

The result of the study reported in this paper is the proposed mathematical model of technological processes occurring in the reactor for acetic acid synthesis. The initial parameters of the reactor considered were the value of the concentration of acetic acid at the reactor outlet, temperature, the level of reaction mass, and pressure in the reactor. The input parameters included the amount of methanol and carbon monoxide supplied. Material and thermal balances of reactor technological processes were used to construct the mathematical model of the reactor. Fisher criterion was applied to test the mathematical model for adequacy. At the specified 5 % level of significance, the value of Fisher criterion for the concentration of acetic acid, temperature, and the level of reaction mass in the reactor does not exceed its critical value for a stationary mode. The reproducibility of the modeling results was tested using the Cochran criterion. The value of the Cochran criterion, at the predefined 5 % level of significance, for the concentration of acetic acid, temperature, and the level of reaction mass in the reactor does not exceed its critical value for different modes. The relative error for the modeled output parameters was calculated. The relative error of the initial parameters did not exceed the level of 10 %. The model built makes it possible to calculate with satisfactory accuracy the value of the concentration of acetic acid at the reactor output, the temperature and level of the reaction mass in the reactor under a stationary mode. The resulting model could be used to automate the control of technological processes in the acetic acid synthesis reactor under a stationary mode. The study results open additional opportunities to manage the stationary mode of the reactor

Keywords: static mathematical model of acetic acid synthesis reactor, automatic control, technological processes

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BUILDING A MATHEMATICAL MODEL OF TECHNOLOGICAL PROCESSES IN THE ACETIC ACID SYNTHESIS REACTOR

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1. Introduction

The production of acetic acid has acquired great importance for people. Acetic acid and its derivatives are widely used in a variety of industries. Acetic acid is utilized in large quantities in the production of acetyl cellulose, when obtaining semi-finished products in fine organic synthesis as an acetylated means, in the textile industry, as well as to obtain its derivatives. Acetyl cellulose is used to make acetate fiber, plastics, varnishes, non-combustible film, and so on. Acetic acid is applied in pharmaceuticals to produce various medicines. Acetic acid salts are used in printing. The most common techniques for obtaining acetic acid in the industry are the oxidation of n-butane in the presence of a cobalt catalyst and methanol carbonylation in the presence of a rhodium catalyst. For modern large-scale production of acetic acid to be cost-effective, it is necessary to use automated control systems.

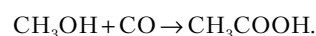
To manage such complex systems, it is necessary to build a model that adequately reflects the properties of the control object. The presence of a mathematical model makes it possible to use optimal and predictive systems for control, which improves production efficiency and enables resource-saving. In many cases, the parameters for such a model are determined directly during the operation of the object, that is, identification by input and output signals is carried out.

It seemed relevant to construct a static mathematical model for the stationary mode of the acetic acid synthesis reactor because it interconnects all the technological parameters of the control system.

2. Literature review and problem statement

The development of improvement of the process of production of acetic acid is described in [1]. To reach the required concentration of acetic acid, it is necessary to control the supply of reagents from which the reaction mixture in the synthesis reactor [2] is formed. However, the issues of optimizing the process of adding a catalyst to the reactionary medium remained unresolved. The option to overcome the difficulties is to add a rhodium-based homogeneous liquid-phase catalyst to the reactor reaction medium. Therefore, to produce acetic acid, Monsanto uses a rhodium-based homogeneous liquid-phase catalyst, which contributes to the formation of acetic acid as a result of methanol carbonylation with high selectivity and at low pressure [3].

The general stoichiometry of acetic acid synthesis was investigated in [4]:



There are the results of studying the methanol carbonylation kinetics, catalyzed by rhodium in the presence of a promotor, which have a number of interesting and unusual properties. The first reaction order was established at a high water content (more than 8 %) in the catalyst concentration and the concentration of iodide methyl [5]. For catalyst components, it was found that the reaction rate was directly proportional to concentrations of rhodium and iodide [6]. It was shown in [7] that the kinetics of methanol carbonylation are identical to the rhodium complex on a solid basis and homogeneous liquid-phase catalytic systems. Therefore, one

can get a heterogeneous analog of a homogeneous catalyst. This suggests that, despite the obvious physical differences between these catalysts, a similar reaction mechanism is likely to work. The stage of oxidative addition of methyl iodide to the rhodium complex is decisive, while other stages are performed much faster [8].

Similar technology is applied in production at many enterprises of the world at present. Such production of acetic acid is characterized by a relatively high degree of automation with complete absence, however, of any model support, which, under modern conditions, is considered a significant drawback.

It is the presence of sufficiently reliable and complete models of technological processes of complex chemical productions that makes it possible to perform with maximum efficiency the necessary periodic modernization of existing automation tools. That also makes it possible to maintain at a predefined level the quality of products and the profitability of production in the face of increasing wear of equipment and the effect of other perturbing factors.

The results of actual measurements of the object under study and the results of calculations were compared in [9]. The authors of work [10] prove the need to introduce corrections given the discrepancy of the above results. Then they check the adequacy of the calculated mathematical model.

The authors of [10] modeled the oxidation of depleted mixtures of methane-air and hydrogen-air in catalytic and non-catalytic reactors with a compacted layer. The possibility of applying a single-stage reaction to describe the processes occurring in the reactor was investigated, provided that the relevant kinetic data were obtained from sufficient experimental data. Acquired data should be available for the same reactor and operating conditions. However, the use of kinetic data for different working conditions could lead to significantly false results. Work [12] described the dynamic modeling of the reactor of catalytic oil reforming using material and thermal balance. With the help of modeling, two transitional regimes were studied: start-up and temperature disturbance at the inlet. It was found that the temperature takes longer to achieve a quasi-stationary state than the concentration of each compound. The disadvantages of that study include the lack of research for the level of reaction fluid in the reactor. The authors of [13] developed and considered the methodology of online optimization of the operation of two connected capacitive reactors of continuous action with a stirrer. The concepts of automatic detection of the stationary state, coordination of data, detection of gross errors, assessment of a dispersion-covariational matrix, the evaluation of parameters and optimization were presented. However, the disadvantages of that method include a complicated procedure for detecting the presence of a stationary state in reactors.

