Математична модель динаміки процесу гомогенної реакції першого порядку в каскаді реакторів ідеального змішування побудована рівнянням зміни мольної частки речовини з часом і зміною внутрішньої енергії ідеального потоку речовини. Розрахунок по моделі здійснено за методом Рунге-Кута третього порядку для реакції гідролізу оцтового ангідриду. Отримано профілі температур динаміки процесу, розраховано вартісний показник

Ключові слова: динаміка процесу, каскад реакторів ідеального змішування, оцтовий ангідрид, ступінь перетворення

Математическая модель динамики процесса гомогенной реакции первого порядка в каскаде реакторов идеального смешения построена уравнением изменения мольной доли вещества со временем и изменением внутренней энергии идеального потока вещества. Расчет по модели осуществлен методом Рунге-Кута третьего порядка для реакции гидролиза уксусного ангидрида. Получены профили температур динамики процесса, рассчитан стоимостной показатель

Ключевые слова: динамика процесса, каскад реакторов идеального смешения, уксусный ангидрид, степень превращения

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MATHEMATICAL MODELING OF THE DYNAMICS OF HOMOGENEOUS REACTIONS IN THE CASCADE OF PERFECT MIXING REACTORS

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1. Introduction

Design of technological processes and application of mathematical tools makes it possible to receive optimal conditions for their conducting, parameters of construction. That is why the development of mathematical models for technological processes, verification of their effectiveness and adequacy play important role in the further development of technologies. Modeling (in the broadest sense) is one of the basic methods of research in many areas of knowledge as with its help one can provide a reliable assessment of characteristics of quite complex systems. As an appropriate method, mathematical modeling is used to substantiate decisions in various areas of engineering. Existing and designing systems can be effectively explored by employing mathematical models (analytical and simulating), which are realized on modern computers. Specifically, in the area of chemical reaction equipment they have become the much-required tools for the experimenter to work with a model of the system. One of the typical chemical reactors with a set of nonlinear dynamic characteristics is the perfect mixing reactor of continuous action (PMR-C). Of special scientific and practical interest is examining it in real time by the means of mathematical modeling. The development of mathematical model, however, is often complicated by the limited knowledge of the course of the process, high sensitivity and nonlinear behavior of reactor [1]. On the other hand, mathematical models are convenient to apply for analysis of the system's behavior, the mechanism of action, the simulation of the process.

In this regard, it is interesting to explore the known process of hydrolysis of acetic anhydride to the acetic acid in PMR-C by mathematical means. World production of acetic acid is currently over 4.0 million t per year. Acetic acid is one of the basic products of industrial organic synthesis and its derivatives are widely used in food, chemical and other industries. That is why examining the hydrolysis process of acetic anhydride in PMR-C with the application of modern mathematical models is not only a relevant task that requires solution. It also allows predicting the optimal parameters for carrying out the process, as well as cost indicators.

2. Literature review and problem statement

Studying the stationary reactions with a single path in PMR-C has been the subject of research by many authors. Multicriteria problems were partially proposed, but the convenience and ease of applying these analytical tools and the required calculation of additional criteria significantly limits the simple search for solution [2]. Article [3] presents a mixed mathematical model for the reaction between hydro-

