Computer modeling system of chemical processes in tubular reactors

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Abstract. A computer modeling system of chemical processes in tubular reactors has been developed. The system helps researchers (technologists, designers) to determine rational modes of operation of tubular reactors, which ensure compliance with the requirements for efficiency indices of chemical processes carried out by various mechanisms. The system includes a module for setting the mechanism of the chemical process, modules for structural synthesis and parameters adjustment of the dynamic mathematical model of the chemical process, a library of finite-difference methods for solving the equation of convective transfer of substance, a module for calculating distributions of concentrations of raw substances and reaction products along the length of the reactor and during time, a module for generating and storing a modeling report. The information ware of the system includes databases of geometric parameters of tubular reactors and procedural ranges of technological parameters of chemical processes. Databases allow the system to be adjusted according to the tubular reactor brand. The results of the modeling are presented in tables, 2D and 3D graphs of the concentration distributions of raw substances and reaction products. The system has been tested according to the data of thermal decomposition of ethylene, benzene oxidation, pyrolysis of mixture of ethane, butane and propane, production of vinyl acetate. The testing results have confirmed the adequacy of the proposed mathematical description of chemical processes in tubular reactors and the operability of the created software solution.

1. Introduction
Chemical processes carried out in tubular reactors are the main stages of many chemical productions. Catalytic reforming in gasoline and aromatic hydrocarbon production, sulfur oxide oxidation in sulfuric acid production, carbon oxide conversion, ammonia synthesis, ethylene polymerization, ethylene oxide hydration, and many others are examples of such productions. Reactor operation largely determines plant throughput, quality and cost of produced chemical products [1]. However, tubular reactors are complex design and control objects. They are characterized by distribution of state parameters, non-stationary state, multi-component of inlet and outlet flows and complexity of interaction of components constituting these streams. Various physical and chemical processes (gas-liquid flow movement, heating/cooling, chemical transformations) occur simultaneously in tubular reactors. Multiple complex nonlinear relationships exist between state parameters of outlet flows, on the one hand, and geometric parameters of equipment, thermophysical properties of reaction mass, kinetic and mode parameters of process, on the other hand. There is incomplete information about the object and the disturbances acting
on it. Therefore, operators make control decisions on the basis of their own production experience and experimentally selected technological regulations. This is inevitably accompanied by errors and leads to an increase in the share of defects in the products, overspend of expensive raw materials, an increase in energy consumption, time required for the plant change-over to a new task, and a decrease in throughput. The profitability and competitiveness of production is reduced as a result. Overcoming this production challenge is impossible without the use of computer modeling methods and technologies. Computer modeling allows us to determine rational modes of operation of an object and control the object based on its mathematical model.

Static and dynamic mathematical models of individual chemical processes in tubular reactors are presented in the literature [2–6]. Analysis of the models has showed that they are deterministic and include the equations of mass and heat balances, the kinetic equations, and the equations of temperature dependence of reaction rate constants. The tanks-in-series model and plug flow reactor model are used to describe the flow structure [2, 4]. Isothermal and non-isothermal process conditions are modeled [4, 6]. Software solutions for modeling chemical technological processes and systems (e.g. chemical simulators Chemcad, Aspen Plus, Aspen Hysys) include modules for calculating compositions and temperatures of outlet flows, and reagent conversion degrees in liquid phase and gas phase continuous tubular reactors [7]. The plug flow reactor model is used to calculate mass and heat balances of chemical processes. Various thermal modes of operation of tubular reactors (isothermal, adiabatic, with a given heat load, etc.) are simulated. The practice of using the software solutions for modeling various chemical processes in tubular reactors, designing appropriate equipment confirms their high efficiency and compliance with the level of modern chemical production. However, the software modeling solutions are largely focused on tubular reactor design problems. They have a user interface that is complex for production staff, limited ability to calculate non-stationary modes of operation of tubular reactors and 3D visualization of modeling results (component concentration fields), relatively high cost of acquisition. Thus, the development of a computer modeling system for chemical processes in tubular reactors to solve the problems of creating new high-efficiency chemical processes and improving existing chemical processes is relevant. Chemical processes carried out by various mechanisms take place in tubular reactors. Therefore, the modeling system should be adjusted to the mechanisms and characteristics of chemical processes, implement structural and parametric synthesis and numerical analysis of mathematical models of chemical processes, 2D and 3D visualization and preservation of modeling results.