Constructed mathematical models of processes are used to interpret data from sensors, to select sensors for controlling chemical processes, to forecast the temperature regime of technological processes.

However, these mathematical models of reactors do not reflect the real processes that occur in the reactor of acetic acid synthesis. Neuro-fuzzy systems and neural networks can be used to build control systems. Fuzzy control uses a preset standard or fuzzy open path of the control object to derive a set of fuzzy rules "if-then" that are part of the corresponding fuzzy controller. The authors of work [14] considered the problem of multicritical optimization of process

control with a deterministic approach and in a fuzzy setting. When solving a multicritical problem in a fuzzy statement, the adequacy of the solution improves but the disadvantages of the proposed method include the need to use only highly qualified personnel to manage production. With a small amount of data from a passive experiment, the construction of control systems is complicated. In [15], a problem of evaluating the parameters of the regression equation for a small sample of the source data was solved when the observation conditions are fuzzy.

Several attempts are known aimed at building a mathematical model of the acetic acid synthesis reactor based on methanol carbonylation with a rhodium catalyst. Paper [16] outlines attempts to construct a model of technological processes in the reactor using the DIVA modeling environment. However, the cited paper lacks a static model of the occurring processes. The authors of work [17] tried to build a holistic static mathematical model of technological processes occurring in the reactor. The model was calculated with certain assumptions with rather large errors in the implementation of calculations. The model did not adequately reflect the processes occurring in the reactor. Experimental and statistical models for the acetic acid synthesis reactor during the start-up period [18] were calculated; neural networks were modeled to control the reactor during the start-up period [19]. None of the proposed models made it possible to determine the connection between the technological parameters of the acetic acid synthesis reactor for a stationary mode. Accordingly, the proposed models did not make it possible to improve the operation of the automated reactor control system for a stationary mode. In this regard, there is a task to devise the appropriate model support.

3. The aim and objectives of the study

The purpose of this work is to build a mathematical model of technological processes that occur in the reactor of acetic acid synthesis based on methanol carbonylation in the presence of a rhodium catalyst. The mathematical model to be constructed could be subsequently used to improve the operation of the automatic reactor control system under a stationary mode.

To accomplish the aim, the following tasks have been set:

- to derive equations of the concentration of acetic acid, temperature, the level of reaction mass, pressure in the reactor of acetic acid synthesis;

- to build and analyze a system of equations that form the mathematical model of the reactor of acetic acid synthesis. Based on the results of the construction of a static mathematical model, additional opportunities open up for managing the stationary mode of the reactor;

- to incorporate the mathematical model into a computer-integrated control system for the acetic acid synthesis reactor.

4. The study materials and methods

Material and thermal balances of reactor technological processes were used to construct a mathematical model of acetic acid synthesis reactor. For quantitative and statistical evaluation of mathematical model parameters, calculations were performed in the software Microsoft Office Excel for Microsoft Windows (USA).

As a control object, the reactor of acetic acid synthesis based on methanol carbonylation in the presence of a rhodium catalyst was considered (Fig. 1).

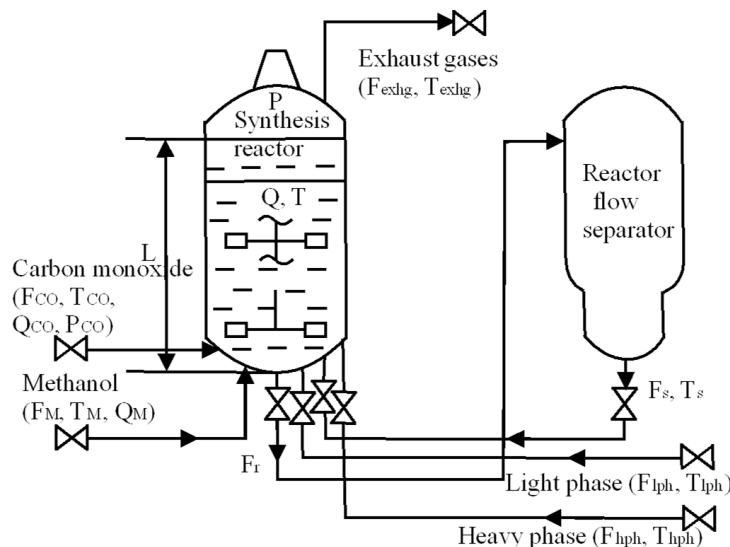


Fig. 1. Acetic acid synthesis reactor based on methanol carbonylation in the presence of a rhodium catalyst

To ensure the normal progress of the technological process in the reactor of acetic acid synthesis, the norms of technological regulations are observed. To do this, they regulate the input parameters and control the output and perturbing parameters, using control-registering equipment with linear static characteristics and a short time of transition processes. The output coordinates of the synthesis reactor as a control object are:

- pressure in reactor P ;
- level in reactor L ;
- the temperature of the synthesis reaction T ;
- the concentration of acetic acid in the reaction fluid Q .

The input coordinates of the synthesis reactor as a control object are:

- methanol consumption F_M ;
- carbon monoxide consumption F_{CO} .

Perturbing coordinates include:

- methanol temperature T_M ;
- carbon monoxide temperature T_{CO} ;
- the flow rate of reactionary fluid at the outlet of separator F_s ;

- the flow rate of the light phase of condensate after a decanter of the distillation column of light fractions F_{lph} ;

- the flow rate of the heavy phase of condensate after a decanter of the distillation column of light fractions F_{hph} ;

- the temperature of the bottom fluid T_s at the inlet to the reactor from the separator;

- the temperature of the flow of the light phase of condensate after a decanter of the distillation column of light fractions T_{lph} ;

- the temperature of the flow of the heavy phase of condensate after a decanter of the distillation column of light fractions T_{hph} ;

- the concentration of methanol supplied to the reactor Q_M ;

- the concentration of carbon monoxide supplied to the reactor Q_{CO} .

It is accepted during the calculations that:

- the target component (the component formed in the reaction of methanol carbonylation) in the input flows of methanol and carbon monoxide is absent;
- the reaction mixture in the reactor of acetic acid synthesis is perfectly stirred;
- the reactor content is in the liquid phase;
- all gas entering the reactor is instantly mixed with the liquid;
- the heat capacity of the walls and other components of the reactor is neglected.

The structural-logical scheme of the synthesis reactor is shown in Fig. 2.

