Optimization of contact reactor

D. CHMÚRNY

Department of Automation and Control, Slovak Technical University,
880 37 Bratislava

A method of optimum temperature determination in a contact reactor for the oxidation of sulfur dioxide, produced by burning hydrogen sulfide, to sulfur trioxide is described. On the basis of the equation of reaction rate and material balance, some general relationships between the temperatures in reactor and furnace for H_2S burning and other quantities (concentration, gas flow, air temperature, and degree of conversion) have been derived. These relationships are founded on plant experiments and have been linearized. The coefficients of linear relations have been determined by regression analysis. The method may be used for optimum control of sulfuric acid production or other chemical productions.

Описан метод определения оптимальных температур в контактном реакторе для окисления двуокиси серы, получаемой сжиганием сероводорода, в трехокись серы. Исходя из уравнения скорости химической реакции и материального баланса, выведены общие соотношения между температурами в реакторе и в печи для сжигания H_2S, концентрацией, потоком газа, температурой воздуха и степенью конверсии. Соответствующие соотношения были найдены на основании производственных измерений и превращены в линейные функции. Коэффициенты прямых были определены при помощи корреляционной связи. Метод можно использовать для оптимального управления производством серной кислоты или других химических производств.

The waste gas from crude oil processing is used for the production of sulfuric acid. Hydrogen sulfide is oxidized in a furnace to give sulfur dioxide which is led through a contact reactor where it is oxidized on contact substance to yield sulfur trioxide. On passing through the first, second, and third layer of catalyst, the gas is cooled to the required temperature by introducing cold air (Fig. 1).

Theoretical

In this case a mathematical model must be set up for the process of SO_2 oxidation (Fig. 1). For varying and non-controlled quantities C_1, w, and T_{air} (concentration
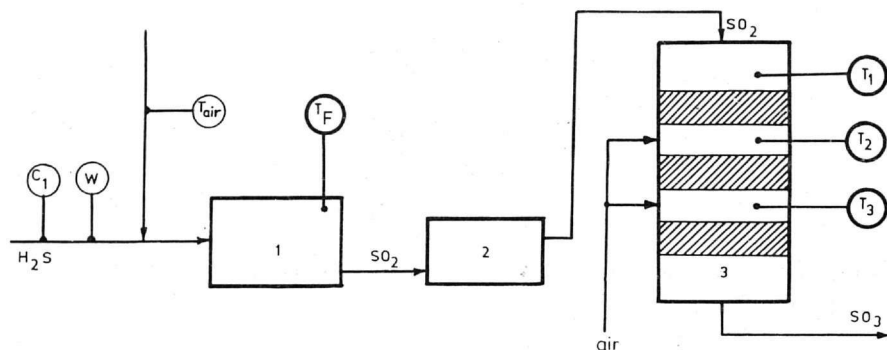
Fig. 1. Block diagram for SO_3 production from gas containing H_2S.
1. Burning furnace for H_2S; 2. steam generator; 3. contact reactor.

of gaseous H_2S, amount of H_2S fed into furnace, and air temperature, respectively) it is necessary to find out such values of T_1, T_2, T_3, and T_F (temperatures of gas corresponding to the inlet into the first, second, and third layer of catalyst and temperature in furnace) that X, *i.e.* the degree of conversion, is maximum.

The mathematical description of the i-th layer of catalyst with air feed (Fig. 1) assumes the following form [1]

$$\tau_i = \int_{X_{ii}}^{X_{if}} \frac{a T^* P_0}{273 \, kT} \left(\frac{X}{X_e - X}\right)^{0.8} \frac{1 - 0.5 \, aX}{b - 0.5 \, aX} \, dX \qquad (1)$$

The process proceeds in the layer adiabatically and the temperature changes linearly with the degree of conversion

$$T_{if} - T_{ii} = \lambda (X_{if} - X_{ii}) \qquad (2)$$

The meaning of individual symbols is as follows: T^* — absolute temperature [K], P_0 — atmospheric pressure, P — pressure in a layer of catalyst, T_i — initial temperature of a layer of catalyst [°C], T_f — final temperature of a layer of catalyst [°C], λ — change in the degree of conversion $\Delta X = 1$ under adiabatic conditions, X_i — initial degree of oxidation in a layer of catalyst, X_f — final degree of oxidation in a layer of catalyst, $\tau = V_c / \dot{V}_g$ — fictitious contact time [s], a — initial content of SO_2 in gas mixture [volume fraction], b — initial content of O_2 in gas mixture [volume fraction], V_c — volume of catalyst [m^3], V_g — volume flow of gas mixture passing through catalyst referred to normal conditions [m^3 s^{-1}], $k = k_0 \, e^{-\frac{E}{RT^*}}$ — rate constant. For equilibrium it holds [1]