gen peroxide and sodium thiosulfate based on the modified equations by hierarchical principle of modeling. The mathematical description provided, however, was not confirmed by experimental data and, therefore, it cannot be employed to describe actual processes. Authors of papers [4, 5] proposed a mathematical model to represent a first order homogeneous reaction that occurs in the *N* sequentially connected PMR-C. The model is formulated based on the material and energy balance under condition of adiabatic mode. In this case, the authors used defined parameters, that is, experimental data on the distribution of time over which the mixture had been in a cascade of the examined PMR-C. It is necessary to note that in the course of reaction, the speed of flows of two liquid phases does not change. The model proposed, however, does not allow considering dynamics of the process. Article [6] examines mathematical models of various types for quasi-stationary state under unisothermal and non-adiabatic modes. The main difficulty of calculation in this case is connected with the necessity of finding a large number of specified parameters by experimental means, which narrows their universality. Effective control over the concentration of reagent in PMR-C can be achieved only through an accurate model. Paper [7] attempts to facilitate difficulties in modeling by applying the techniques of "artificial intelligence" based on neural, fuzzy and neural-fuzzy methods. Actually, the simulation results demonstrate effectiveness of these very modeling methods. However, soft computing techniques, namely with the use of neural, fuzzy and neural-fuzzy methods, can describe the process only approximately, by employing data sets at the input and output of the system. Other authors [8] applied the classical model of PMR-C under isothermal mode to describe the reaction of hydrogen iodide formation. Thermodynamic properties of the reagents are calculated as a ratio of intensive variables to those extensive. As stated by the authors, for the chosen process at clearly predefined parameters, the model is quite simple, but has a narrow scope of applicability. Article [9] presents two different strategies to control and manage temperature in PMR-C. Underlying the proposal is a combination of new algorithm for social-political optimization and the concept of gain planning. The calculation is carried out using the method of least squares and approaches of fuzzy logic. The results showed that both proposed controllers were more accurate and demonstrated high performance efficiency compared to the fixed proportional-integral-differential regulator. Paper [10] addresses modeling of PMR-C with regard to the typical nonlinear system with lumped parameters. A mathematical model is built based on material balance in the form of a system of ordinary differential equations. The calculation was conducted for certain stationary state; optimal volumetric flow rate was determined. However, the model can neither analyze dynamics of the process nor define its thermodynamic parameters.

It appears relevant to develop such a mathematical model for the dynamics of PMR-C by whose means it would be easy to calculate basic parameters of the course of the process and perform its simulation.

3. The aim and tasks of the study

The aim of present study is to explore the dynamics of process of first order homogeneous reaction in the cascade of PMR-C by mathematical means. To predict quantitative characteristics for the process of acetic anhydride hydrolysis.

To achieve the set aim, the following tasks are to be solved:

– to develop a mathematical model of the dynamics of process of first order homogeneous reaction in the cascade of PMR-C and verify its adequacy;

– to calculate by the mathematical model the process of acetic anhydride hydrolysis, to define a change in temperature over time for each reactor;

– to analyze an impact of the reaction mixture volume to the depth of the course of the process;

– to assess relative estimated cost of conducting the process of acetic anhydride hydrolysis depending on the temperature of the process.

4. Basics of mathematical modeling of the dynamics of homogeneous reactions in PMR-C

First, a mathematical model makes it possible to significantly reduce the large amount of data by expressing them through a function, which can be defined by only a few parameters. Second, it provides for the prediction of progress of the process under these or other conditions, to detect the optimal ones. In addition, using it enables analysis of technological scheme from the technical-economic point of view. Moreover, based on the results of mathematical modeling, it is possible to predict possible additional costs and to define recommendations on how to eliminate them [11, 12].

Mathematical model of the dynamics of homogeneous reaction in PMR-C is built based on the thermal and material balance. It is represented in the form of equations of a change in the molar share of substance over time and a change in the inner energy of ideal flow of substance.

In this case, the following assumptions are taken into account:

1) physical magnitudes of the substance are constant;
2) total reaction volume is constant;
3) the level of fluid in the reactors is the same;
4) homogeneous reaction is the reaction of first order;
5) flow rate for each of the reactors is the same.

$$\frac{dn_i}{d\tau} = F_i^{in}C_i^{in} - F_i^{out}C_i^{out} - r(T,n_i)V,$$

$$U\left(T,n_i\right) = \sum n_i(c_{v,i}(T-T_0)+u_{0,i}),$$

where F_i^{in}, F_i^{out} is the volumetric substance consumption at the inlet and outlet of reactor, respectively, m^3/h; C_i^{in}, C_i^{out} is the concentration of reagent at the inlet and outlet of reactor, respectively, mol/m^3; $r(T,n_i)$ is the speed of reaction, mol/m^3hour; V is the reaction volume, m^3; $u_{0,i}$ is the molar inner energy of substance at temperature T_0, J.