The structural-logical scheme of the reactor of acetic acid synthesis (Fig. 2) shows the input, output, and perturbing coordinates.

To check the adequacy of the model, experimental data from a passive experiment were used, obtained in the study of the stationary mode of operation of the acetic acid synthesis reactor based on methanol carbonylation in the presence of a rhodium catalyst. When obtaining passive experiment data, parallel measurements were carried out at each experimental point.

The values of input, output, and perturbing coordinates for the stationary mode of the reactor are given in Table 1.

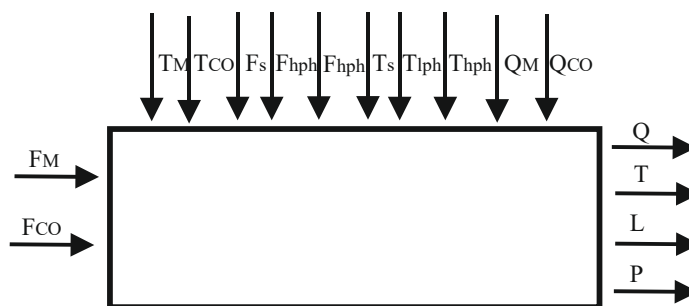


Fig. 2. Structural-logical diagram of the reactor

Table 1

Values of input, output, and perturbing coordinates for the stationary mode of the reactor

Input, output, and perturbing coordinates	Numerical values									
F_M , kg/h	9,175	9,050	8,950	9,000	9,125	8,975	9,125	8,950	8,950	
F_{CO} , kg/h	9,620	9,350	9,404	9,610	9,470	9,425	9,350	9,350	9,420	
F_s , kg/s	32.2	32.1	33.6	34.1	33.6	33.4	33.4	33.2	33.1	
F_{lph} , kg/s	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	
F_{hph} , kg/s	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	
T_M , °C	110	118	115	100	117	140	105	120	140	
T_{CO} , °C	40.6	40	38	38.5	42.3	39.8	40	37.5	40	
T_s , K	401.2	404.0	387.3	384.6	387.2	388.2	391.1	390.1	391.2	
T_{lph} , K	313.0	313.0	313.0	313.0	313.0	313.0	313.0	313.0	313.0	
T_{hph} , K	323.0	323.0	323.0	323.0	323.0	323.0	323.0	323.0	323.0	
Q_M	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	
Q_{CO}	0.97	0.97	0.97	0.97	0.97	0.97	0.97	0.97	0.97	
Q	0.668	0.648	0.660	0.652	0.654	0.668	0.667	0.657	0.657	
T , °C	187.5	187.5	185.9	186.1	186.2	186.2	186.3	186.4	186.5	
L , %	75	75	77	77	77	77	77	77	77	
P , MPa	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	

Data regarding the tools to control the input, output, and perturbing coordinates, and to measure the input, output, and perturbing coordinates for the stationary mode of the reactor are given in Table 2.

The following data were used to calculate the static mathematical model of the acetic acid synthesis reactor:

- ρ is the density of acetic acid, $\rho=987.5 \text{ kg/m}^3$ [17];
 - S_a – the cross-sectional area of the reactor, $S_a=10.51 \text{ m}^2$ [20];
 - K_0 – reaction rate constant, $K_0=0.037 \text{ 1/s}$ [20];
 - E – reaction activation energy, $E=7,830 \text{ J/mol}$ [20];
 - R – universal gas constant is equal to $8.31 \text{ J/(mol}\cdot\text{K)}$;
 - S – cross-sectional area of the regulating body (valve hole), $S=0.00129 \text{ m}^2$ [20];
 - g – free-fall acceleration 9.8 m/s^2 ;
 - C_M – specific heat of methanol entering the reactor, $C_M=3,070 \text{ J/(kg}\cdot\text{K)}$;
 - C_{CO} – specific heat of carbon monoxide entering the reactor, $C_{CO}=1,050 \text{ J/(kg}\cdot\text{K)}$;
 - C_s – specific heat of the flow of bottoms from the separator to the reactor, $C_c=2,870 \text{ J/(kg}\cdot\text{K)}$;
 - C_{lph} – specific heat of the light phase of the condensate after a decanter of the column distillation of light fractions, $C_{lph}=4,180 \text{ J/(kg}\cdot\text{K)}$;
 - C_{hph} – specific heat of the heavy phase of the condensate after a decanter of the column distillation of light fractions, $C_{hph}=578 \text{ J/(kg}\cdot\text{K)}$;
 - r – specific heat of reaction, $r=2,325 \text{ J/kg}$;
 - C – the specific heat of the reaction mixture in the reactor, $C=2,230 \text{ J/(kg}\cdot\text{K)}$ [16];
 - G – Henry constant, $G=12,977,157.67 \text{ Pa}$;
 - β_p – mass transfer coefficient,
- $\beta_p=0.25 \text{ kg}/(\text{m}^2\cdot\text{s}(\text{kg}/\text{m}^3))$ [21].

According to [22], α is the coefficient characterizing the degree of opening of the drain channel hole: $\alpha=0.6$.

Data regarding the tools to control the input, output, and perturbing coordinates, and to measure the input, output, and perturbing coordinates for the stationary mode of the reactor

Input, output, and perturbing coordinates	Control tools	Measurement means
F_M	disk diaphragm, controller	Diffmanometer
F_{CO}	disk diaphragm, controller	Diffmanometer
F_s	disk diaphragm, controller	Diffmanometer
F_{lph}	disk diaphragm, controller	Diffmanometer
F_{hph}	disk diaphragm, controller	Diffmanometer
T_M	controller	Calibration thermocouple «E»
T_{CO}	controller	Calibration thermocouple «E»
T_s	controller	Calibration thermocouple «E»
T_{lph}	controller	Calibration thermocouple «E»
T_{hph}	controller	Calibration thermocouple «E»
Q_M	controller	Chromatograph
Q_{CO}	controller	Chromatograph
Q	controller	Chromatograph
T	controller	Calibration resistance thermometer RT100-
L	controller	Diffmanometer
P	controller	Diffmanometer

For the studied initial parameters of the static mathematical model of the acetic acid synthesis reactor, three criteria are checked and analyzed:

- a) Fisher criterion (model adequacy check);
- b) Cochran criterion (verification of the reproducibility of experiments);
- c) relative error.