$$X_e = \frac{K_e}{K_e + \sqrt{\frac{1 - \frac{aX_e}{2}}{P\left(b - \frac{aX_e}{2}\right)}}}$$

where P is the gas pressure at catalyst [Torr] and K_e is equilibrium constant (temperature function) [Torr$^{-0.5}$]. The degree of conversion does not change between layers

$$X_{if} = X_{(i+1)i} \tag{3}$$

If cold air is introduced between layers, the temperature of reaction mixture changes according to the equation

$$T_{(i+1)i} = T_{air} + \frac{\dot{V}_i^*}{\dot{V}_{i+1}} (T_{if} - T_{air}) \tag{4}$$

Simultaneously, the composition of reaction mixture changes according to the following equations

$$a_{i+1} = \frac{\dot{V}_i}{\dot{V}_{i+1}} a_i \tag{5}$$

$$b_{i+1} = 0.21 - \frac{\dot{V}_1}{\dot{V}_{i+1}} (0.21 - b_1) \tag{6}$$

The individual symbols denote: T_{air} — temperature of cold air [K], $\dot{V}_i$ — volume flow of reaction mixture in the i-th layer referred to normal conditions, $\dot{V}_{i+1}$ — volume flow of reaction mixture in the $(i + 1)$-th layer after introduction of cold air referred to normal conditions, the sign (*) signifies that the volume flow is referred to normal conditions.

If a real contact reactor is investigated, the amount of catalyst in layers and the volume flow of reaction mixture through the i-th layer per unit time are known.

Thus, the contact time in the i-th layer may be determined from the expression

$$\tau_i = \frac{O_i}{\dot{V}_i} \xi \tag{7}$$

where O_i, $\dot{V}_i$, and ξ are the volume of contact substance in the i-th layer [m^3], volume flow of reaction mixture passing through the i-th layer referred to normal conditions [m^3 s^{-1}], and effectivity factor [2], respectively. If we calculate τ_i from eqn (7), we are able to determine the final degree of conversion in the i-th layer X_{if} [3] by means of eqn (1) and tables for the preset values of a_i, b_i, T_{ii}, and X_{ii}.

For overall contact time it may be written

$$\tau = \sum_{i=1}^{n} \tau_i \qquad (i = 1, 2, ..., n) \qquad (8)$$

It is obvious from eqns (1), (2), and (7) that T_{1i}, a_1, b_1, and $\dot{V}_1$ predominantly influence the degree of conversion in the first layer while the degree of conversion in each subsequent layer is affected by the initial temperature of reaction mixture in front of the layer which is given by eqn (4) and depends on the amount and temperature of the air let in.

In view of the material and heat balance of a furnace for burning H_2S, it may be proved that the content of O_2 in gas is governed by the equation

$$b = 21\left(1 - \frac{d}{100}\right) - \left\{ \frac{21\left(1 - \frac{d}{100}\right)}{C_1} + \left[1.5 - 0.105\left(1 - \frac{d}{100}\right)\right] \right\} a \qquad (9)$$

where C_1 is the content of H_2S in gas [%] and d is the content of H_2O in air [%]. On the other hand, the content of SO_2 in gas is given by the following equation

$$a = \frac{T_g - T_{air}}{\dfrac{T_c - T_{air}}{C_1} + \dfrac{T_{air}}{200} + 167.3} \qquad (10)$$

where T_g, T_{air}, and T_c are temperatures of gas in burning zone of furnace, air, and gaseous H_2S, respectively [°C].

It ensues from eqns (9) and (10) that the temperature in burning zone of furnace can principally characterize the composition of the gas flowing into the first layer of contact substance.

Practical

All quantities operative in the processes involving SO_2 transformations may be divided into: a) controlled, b) non-controlled (actuating quantities or disturbance quantities).

The investigation of the effect of these quantities on the oxidation of SO_2 may be carried out, provided the mathematical description of this process is available, by the method of finding the optimum in a mathematical model of this process with successive transmission of the optimum from model to real object.

The Box—Wilson method was used for finding the optimum in the model.