5. Calculation by the mathematical model of the process of acetic anhydride hydrolysis

The mathematical model devised is for the first time applied to calculate the cascade line of reactors, to understand their action depending on the parameters of long-known

process of acetic anhydride hydrolysis with the aim of its optimization. Therefore, the main task was to conduct a computational experiment for the process of acetic anhydride hydrolysis in sequentially connected PMR-C (n=5) (Fig. 1).

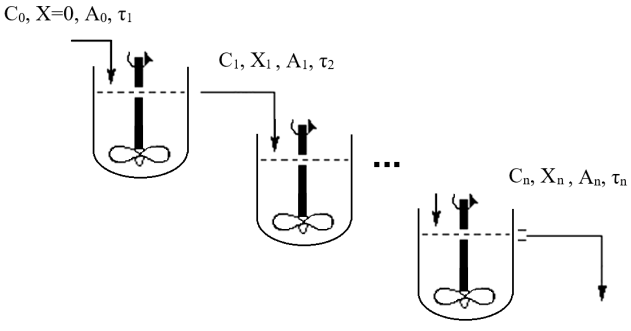

Fig. 1. General scheme of cascade perfect mixing reactor of continuous action

In Fig. 1, A_0, A_1,..., A_n is the molar flow rate, mol/h; C_0, C_1,..., C_n is the concentration of reagent, mol/m^3; X_0, X_1,..., X_n is the conversion of reagent; τ_1, τ_2,..., τ_n is the time constant, h; V_0, V_1,..., V_n is the volume of each reactor, m^3.

Relation between the conversion of reagents and molar flow rate is expressed through equation:

$$A_i = A_0(1-X_i).$$

Molar balance of the reagent, given its consumption in the process, is calculated as:

$$A_i^{in} = A_i^{out} + (-r_n)V_n.$$

Then the volume of each reactor can be expressed as:

$$V_n = \frac{A_i^{in} - A_i^{out}}{(-r_n)}.$$

By consistently substituting the values of A_1, A_2, ..., A_n and considering $\tau = V/F = VC/A$, we shall calculate molar balance of the reagent through concentrations for each reactor.

For the reactor with defined volume, the conversion degree of acetic anhydride is expressed as a differential equation of first order and is calculated by the change in its concentration over time (reaction by acetic anhydride of first order) [13]. Thus, the concentration of acetic anhydride at the ouylet was calculated by expression:

$$C_{ac.an.(i)(out)} = \frac{C_{ac.an.(i)(in)}}{1+\frac{k\cdot V}{A}} = \left(1+\frac{k\cdot V}{A}\right)^{-1} C_{ac.an.(i-1)(out)},$$

where $C_{ac.an.(i)(out)}$ is the concentration of acetic anhydride at the outlet of reactor, mol/m^3; $C_{ac.an.(i)(in)}$ is the concentration of acetic anhydride at the inlet to reactor, mol/m^3, A is the molar flow rate, mol/h, V is the volume of reactor, k is the Arrhenius constant, s^{-1}:

$$k(T) = k_0 \cdot e^{\frac{-E_A}{RT}}.$$

We shall reduce the mathematical model to a system of ordinary differential equations:

$$\frac{dC_{ac.an.(i)}}{d\tau} = \frac{F_i^{вх}C_{ac.an.(i)(in)} - F_i^{вих}C_{ac.an.(i)(out)}}{V_{(i)}} - k_0 C_{ac.an.(i)} e^{\frac{-E_A}{RT}},$$

$$\frac{dT_{(i)}}{d\tau} = \frac{mc_p(T_0 - T_{(i)}) - \Delta H(T)\cdot k_0 C_{ac.an.(i)} e^{\frac{-EA}{RT}} + Q_{in}}{V\rho C_p}.$$

Calculation by the model was conducted by the Runge-Kutta method of third order at the following initial data: the number of rectors: five, of volume 150, 200, 300, 400, 500 ml, respectively. Thermal consumption for the reactor insulation was neglected (Q_{in}).