Fisher criterion was used to determine the adequacy of the resulting model.

$$F = \frac{S_{mad}^2}{S_{repr}^2}, \tag{1}$$

where S_{mad}^2 is the variance of inadequacy; S_{repr}^2 is the variance of reproducibility.

The variance of reproducibility was calculated according to the formula:

$$S_{repr}^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2}{f}, \tag{2}$$

where y_i is the sample data, \bar{y} is the mean, f is the number of degrees of freedom.

The variance of inadequacy was calculated according to the formula:

$$S_{mad}^2 = \frac{\sum_{i=1}^n (y_{exp} - y_{calc})^2}{f}, \tag{3}$$

where y_{exp} are the data from a passive experiment; y_{calc} are the data from calculations by model; f the number of degrees of freedom.

According to the table of critical points of Fisher and the predefined level of significance $\alpha=0.05$ and the number of degrees of freedom, the critical value F_{cr} was determined. If

$F_{obs} < F_{cr}$, a decision about the adequacy of the calculated model was made.

Table 2

As a criterion for the reproducibility of experiments, the Cochran criterion was used. To do this, the ratio of maximum variance to the sum of all variances was determined.

5. Results of studying the construction of a mathematical model for the acetic acid synthesis reactor

5.1. Deriving equations for the concentration of acetic acid, temperature, the level of reaction mass, pressure in the acetic acid synthesis reactor

In order to build a general mathematical model of the acetic acid synthesis reactor based on any initial coordinate, partial mathematical models were constructed for each initial coordinate.

To derive a partial mathematical model based on the concentration of the target component, the equation of material balance of the acetic acid synthesis reactor was built for the target component.

The balance equation takes the following form:

$$dm_1 + dm_2 + dm_r + dm_s = dm_v + dm, \tag{4}$$

where dm_1 is the mass of the reacting component entering the reactor with a methanol flow, dm_2 is the mass of the reacting component entering the reactor with a stream of carbon monoxide, dm_r – the mass of the target component formed in the reaction, dm_s – the mass of the target component discharged from the separator to the reactor, dm_v – the mass of the target component that accumulates in the reactor of volume V , dm – the mass of the target component discharged from the reactor;

$$dm_1 = F_M \cdot Q_M dt, \tag{5}$$

where F_M is the mass consumption of methanol into the reactor, Q_M – the concentration of methanol supplied to the reactor, dt – time.

$$dm_2 = F_{CO} \cdot Q_{CO} dt, \tag{6}$$

where F_{CO} is the mass consumption of carbon monoxide in the reactor, Q_{CO} is the concentration of carbon monoxide supplied to the reactor.

$$dm_p = VK\rho(Q_{\max} - Q)dt, \tag{7}$$

where V is the reactor volume, K is the speed of the chemical reaction, ρ is the density of the reaction mixture, Q_{\max} is the maximum concentration of the target component, Q is the concentration of the target component.

$$K = K_0 \exp\left(-\frac{E}{RT}\right), \tag{8}$$

where K_0 is the constant of the rate of chemical reaction, E is the activation energy of the reaction, R is the universal gas constant, T is the reaction temperature.

$$dm = FQdt, \tag{9}$$

$$dm_v = V\rho dQ, \tag{10}$$

$$dm_s = F_s Q dt, \tag{11}$$

where F is the consumption of the reaction mixture, F_s is the fluid flow from the separator to the reactor.

After substitution of the specified expressions of mass in the equation of thermal balance (2), one obtains:

$$F_M Q_M dt + F_{CO} Q_{CO} dt + F_s Q dt + V\rho K(Q_{\max} - Q)dt = V\rho dQ + FQdt. \tag{12}$$

For further research, it is necessary to take into consideration that [13]

$$F = \rho\alpha S \sqrt{2gL + \frac{P}{\rho}}, \tag{13}$$

where $\alpha=0.6\div0.8$ is the coefficient of fluid leakage through the regulatory body, S is the area of the cross-section of the

regulatory body (valve opening), L is the level of the reaction mixture, P is the value of excess pressure in the reactor, g is the acceleration of free fall.

If one replaces the expression of the amount of F coming out of the reactor using formula (13) and divide the left- and right-hand sides of equation (12) by dt , the expression takes the following form:

$$F_M Q_M + F_{CO} Q_{CO} + F_s Q + S_a L \rho Q_{\max} \times K_0 \exp\left(-\frac{E}{RT}\right) - S_a L \rho Q K_0 \exp\left(-\frac{E}{RT}\right) = S_a L \rho \frac{dQ}{dt} + Q\rho\alpha S \sqrt{2gL + \frac{P}{\rho}}, \tag{14}$$

where S_a is the cross-sectional area of the reactor.

Equation (14) is a nonlinear mathematical model of the acetic acid reactor for the concentration of the target component.

After linearization of the nonlinear partial mathematical model of the reactor for the concentration of target component (14), the equation for a stationary mode or a static partial mathematical model of the reactor for the concentration of a target component is built:

$$F_M Q_M + F_{CO} Q_{CO} + F_s Q + \rho S_a L K_0 \exp\left(-\frac{E}{RT}\right) Q_{\max} - \rho S_a L Q K_0 \exp\left(-\frac{E}{RT}\right) = Q\rho\alpha S \sqrt{2gL + \frac{P}{\rho}}. \tag{15}$$

Hence, the expression for concentration:

$$Q = \frac{F_M Q_M + F_{CO} Q_{CO} + \rho S_a L K_0 Q_{\max} \exp\left(-\frac{E}{RT}\right)}{\rho\alpha S \sqrt{2gL + \frac{P}{\rho}} - F_s + \rho S_a L K_0 \exp\left(-\frac{E}{RT}\right)}. \tag{16}$$

In order to build a partial mathematical model of the reactor of acetic acid synthesis based on temperature, the equation of thermal balance was constructed.

