (27), with consideration of (26) is a complete mathematical model of the process for non-stationary conditions.

6. Block-flowsheet of optimal conduction of the process in non-stationary conditions:

7. Results of calculation:

At difference of polystyrene productivity from its stationary value, changing a value of θ on the account of increasing purity of the styrene feed into a reactor or amount of initiator, we'll be able to regulate the process and obtain the required yield of a target product.

Conclusion

The developed algorithms of a choice for optimal conducting the processes of ethylene region with own non-stationarity function found out for each of them permit to calculate operatively the regimes of work in non-stationary industrial conditions for the purpose to receive demanded values of productivities of the target products obtained already at optimization of CTC, but in stationary conditions.

As the processes of ethylene region do not work synchronously and periods of changing catalyst's activity do not coincide in time, in addition the reasons of destroying stationarity in

each process are different, it is impossible to make up a general function of control for a whole region. However the mathematical models of the processes developed with consideration for non-stationary activity of catalyst's possess a flexible structure, i.e. in the course of time the process of self-adjustment of these models takes place. Adjusting mathematical models is carried out both periodically through certain intervals of time or disagreement between calculated and experimental values exceeds the definite values given beforehand. At similar approach the region becomes a flexible chemical-technological system maintaining own work capacity even at possible outward and inner effects.

A general flowsheet of control for ethylene region in CTC is shown in a Figure, where every process proceeding under non-stationary conditions corresponds to control block of its own, using non-stationarity function, concrete for this process.

General flowsheet for control of the ethylene region of CTC.

References

1. Osmanova I.I. Solution of the problems of non-stationarity of the processes of ethylene region of the chemical-technological complex on processing cracking and pyrolysis gases. Azerb. chem. journ. 2019. No 3. P. 75–83.
2. Aliyev A.M., Osmanova I.I., Balayev I.V., Huseynova A.M., Safarov A.R. The method of control for the process of dealkylating toluene by water vapor. Scienc. News. Sumgait University. 2018. No 3. P. 42–48.
3. Aliyev A.M., Osmanova I.I., Safarov A.R., Huseynova A.M., Aliyeva X.A. Blok-skhemata optimalnogo upravleniia protsessom alkilirovaniia benzola etilenom v nestatsionarnykh usloviakh. Abstracts of Scien. conf. "Nagiye Readings" dedicated to the 110th anniversary of academician M.Nagiev. Baku. 2018. P. 133.
4. Aliyev A.M., Osmanova I.I., Safarov A.R., Huseynova A.M., Aliyeva Kh.A. Control of the process of ethylbenzene dehydration to styrene under non-stationary conditions. Azerb. chem. journ. 2018. No 1. P. 17–22.
5. Aliyev A.M., Osmanova I.I., Safarov A.R., Huseynova A.M., Balayev I.V. Control of the process of styrene polymerization in non-stationary conditions. Azerb. chem. journ. 2018. No 3. P. 33–37.

Additional remarks for references

1. $C_{p\text{ mid}}$ – middle heat capacity of components, kcal/kmol⁻¹·deg⁻¹;
2. $C_{p\text{ st}}$, $C_{p\text{ EB}}$ – heat capacities of styrene and ethylbenzene, kcal/kmol·deg⁻¹;
3. K_D – constant of diffusion exchange;
4. K_{eff}^j – effective constant of j -th reaction velocity;
5. N_o – feeding velocity of ethylbenzene, kmol/h;
6. $N_{w.v.}$ – amount of water vapor, kmol/h;
7. n_B – mole velocity of benzene, mol/s;
8. P_{TOL} – partial pressure of toluene;
9. w_g , w_l – linear velocities of gas and liquid flows, mol m⁻³·s⁻¹;
10. w_{BENZ} , w_{XYL} – benzene and xylene formation velocity, mol m⁻²·h⁻¹;
11. w_{TOL}^{Σ} – toluene summary conversion velocity, mol/(m²·h);
12. X_B , X_{PAB} , X_B – partial moles of benzene, polyalkylbenzene and ethylbenzene;
13. γ_l – special weight of liquid phase, kg/m³;
14. G_{cc}^f – expenditure of fresh catalyst's complex, kg/h;
15. N_T – current amount of ethylbenzene, kmol/h.

KREKİNG VƏ PİROLİZ QAZLARININ EMALININ KİMYƏVİ TEXNOLOJİ KOMPLEKSİNİN ETİLEN REQİONU PROSESLƏRİNİN QEYRİ-STASİONARLIĞINI NƏZƏRƏ ALMAQLA ÜMUMİ İDARƏ SXEMİ

I.I.Osmanova

Məqalədə KTK-in etilen regionu proseslərinin qeyri-stasionar şəraitdə əvvəl təklif edilmiş [1] sxemi üzrə hesablanmış idarə olunmasının gedişi və nəticələri təqdim olunub. Proseslərin qeyri-stasionar şəraitdə optimal idarə olunması məsələsi həll olunub və aparılan iş nəticəsində KTK-in etilen regionunun qeyri-stasionar şəraitdə baş verməsini nəzərə almaqla ümumi idarə sxemi işlənilib hazırlanıb.

Açar sözlər: qeyri-stasionar, idarə olunma funksiyası, məhsuldarlıq, dinamika, aktivlik, blok-sxem, ümumi idarə sxemi.

ОБЩАЯ СХЕМА УПРАВЛЕНИЯ ЭТИЛЕНОВЫМ РЕГИОНОМ ХИМИКО-ТЕХНОЛОГИЧЕСКОГО КОМПЛЕКСА ПО ПЕРЕРАБОТКЕ ГАЗОВ КРЕКИНГА И ПИРОЛИЗА С УЧЕТОМ НЕСТАЦИОНАРНОСТИ ПРОТЕКАЮЩИХ В НЕМ ПРОЦЕССОВ

И.И.Османова

В статье представлены ход и результаты управления процессами этиленового региона ХТК по предложенной ранее [1] схеме их расчетов в нестационарных условиях. Решены задачи их оптимального управления и на основании проделанной работы разработана общая схема управления этиленовым регионом ХТК с учетом нестационарности протекающих в них процессов.

Ключевые слова: нестационарность, функции управления, производительность, динамика, активность, блок-схема, общая схема управления.