According to eqns (1), (2), (9), and (10), the variables T_F, T_1, T_2, and T_3 belong among controlled quantities whereas the variables C_1, w, and T_{air} are non-controlled quantities according to eqns (1), (7), (9), and (10).

Table 1 contains the values of T_F, T_1, T_2, T_3, C_1, w, and T_{air} which were obtained in a plant producing sulfuric acid by wet catalysis. At the same time, the values of controlled

and non-controlled quantities as well as the values of T_c, a, and b are presented. As obvious from Table 1, the investigated region represents a relatively small portion of response surface, which enables us to describe the dependence of the degree of conversion on controlled parameters by the following linear relationship

$$X = f(T_F, T_1, T_2, T_3) \tag{11}$$

The linear character of regression equations for four controlled parameters allows to use the matrix for scheduling experiments of the type 2^{q-1}, *i.e.* 2^{4-1}; q being the number of variables.

The aim of further work was to detect the effect of non-controlled parameters on controlled parameters which may be represented by the linear relationship

$$T_i = f(C_1, w, T_{air}) \tag{12}$$

$$(i = F, 1, 2, 3)$$

Table 1

Average values of controlled and non-controlled parameters in the period of one month

Parameters	Basic value 0	Interval of fluctuations	Upper limit +1	Lower limit −1
Controlled parameters				
T_F [°C]	920	80	1000	840
T_1 [K]	717	15	732	702
T_2 [K]	781	20	801	761
T_3 [K]	765	15	780	750
Non-controlled parameters (disturbances)				
C_1 [% volume]	90	7	97	83
$\dot{w}$ [m³ s⁻¹]	0.047	0.013	0.06	0.034
T_{air} [K]	295	10	305	285
T_c [°C]	30	5	35	25
a [% SO_2]	5.9	0.1	6.0	5.8
b [% O_2]	11.05	0.15	11.2	10.9

For limitation
1. Controlled parameters

$T_F \leqq 1000°C$	$T_F \geqq 840°C$	$T_2 \leqq 801$ K	$T_2 \geqq 761$ K
$T_1 \leqq 732$ K	$T_1 \geqq 702$ K	$T_3 \leqq 780$ K	$T_3 \geqq 750$ K

2. Non-controlled parameters

$C_1 \leqq 97$	$C_1 \geqq 83$
$\dot{w} \leqq 0.06$	$\dot{w} \geqq 0.034$
$T_{air} \leqq 305$	$T_{air} \geqq 285$

Similarly, the matrix for experiment scheduling, used for non-controlled parameters, may be represented by a form of the 2^{3-1} type. The coefficients in eqns (11) and (12) were determined from the following equation [3]

$$b_i = \frac{\sum_{u=1}^{N} Z_{iu} X_u}{N} \qquad (13)$$

where u, N, i, and Z_{iu} stand for experiment number, number of the experiments performed, index denoting variable parameter, and code-character in scheduling matrices, respectively.

While the non-controlled parameters are preset by each line of scheduling matrix, the scheduling matrix for the controlled parameters was set up on a digital computer MINSK 22 (Department of Computers, Slovak Technical University, Bratislava). The results of these calculations are given in Table 2.

If we use the data of Table 2 and eqn (13), we obtain the equations giving the dependence of the degree of conversion on controlled quantities for all four experiments expressed in terms of the matrix for non-controlled parameters

$$\hat{X}_1 = a_1 + b_1 T_F + c_1 T_1 + d_1 T_2 + e_1 T_3$$
$$\hat{X}_2 = a_2 + b_2 T_F + c_2 T_1 + d_2 T_2 + e_2 T_3$$
$$\hat{X}_3 = a_3 + b_3 T_F + c_3 T_1 + d_3 T_2 + e_3 T_3 \qquad (14a)$$
$$\hat{X}_4 = a_4 + b_4 T_F + c_4 T_1 + d_4 T_2 + e_4 T_3$$

The coefficients of eqns (14) were calculated on a computer MINSK 22

$$\hat{X}_1 = 0.769025 - 0.3787499\ T_F + 0.022875\ T_1 + 0.02287499\ T_2 + 0.024625\ T_3$$
$$\hat{X}_2 = 0.88540 - 0.02550\ T_F + 0.01600\ T_1 + 0.01324999\ T_2 + 0.01224999\ T_3$$
$$\qquad (14b)$$
$$\hat{X}_3 = 0.77365 - 0.03874999\ T_F + 0.02350\ T_1 + 0.02225\ T_2 + 0.2449999\ T_3$$
$$\hat{X}_4 = 0.875525 - 0.02762499\ T_F + 0.17375\ T_1 + 0.014375\ T_2 + 0.01387499\ T_3$$