$$dq_1 + dq_2 + dq_{\text{reac}} + dq_s + dq_{\text{lph}} + dq_{\text{hph}} = dq_v + dq + dq_{\text{exhg}}, \tag{17}$$

where dq_1 is the amount of heat entering the reactor with a methanol flow, dq_2 – the amount of heat entering the reactor with the flow of carbon monoxide, dq_{reac} – the amount of heat released as a result of the reaction, dq_v – the amount of heat accumulated in the reactor of volume V , dq – the amount of heat emanating from the reactor with the target component, dq_{exhg} – the amount of heat released with exhaust gases, dq_s – the amount of heat entering the reactor with the flow of bottoms from the separator, dq_{lph} – the amount of heat entering the reactor with the flow of the light phase of condensate after the light fraction distillation column decanter, dq_{hph} – the amount of heat entering the reactor with the flow of the heavy phase of condensate after the light fraction distillation column decanter;

$$dq_1 = F_M C_M T_M dt, \quad (18)$$

where F_M is the methanol flow rate, C_M – the heat capacity of a methanol flow, T_M – the methanol flow temperature at the input of the reactor

$$dq_2 = F_{CO} C_{CO} T_{CO} dt, \quad (19)$$

where F_{CO} is the flow rate of carbon monoxide, C_{CO} – the heat capacity of the carbon oxide flow, T_{CO} – the temperature of the carbon oxide flow at the inlet of the reactor.

$$dq_{reac} = r \rho V K Q dt, \quad (20)$$

where r is the reaction specific heat; $V = S_a L$ – the volume of fluid in the reactor.

$$dq_v = m C dT = \rho V C dT = \rho S_a L C dT, \quad (21)$$

where m is the mass of liquid in the reactor; C – the heat capacity of liquid in the reactor; dT – a temperature change in the reactor.

$$dq = F C T dt, \quad (22)$$

where F is the flow rate of liquid from the reactor, determined according to (13), T – the temperature in the reactor;

$$dq = \rho \alpha S \sqrt{2gL + \frac{P}{\rho}} C T dt, \quad (23)$$

$$dq_{exhg} = F_{exhg} C_{exhg} T_{exhg} dt, \quad (24)$$

where F_{exhg} is the flow rate of exhaust gases, C_{exhg} – the heat capacity of the flow of exhaust gases, T_{exhg} – the flow rate of exhaust gases

$$dq_s = F_C C_C T_C dt, \quad (25)$$

where F_C is the flow rate of bottoms from the separator to the reactor, C_C – the heat capacity of the flow of bottoms from the separator to the reactor, T_C – the temperature of the flow of bottoms from the separator to the reactor

$$dq_{lph} = F_{lph} C_{lph} T_{lph} dt, \quad (26)$$

where F_{lph} is the flow rate of the light phase of condensate after the light fraction distillation column decanter, C_{lph} – the heat capacity of a flow of the light phase of condensate after the light fraction distillation column decanter, T_{lph} – the flow temperature of the light phase of condensate after the light fraction distillation column decanter

$$dq_{hph} = F_{hph} C_{hph} T_{hph} dt, \quad (27)$$

where F_{hph} is the flow rate of the heavy phase of condensate after the light fraction distillation column decanter, C_{hph} – the heat capacity of the heavy condensate phase flow after the light fraction distillation column decanter, T_{hph} – the flow temperature of the heavy phase of condensate after the light fraction distillation column decanter.

Considering the above, the equation of thermal balance in technological variables takes the form:

$$\begin{aligned} & F_s C_s T_s dt + F_{lph} C_{lph} T_{lph} dt + F_{hph} C_{hph} T_{hph} dt + \\ & F_M C_M T_M dt + F_{CO} C_{CO} T_{CO} dt + \\ & + r \rho S_a L K_0 Q \exp\left(-\frac{E}{RT}\right) dt = F_{exhg} C_{exhg} T_{exhg} dt + \\ & + \rho S_a L C dT + \rho \alpha S \sqrt{2gL + \frac{P}{\rho}} C T dt. \end{aligned} \quad (28)$$

Divide the left- and right-hand sides of equation (28) by dt and neglect the flow of exhaust gases. Taking that into consideration, the equation of thermal balance in technological variables takes the form:

$$\begin{aligned} & F_s C_s T_s + F_{lph} C_{lph} T_{lph} + F_{hph} C_{hph} T_{hph} + F_M C_M T_M + \\ & + F_{CO} C_{CO} T_{CO} + r \rho S_a L K_0 Q \exp\left(-\frac{E}{RT}\right) = \\ & = S_a L C \frac{dT}{dt} + \rho \alpha S \sqrt{2gL + \frac{P}{\rho}} C T, \end{aligned} \quad (29)$$

where S is the area of the cross-section of the regulatory body on the line of selection of reaction fluid.

After linearization of the nonlinear partial mathematical model of the acetic acid reactor for temperature (29), the equation for a stationary mode or a static partial mathematical model of acetic acid synthesis reactor for temperature is built:

$$\begin{aligned} & F_s C_s T_s + F_{lph} C_{lph} T_{lph} + F_{hph} C_{hph} T_{hph} + F_M C_M T_M + \\ & + F_{CO} C_{CO} T_{CO} + r \rho S_a L K_0 Q \exp\left(-\frac{E}{RT}\right) = \\ & = \rho \alpha S \sqrt{2gL + \frac{P}{\rho}} C T. \end{aligned} \quad (30)$$

To calculate the temperature, special methods were used for solving nonlinear equations.

To construct a mathematical model for level, the equation of material balance was built.

$$dm_1 + dm_2 + dm_{lph} + dm_{hph} = dm_v + dm, \quad (31)$$

where dm_1 is the mass entering the reactor with a methanol flow, dm_2 – the mass entering the reactor with a flow of liquid from the separator, dm_v – the mass that accumulates in the reactor of volume V , dm – the mass of reaction fluid discharged from the reactor, dm_{lph} – the mass entering the reactor with a stream of the light phase of condensate after the light fraction distillation column decanter, dm_{hph} – the mass entering the reactor with the flow of the heavy phase of condensate; after the light fraction distillation column decanter.

$$dm_1 = F_M dt, \quad (32)$$

where F_M is the mass flow rate of a methanol flow.

$$dm_2 = F_s dt, \quad (33)$$

F_s is the mass flow rate of bottoms from the separator to the reactor.

$$dm_v = \rho S_a dL, \tag{34}$$

where S_a is the reactor cross-sectional area;

$$dm = F dt = \rho \alpha S \sqrt{2gL + \frac{P}{\rho}}, \tag{35}$$

where F is the flow rate of liquid from the reactor, determined from (11).

$$dm_{lph} = F_{lph} dt, \tag{36}$$

where F_{lph} is the mass flow rate of the light phase of condensate after the light fraction distillation column decanter.

$$dm_{hph} = F_{hph} dt, \tag{37}$$

where F_{hph} is the mass flow rate of the heavy phase of condensate after the light fraction distillation column decanter.