6. Results of calculating the process of acetic anhydride hydrolysis by the mathematical model

In order to verify the adequacy of mathematical model to describe the experimental data, we calculated a change in the concentration of acetic anhydride over time by the model based on the initial data that correspondes to experimental data [14] (Fig. 2). Initial concentration of acetic anhydride is 400 mol/m^3. In order to achieve a reliable result in the calculation by the mathematical model, while calculating a total volume of reactor, we considered the mean weighted value of reaction volume magnification factor:

$$\overline{\alpha} = \sqrt{\Sigma V_i \alpha_i / \Sigma V_i},$$

where α_i is the degree in the increase of reaction volume for each reactor.

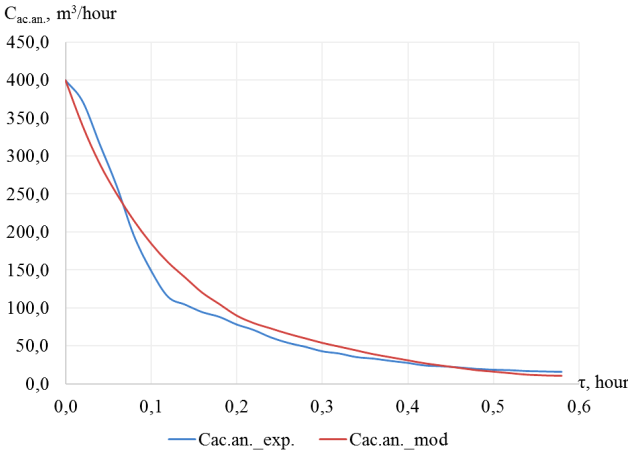

Fig. 2. Comparison of dependence of change in the concentration of acetic anhydride in the perfect mixing reactor over time by the model to experimental data

The adequacy of calculation by the mathematical model to the experimental data was tested by the Fisher criterion whose computed value turned out to be less than the tabular one, which indicates the reliability of calculation by the mathematical model.

It is important to predict temperature change over time for each of the reactors with defined volume. As a result of calculation by the mathematical model, we obtained values of change in temperature over time (Fig. 3).

Fig. 3 shows that temperature in the reactor over time increases by gradient, and then it takes a constant value. Thus, the optimal value of temperature for the calculated cascade of reactors is 303–373 K.

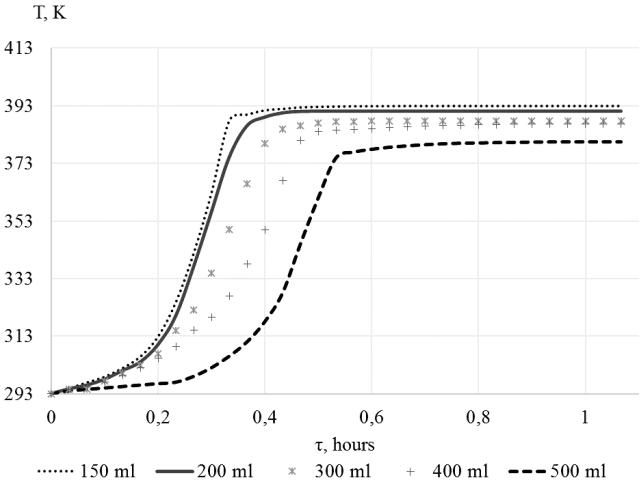

Fig. 3. Dependence of change in temperature in the process of acetic anhydride hydrolysis over time in the cascade of perfect mixing reactors

An essential characteristic of any technological process is its cost. Thus, for the estimated cost of PMR-C we considered the relative indicator of consumption, taking into account the requirement to achieve the 90 % conversion of acetic anhydride. The overall estimated costs per year were determined according to equation [15] (as the amount spent both on PMR-C of the defined volume and the heat cost):

$$B(T)=1.4\cdot V+29.2\cdot\left(T-298\right).$$

Provided that a reactor receives the 1-molar solution of acetic anhydride, then in the case of the 90 % conversion, the reactor should yield the 0.1 molar solution, with a flow rate of 1 m^3/s, E_A=50.2 kJ/mol:

$$\frac{C_{ac.an.(i)(in)}}{C_{ac.an.(i)(out)}}=1+\frac{k\cdot V}{A},$$

hence, we find the relationship between volume and temperature,

$$V=\frac{A\left(\frac{C_{ac.an.(i)(in)}}{C_{ac.an.(i)(out)}}-1\right)}{k},$$

$$V=6.7\cdot10^{-6}e^{6038/T},$$

$$T=\frac{6038}{\ln\left(\frac{6.7\cdot10^{-6}}{V}\right)},$$

then

$$B(T)=9.4\cdot10^{-6}e^{6038/T}+29.2\cdot\left(T-298\right),\ \text{UAH thousand},$$

$$B'(T)=29.2-0.05675\cdot T^{-2}\cdot e^{6038/T},\ \text{UAH thousand},$$

whose minimum is achieved at T=341 K and amounts to UAH 1.7 million.

The cost of conducting the process of acetic anhydride hydrolysis depending on the temperature change (Table 1), calculated for the total reaction volume, is shown in Fig. 4.

Table 1

Impact of temperature on the cost of the process of acetic anhydride hydrolysis in the cascade of perfect mixing reactors of continuous action

No.	T, K	Cost, UAH mln.	No.	T, K	Cost, UAH mln.
1	293	8,23	17	350	1,81
2	295	7,19	18	354	1,88
3	297	6,31	19	358	1,95
4	299	5,57	20	362	2,03
5	302	4,65	21	366	2,12
6	306	3,72	22	370	2,22
7	310	3,05	23	374	2,32
8	314	2,58	24	378	2,42
9	318	2,24	25	382	2,52
10	322	2,01	26	386	2,63
11	326	1,86	27	390	2,74
12	330	1,77	28	394	2,85
13	334	1,72	29	398	2,96
14	338	1,71	30	402	3,07
15	342	1,72	31	406	3,18
16	346	1,76	32	410	3,29

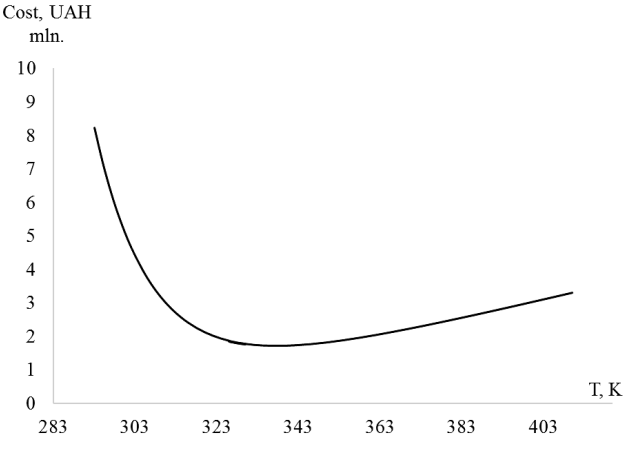

Fig. 4. Dependence of the cost of conducting the process of acetic anhydride hydrolysis on the temperature in the cascade of perfect mixing reactors of continuous action

As illustrated in Fig. 4, the cost of the process of acetic anhydride hydrolysis reduces with changing the temperature from 293 K to 341 K, and then it gradually increases. It is the optimum in Fig. 4 that shows the counteraction of material balance (at low temperatures) and thermal balance

(at high temperatures), which affects technical indicators, and, through them, the cost of the process.

The total amount of substance at the outlet from the cascade of reactors is calculated by formula:

$$\Sigma n_i = n_{0ac.an.}(1+\alpha X_i).$$

Taking into account the Mendeleyev-Klapeyron equation and the reaction kinetics equation ($r = kC_{ac.an.(i)}$), we receive

$$n_{0ac.an.}(1+\alpha X_i) = kPV(1-X_i)/RT.$$

As a result of calculation for each of the reactors and the cascade of reactors, we shall obtain dependence of a degree in the increase of reaction volume on the conversion degree (Fig. 5).