Table 2

Results of the scheduling matrix for controlled parameters and fixed non-controlled parameters preset by the values of each line in the experiment scheduling matrix [1]

u	1	2	3	4
1	0.7989	0.9029	0.8029	0.8949
2	0.7079	0.8499	0.7129	0.8369
3	0.7048	0.8409	0.7069	0.8269
4	0.7129	0.8459	0.7169	0.8329
5	0.8309	0.9309	0.8369	0.9239
6	0.8299	0.9219	0.8359	0.9159
7	0.8329	0.9199	0.8369	0.9139
8	0.7338	0.8709	0.7399	0.8589

The conversion may be expressed as a function of controlled and non-controlled parameters as follows

$$\hat{X} = (A_1 + B_1 T_F + C_1 T_1 + D_1 T_2 + E_1 T_3) + (A_2 + B_2 T_F + C_2 T_1 + D_2 T_2 + E_2 T_3) \; C_1 +$$

$$+ (A_3 + B_3 T_F + C_3 T_1 + D_3 T_2 + E_3 T_3) \; \dot{w} + (A_4 + B_4 T_F + C_4 T_1 + D_4 T_2 + E_4 T_3) \; T_{air}$$

$$(15a)$$

The coefficients of eqns (15) were calculated on a computer MINSK 22

$$\hat{X} = 0.82590 - 0.0324374 \; T_F + 0.0199375 \; T_1 + 0.0181875 \; T_2 + 0.0188125 \; T_3 +$$

$$+ (0.00131249 + 0.00074999 \; T_F + 0.00050 \; T_1 - 0.000125 \; T_2 -$$

$$- 0.00037499 \; T_3) \; C_1 + (- 0.0556249 - 0.00587499 \; T_F + 0.00325 \; T_1 + 0.00437499 \; T_2 -$$

$$- 0.00575 \; T_3) \; \dot{w} + (0.00362499 + 0.0003125 \; T_F - 0.00018749 \; T_1 -$$

$$- 0.0004375 \; T_2 - 0.0004375 \; T_3) \; T_{air} \qquad (15b)$$

Results and discussion

The calculation was carried out according to the mathematical model of the process of SO_2 oxidation described by eqns (15) on a computer MINSK 22. The course of X calculated from eqns (1—10) as well as the course of X calculated from eqns (15) on a digital computer MINSK 22 and on an analogue computer AP-3 is presented in Fig. 2.

Fig. 3 shows the course of conversion X_{meas}, X_{anal}, and X_{lin} for a process executed in a plant where the proposed method of optimum control as well as a comparison of the model accuracy with reality was tested. X_{meas} is the conversion measured by the Reich method in unit operation, X_{anal} is the conversion calculated by analytical procedure from eqns (1—10), and X_{lin} is the conversion calculated on the basis of linear model according to eqns (15). Furthermore, the course of optimal conversion X_{opt} calculated from the linear model of process is depicted in Fig. 3. It appears that the model of process according to eqns (15) is relatively accurate in comparison with reality and the optimum process control enables us to raise the conversion by about 2.5%.

Optimum control of chemical technological systems with model coefficient correction