By substituting the specified mass expressions in the material balance equation (31), and dividing the left- and right-hand sides of the equation by dt , expression (31) takes the form

$$F_M + F_s + F_{lph} + F_{hph} = \rho S_a \frac{dL}{dt} + \rho \alpha S \sqrt{2gL + \frac{P}{\rho}}, \tag{38}$$

where S_a is the cross-sectional area of the reactor.

Equation (38) is a nonlinear mathematical model of the acetic acid reactor for level.

After linearization of the nonlinear partial mathematical model of the acetic acid reactor, the equation for a stationary mode or a static partial mathematical model of the acetic acid synthesis reactor for level was built:

$$F_M + F_s + F_{lph} + F_{hph} = \rho \alpha S \sqrt{2gL + \frac{P}{\rho}}. \tag{39}$$

Hence the expression for the reaction mass level in the reactor:

$$L = \frac{(F_M + F_s + F_{lph} + F_{hph})^2}{2g\rho^2\alpha^2 S^2} - \frac{P}{2g\rho}. \tag{40}$$

To derive a partial mathematical model of the acetic acid synthesis reactor for pressure P , the equation of material balance was built for the component that creates the pressure. Pressure in the acetic acid synthesis reactor is generated by carbon monoxide entering the reactor. The gas accumulates in the reactor in free volume and reacts.

$$dm_2 = dm_{vg} + dm_{reac} + dm_3, \tag{41}$$

where dm_2 is the mass of carbon monoxide entering the reactor; dm_{vg} – the mass of carbon oxide accumulated in the free volume of the reactor; dm_{reac} – the mass of carbon monoxide reacting; dm_3 – the mass of exhaust gases.

The components of equation (41) were determined through the technological parameters

$$dm_2 = F_{CO} dt, \tag{42}$$

where F_{CO} is the carbon monoxide flow rate,

$$dm_{vg} = V_2 d\rho, \tag{43}$$

where V_2 is the free volume of the reactor taken by gas; $d\rho$ is the change in gas density caused by a change in pressure

$$d\rho = \frac{M}{RT} dP, \tag{44}$$

where M is the molar mass of carbon monoxide, R is a universal gas constant, T is the temperature of carbon monoxide, P is the pressure of carbon monoxide.

$$dm_p = \beta_p S_a Q_n dt, \tag{45}$$

β_p is the mass exchange coefficient, S_a is the area of contact of gas with a liquid phase, Q_n is the equilibrium concentration of gas dissolved in solution;

$$dm_3 = F_{exhg} dt, \tag{46}$$

where F_{exhg} is the exhaust gas consumption.

Chemical conversion in the reactor could occur only after the gaseous reagent dissolves in the solution inside the reactor. Given that the reaction rate is much higher than the rate of dissolution of gas in the liquid, it can be argued that the speed of the process in the reactor would be determined precisely by the speed of gas dissolution. This process is subject to Henry's law [12]

$$Q_n = \frac{PQ_g}{G} = kQ, \tag{47}$$

where P is the pressure in the reactor, Q_g is the concentration of the reagent in the gas phase, G is Henry's constant, Q is the concentration of the target component, k is the coefficient, Q_n is the concentration of gas dissolved in the solution.

Taking the above into consideration, the equation of material balance takes the form

$$F_{CO} dt = \frac{V_2}{RT} dP + \beta_p S_a \frac{P}{G} dt + F_{exhg} dt. \tag{48}$$

Equation (48) is a nonlinear mathematical model of the acetic acid reactor for pressure.

As a rule, the concentration $Q_g=1$, that is, the gaseous reagent is fed in its pure form. If one neglects F_{exhg} , the consumption of exhaust gases, that is, assuming $F_{exhg}=0$ and dividing equation (48) by dt

$$F_{CO} = \frac{V_2}{RT} \frac{dP}{dt} + \beta_p S_a \frac{P}{G}. \tag{49}$$

After linearization of the nonlinear partial mathematical model of the acetic acid reactor, the equation for a stationary mode or a static partial mathematical model of acetic acid synthesis reactor for pressure is built:

$$F_{CO} = \beta_p S_a \frac{P_0}{G}. \tag{50}$$

Hence the expression for pressure:

$$P = \frac{F_{CO} G}{\beta_p S_a}. \tag{51}$$

The expressions derived relate the initial parameters of the reactor to the input and perturbing parameters.

5. 2. Construction and analysis of the system of equations that form the mathematical model of the reactor of acetic acid synthesis

Having built equations for the concentration of acetic acid, the temperature and level of reaction mass, as well as pressure in the reactor, a system of equations is constructed, which represent a static mathematical model of the acetic acid synthesis reactor:

$$\left\{ \begin{aligned}
 Q &= \frac{F_M Q_M + F_{CO} Q_{CO} + \rho S_a L K_0 Q_{\max} \exp\left(-\frac{E}{RT}\right)}{\rho \alpha S \sqrt{2gL + \frac{P}{\rho}} - F_s + \rho S_a L K_0 \exp\left(-\frac{E}{RT}\right)}, \\
 F_s C_s T_s + F_{lph} C_{lph} T_{lph} + F_{hph} C_{hph} T_{hph} + F_M C_M T_M + \\
 + F_{CO} C_{CO} T_{CO} + r S_a L K_0 Q \exp\left(-\frac{E}{RT}\right) &= \\
 &= \rho \alpha S \sqrt{2gL + \frac{P}{\rho}} CT; \\
 L &= \frac{(F_M + F_s + F_{lph} + F_{hph})^2}{2g\rho^2 \alpha^2 S^2} - \frac{P}{2g\rho}; \\
 P &= \frac{F_{CO} G}{\beta_p S_a}.
 \end{aligned} \right. \quad (52)$$

The results of studying the initial parameters of the constructed mathematical model of the acetic acid synthesis reactor based on methanol carbonylation in the presence of a rhodium catalyst in accordance with the criteria by Fisher, Cochran, and relative error are given in Table 3.