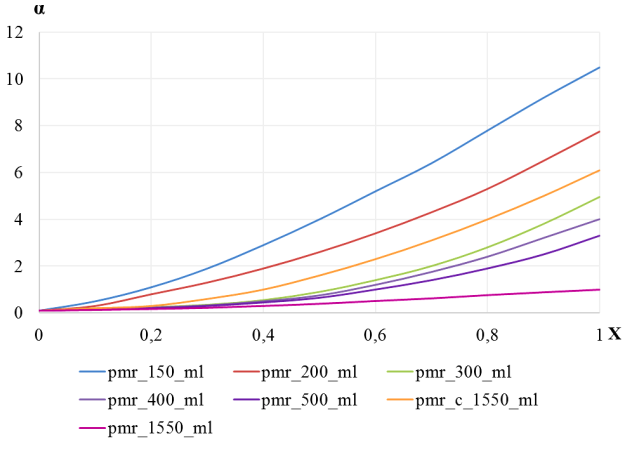

Fig. 5. Dependence of a degree in the increase of reaction volume on the conversion degree

7. Discussion of results of the computational experiment

A perfect mixing reactor of continuous action (PMR-C) is a typical chemical reactor with a set of nonlinear dynamic characteristics. It is important to study it in real time by the means of mathematical modeling. In the present study, by the means of mathematical modeling, we explored dynamics of the process, making it possible to define the parameters of the process at any time, and to observe the process as a whole. Results of the calculation by the mathematical model provide information about the optimum temperature for conducting the process, as well as its cost. The obtained data might be used to optimize the real objects at a laboratory scale.

It is obvious that with the increased volume of the mixture, the reaction rate grows. At the same time, the speed of achieving the necessary degree of conversion decreases. In other words, at the increased reaction volume, the depth of the course of reaction decreases. Thus, Fig. 5 shows a decrease in the degree of reagent conversion in some reactors of volume 150 ml (pmr_150_ml), 200 ml (pmr_200_ml), 300 ml (pmr_300_ml), 400 ml (pmr_400_ml), 500 ml (pmr_500_ml). Fig. 5 also shows the curve for the cascade of perfect mixing reactors of total volume 1550 ml (pmr_c_1550 ml) and the perfect mixing reactor of volume 1550 ml (pmr_c_1550_ml). For the cascade of reactors, the speed of achieving maximum degree of conversion compared with one perfect mixing reactor of the same volume is much higher. That is why it is advisable to recommend, for considerable reaction volumes in industry, applying the cascade of reactors or the ideal-displacement reactor.

The obtained data might be used to optimize the real objects at a laboratory scale. We plan to conduct additional field experiments and analyze the applicability of mathematical model to the selected process. In the future, it may become necessary to observe the process at industrial scale and to assess effectiveness of the mathematical model for the real process.

8. Conclusions

1. We examined the dynamics of the process of first order homogeneous reaction in the cascade of perfect mixing reactors of continuous action (PMR-C) by the mathematical means. A mathematical model of the dynamics of the process is built based on the material and thermal process taking into account the kinetics of the process. This is a system of ordinary differential equations. The adequacy of calculation by the mathematical model to the experimental data was verified by the Fisher criterion whose computed value turned out to be less than the tabular one, which indicates the accuracy of calculation by the mathematical model.

2. We calculated by the mathematical model the process of acetic anhydride hydrolysis in PMR-C by the Runge-Kutta method of third order. The temperature profiles were obtained for the dynamics of the process of acetic anhydride hydrolysis for 5 sequentially connected PMR-C reactors. The temperature gradient in the reactor increases over time; consequently, it takes on a constant value. Thus, for the calculated cascade of reactors, the optimal value of temperature is 303–373 K.

3. We analyzed effect of the volume of reaction mixture to the depth of the course of the process. It was found that with an increase in the reaction volume, the degree of reagent conversion decreases. For the cascade of reactors, the speed of achieving maximum degree of conversion compared with one perfect mixing reactor of the same volume is much higher. That is why it is advisable to recommend, for considerable reaction volumes in industry, applying the cascade of PMR-C.

4. We calculated the value of cost for conducting the process of acetic anhydride hydrolysis depending on the change in temperature; its minimum value is achieved at 341 K and amounts to UAH 1.70 million per year.

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