The model coefficients vary owing to the change in catalyst characteristics. If we want to calculate the optimum values, we must respect this change (Fig. 4).
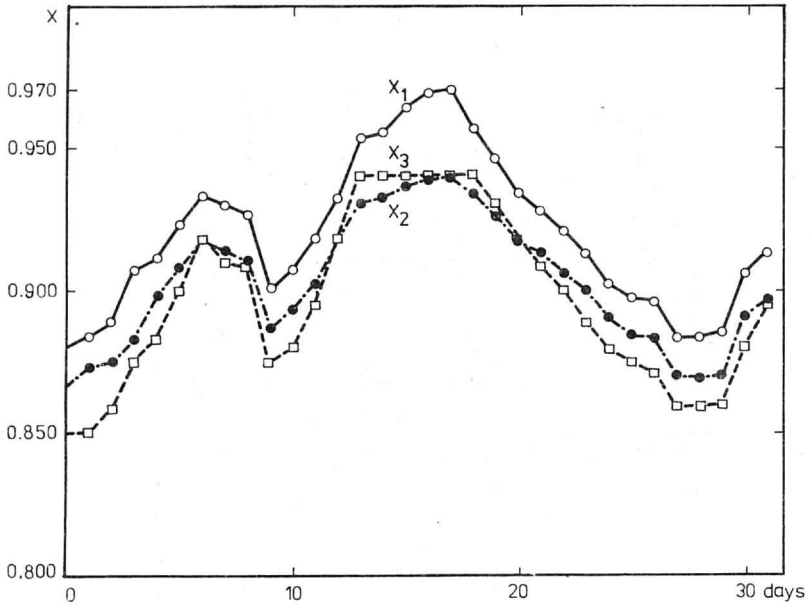
Fig. 2. Course of the degree of conversion (X_1 — calculated with digital computer; X_2 — calculated by analytical method; X_3 — calculated with analogue computer).
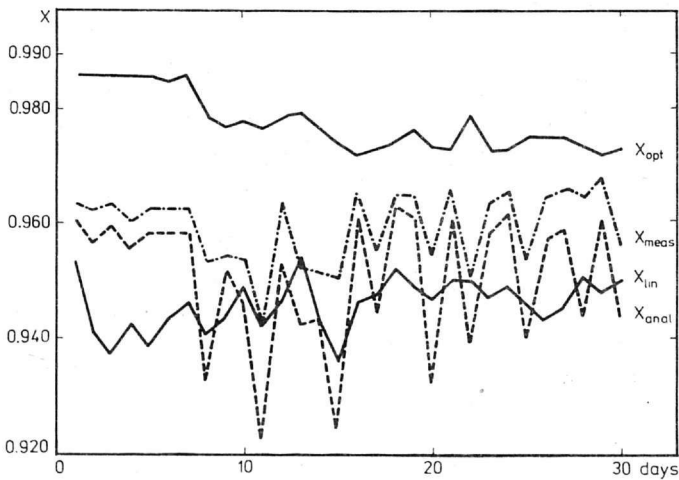Input parameters are given in [3] and have been measured in plant operation.

Fig. 3. Course of the degree of conversion (X_{meas} — conversion obtained in plant operation; X_{anal} — conversion calculated from eqns (1—10) analytically; X_{lin} — conversion calculated on the basis of linear model for non-optimum control; X_{opt} — optimum conversion calculated on the basis of linear model for optimum control).
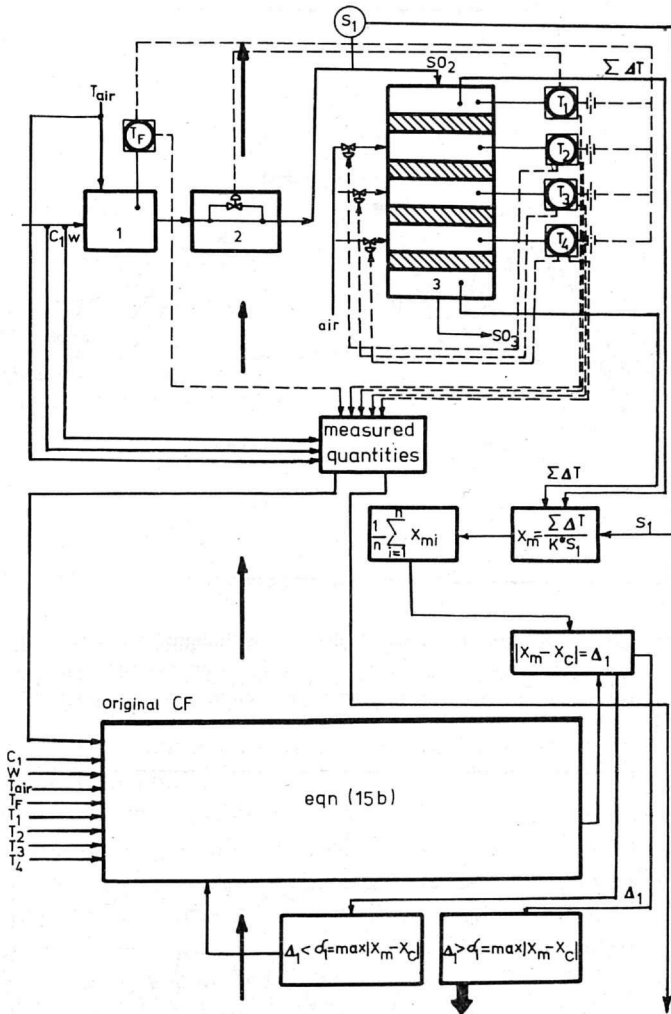
Fig. 4. Block diagram illustrating the optimum control of chemical technological processes with the correction of model coefficients.