Table 3

Initial parameters that are evaluated to test the static mathematical model of the acetic acid synthesis reactor

Estimated parameter	Criterion	Criterion numerical value
Concentration	Fisher's criterion	1.64
	Cochrane's criterion	0.59
	Relative error	0.000005
	The variance of the errors of the experiments	0.000054
	The variance of inadequacy	0.000083
Temperature	Fisher's criterion	0.004
	Cochren's criterion	0.51
	Relative error	0.00001
	The variance of the errors of the experiments, K ²	0.344
	The variance of inadequacy, K ²	0.0013
Level	Fisher's criterion	0.0000002
	Cochren's criterion	0.67
	Relative error	0.000003
	The variance of the errors of the experiments, m ²	0.0037
	The variance of inadequacy, m ²	7·10 ⁻¹⁰
Pressure	Fisher's criterion	-
	Cochren's criterion	-
	Relative error	-

The adequacy of the model under study is to be performed using the Fisher criterion. Adequacy is justified if the following inequality holds

$$F_{tabl} \langle F_{cr}, \quad (53)$$

F_{tabl} is the Fisher criterion calculated for the model under study; F_{cr} is a tabular value of the Fisher criterion at 5 % significance level.

At the predefined level of significance under a stationary mode, F_{cr} is 3.44. Inequality (53) holds for the studied models of the concentration of acetic acid at the reactor outlet, reactor temperature, the reaction mass level in the reactor. Consequently, the constructed models are adequate to the actual technological process of acetic acid synthesis. Inequality (53) does not hold for the examined pressure model.

The results of the studies performed under the same conditions were checked for statistical reproducibility according to Cochran's criterion G .

$$G_{tabl} \langle G_{cr}, \quad (54)$$

G_{tabl} is the Cochran criterion, calculated for the model under study; G_{cr} is a tabular value of the Cochran criterion at 5 % significance level.

At the predefined level of significance under a stationary mode, G_{cr} is 0.68. Inequality (54) holds for the studied models of the concentration of acetic acid at the reactor outlet, reactor temperature, reaction mass level in the reactor. Thus, the process is reproducible. Inequality (54) does not hold for pressure.

The relative errors for all models under study do not exceed 10 percent.

The comparison of data from a passive experiment with data from actual production, calculated using the examined model, is illustrated in Table 4.

Table 4

The average values of reactor output parameters calculated using the mathematical model under study

Estimated parameter	The method of obtaining the output data	Average value
Concentration	Experimental data from the acetic acid synthesis reactor based on methanol carbonylation in the presence of a rhodium catalyst	0.659
	calculated using the mathematical model under study	0.662
Temperature, K	the reactor of acetic acid synthesis based on methanol carbonylation in the presence of a rhodium catalyst	459.51
	calculated using the mathematical model under study	459.51
Level, m	the reactor of acetic acid synthesis based on methanol carbonylation in the presence of a rhodium catalyst	5.26
	calculated using the mathematical model under study	5.26
Pressure, Pa	the reactor of acetic acid synthesis based on methanol carbonylation in the presence of a rhodium catalyst	2,800,000
	calculated using the mathematical model under study	-

As follows from the data in Table 4, there is a satisfactory agreement between the experimental and calculated data.

5. 3. Incorporating the mathematical model into a computer-integrated control system of the acetic acid synthesis reactor

Fig. 3 shows the functional scheme of automation; Fig. 4 depicts the mnemonic circuit of the control system of the acetic acid synthesis reactor [23].

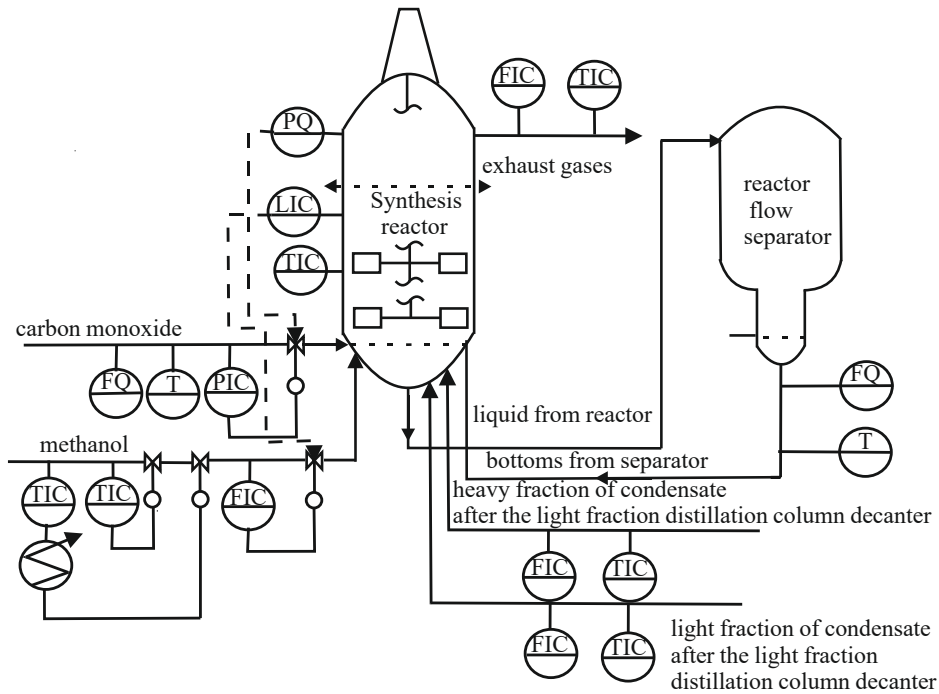


Fig. 3. Functional diagram of automation of acetic acid synthesis reactor control system

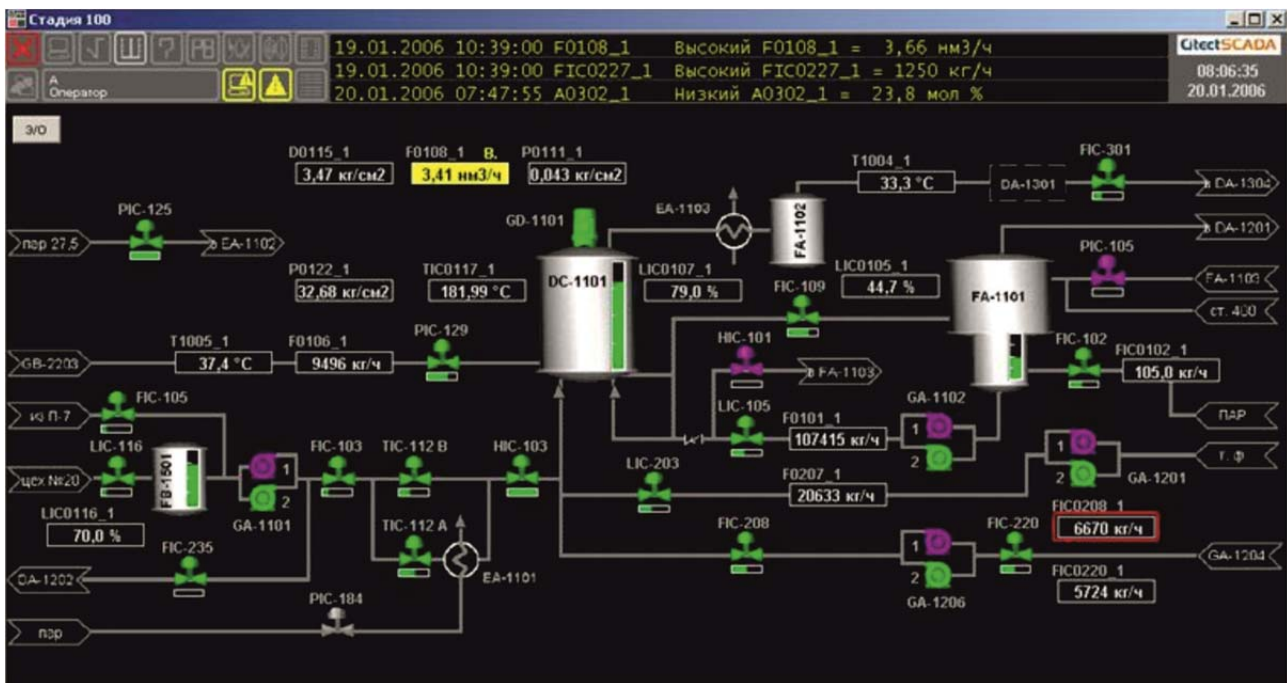


Fig. 4. Mnemonic circuit of a computer-integrated control system of the acetic acid synthesis reactor

According to the presented mathematical model, it is possible to improve the operation of the automatic control system of the acetic acid synthesis reactor under a stationary mode.

6. Discussion of results of constructing a mathematical model of the acetic acid synthesis reactor based on statistical analysis

To improve the operation of automatic control systems for the acetic acid synthesis reactor under a stationary mode, it is

necessary to derive a static mathematical model that binds the input, output, and perturbing reactor parameters. The proposed mathematical model makes it possible to determine the value of the concentration of acetic acid at the reactor outlet (16), the temperature of the reaction mixture (30), the level of the reaction mixture in the reactor (40), and the amount of pressure in the reactor (51). Equations describing the value of the concentration of acetic acid at the reactor outlet, the level of the reaction mixture, and pressure in the reactor are linear algebraic ones. The equation describing the temperature determination of the reaction mixture in the reactor is nonlinear. Static mathematical model (52) adequately, with satisfactory reproducibili-

ty and accuracy, describes the technological processes that take place in the reactor of acetic acid synthesis. This is evidenced by the statistical analysis of the model (Table 3). Fisher's and Cochran's criteria, investigated for the output parameters, accept values less than their critical ones. The Fisher criterion's tabular value at a 5 % significance level is 3.44. For the concentration of acetic acid, the Fisher's criterion $F(0.05)=1.64<3.44$, for the temperature of the reaction mass – $F(0.05)=0.004<3.44$, for the reaction mass level – $F(0.05)=0.013<3.44$. The tabular value of the Cochran criterion at a 5 % significance level is 0.68. For the concentration of acetic acid, the value of Cochran criterion $G(0.05)=0.59<0.68$, for the temperature of the reaction mass – $G(0.05)=0.51<0.68$, for the level of reaction mass – $G(0.05)=0.67<0.68$.

For a stationary mode of the acetic acid synthesis reactor, the range of change in the input data is: for $F_M=(8,950\div 9,175)$ kg/h, and for $F_{CO}=(9,350\div 9,620)$ kg/h. However, for the mathematical model of pressure in the reactor, the criteria of Fisher and Cochran exceed their critical values. This circumstance indicates an obvious drawback of the proposed model. The direction of further research related to its elimination should be focused on a more accurate study of the physical processes occurring in the reactor when bubbling methanol with carbon monoxide. Such a study could clarify the static mathematical model of pressure in the acetic acid synthesis reactor. For the process under study, one can say that the pressure adjustment is secondary.

7. Conclusions

1. Based on material and thermal balances, equations of the concentration of acetic acid, the temperature, level of reaction mass, the pressure in the reactor of acetic acid synthesis dependent on the amount of methanol and carbon monoxide fed under a stationary mode have been built. The equations also take into consideration the perturbing factors

that affect the system. Analytical description for the concentration of acetic acid, the level of reaction mass, the pressure in the reactor was obtained in the form of linear algebraic equations, and for the temperature in the reactor – in the form of a nonlinear equation. The system of composed equations is a static mathematical model of the reactor of acetic acid synthesis.

2. It is shown that the model makes it possible to calculate with satisfactory accuracy the value of the concentration of acetic acid, the temperature and level of reaction mass in the reactor under a stationary mode. Data from a passive experiment were used to check the adequacy of the model and reproducibility of the obtained results. The relative error of the calculated output parameters of the static mathematical model of the acetic acid synthesis reactor did not exceed 10 % of the value. The statistical analysis showed satisfactory adequacy and reproducibility for the investigated output parameters of the static mathematical model of the reactor. The results from constructing the mathematical model used for statistical analysis based on the criteria of Fisher and Cochran showed their less values than the critical ones. The developed static mathematical model of technological processes could be used to improve the operation of the automatic control system for the acetic acid synthesis reactor under a stationary mode.

3. Based on the calculations, it is possible to incorporate the mathematical model constructed into a computer-integrated control system for the acetic acid synthesis reactor.

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