1. Burning furnace for H_2S; *2.* steam generator; *3.* contact reactor; CF — criterion function.

Consider the mathematical model of a process described by the equation

$$X = f(T_F, T_1, T_2, T_3, T_4, T_5, C_1, w, T_{air}) \qquad (16)$$

During a selected time interval we measure n values of each variable and substitute the resulting average value
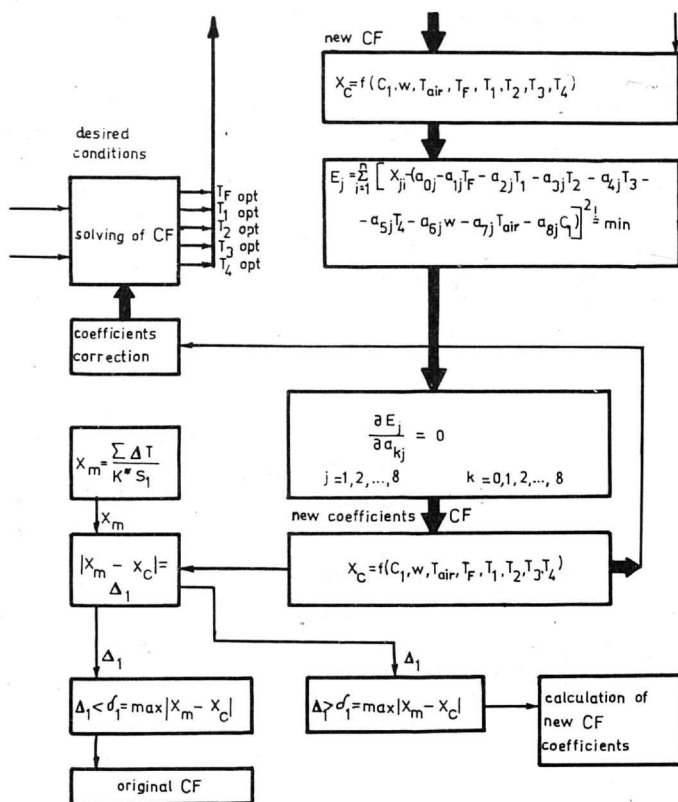
Fig. 4 (Continued)

$$\frac{1}{n}\sum_{i=1}^{n} Z_{ji} = Z_{jm}$$

into eqn (*16*). Since the model coefficients are dependent on time, the average value X_{jm} will not be likely equal to the calculated value X_{jc}.

If the difference

$$|X_{1m} - X_{1c}| = \Delta_1$$

is smaller than the highest acceptable deviation

$$\delta_1 = \max |X_{1m} - X_{1c}|$$

we may use the original criterion function for the calculation of optimum values.

Provided $\Delta_1 > \delta_1$ we must calculate new coefficients. According to the method of multiple linear regression, we shall search for the minimum values of the following expression

$$E_j = \sum_{i=1}^{n} [X_{ji} - (a_0 + a_1 T_F + a_2 T_1 + a_3 T_2 + a_4 T_3 + a_5 T_4 +$$

$$+ a_6 T_5 + a_7 C_1 + a_8 w + a_9 T_{air})]^2 \stackrel{!}{=} \min$$

From the condition of minimum

$$\frac{\partial E_j}{\partial a_{kj}} = 0$$

$$(k = 0, 1, 2, ..., 8), \qquad (j = 1, 2, ..., 8)$$

we obtain normal equations for the calculation of new mathematical model coefficients and thus, we can substitute the model with new coefficients into criterion.

These coefficients should satisfy the following condition

$$\Delta_1 < \delta_1$$

The calculation must be continued until the validity of this condition is achieved

$$\Delta_1 > \delta_1$$

References

1. *Modelirovanie i optimizatsiya kataliticheskikh protsessov*, pp. 75—76. Izd. Nauka, Moscow, 1965.
2. Kafarov, V. V., *Metody kibernetiki v khimii i khimicheskoi tekhnologii*, pp. 173—175. Izd. Khimiya, Moscow, 1971.
3. Chmúrny, D., *Thesis.* Slovak Technical University, Bratislava, 1969.