2. Information description of the modeling object. Statement of investigation problem

Analysis of mechanisms and hardware and process design of various chemical processes carried out in continuous tubular reactors has been performed. It has made it possible to form an information description of the chemical process in the tubular reactor as a modeling object. The information description includes vectors of input parameters $X$, variable parameters $V$ and output parameters $Y$. The information description of the chemical process in the tubular reactor is shown in figure 1.

![Figure 1. Information description of the chemical process in the tubular reactor as a modeling object.](image)

The tubular reactor is characterized by geometric parameters – length $L$ (m) and diameter $D$ (m). The length of the reactor is significantly (more than 20 times) larger than its diameter. The volumetric flow rate through the reactor is $Q$ (l min$^{-1}$).
The inlet flow contains \( n_R \) of raw substances. Volume molar concentration of \( l \)-th raw substance \( A_l \) in the inlet flow is \( C_{i,n} \), \( l = 1 \ldots n_R \) (mol l\(^{-1}\)). Concentration of \( l \)-th component (raw substance, target product or byproduct) in the reactor in initial time point \( t \) equals \( C_{i,n} \), \( l = 1 \ldots n \) (mol l\(^{-1}\)). Here \( n \) is the total number of components in the system. A chemical process involving \( m \) homogeneous chemical reactions (without phase transitions) takes place in the reactor. Each reaction follows the mechanism shown in figure 1. In the scheme of reaction \( \nu_{s,q} \) is amount of \( l \)-th raw substance \( A_l \), which enters into \( s \)-th reaction \((l = 1 \ldots n_R)\), or amount of \( l \)-th substance \( A_l \), which is formed during \( s \)-th reaction (amount of product of \( s \)-th reaction, \( l = n_R + 1 \ldots n \)). Both the raw substances and the products of other reactions may be the starting substances of each reaction. Therefore \( \nu_{s,q} \) is the amount of \( q \)-th product of the other reaction (differ from \( s \)-th reaction), which enters into \( s \)-th reaction \((q = n_R + 1 \ldots n, \ q \neq l)\).

Kinetics of \( s \)-th reaction is characterized by a rate constant \( k \) \((\text{mol} \text{l}^{-1} \text{ min}^{-1})\), where \( p \) is order of the reaction. The rate constant depends on the temperature in the reactor \( T \) (°C). Preexponential factor \( k_0 \) \((\text{mol} \text{l}^{-1} \text{ min}^{-1})\) and energy of activation \( E_\nu \) (J mol\(^{-1}\)) are parameters of this dependence (kinetic parameters of \( s \)-th reaction).

Reactionary mixture moves in reactor at average linear velocity \( u \) (m min\(^{-1}\)). Velocity \( u \) depends on flow rate \( Q \) and cross-sectional area of the reactor \( S = 0.25\pi D^2 \) (m\(^2\)). Current concentration of \( l \)-th component of the reactionary mixture \( C_l \) (mol l\(^{-1}\)) varies along the length of the reactor (by coordinate \( x \) (m)) and during time \( t \) (min).

The outlet flow contains \( n \) components (raw substances, products of reactions). Volume molar concentration of \( l \)-th component in the outlet flow is \( C_{l,\text{out}} \), \( l = 1 \ldots n \) (mol l\(^{-1}\)). Conversion degree of \( l \)-th raw substance is \( \chi_l \), \( l = 1 \ldots n_R \) (%).

The investigation problem of the modes of operation of this chemical technological object is as follows:

using mathematical model of a chemical process in a tubular reactor \( Y = F(\{X,V,x,t\}) \), it is necessary to determine values of variable technological parameters \( C_{i,\text{in}} \in [C_{i,\text{min}},C_{i,\text{max}}] \), \( l = 1 \ldots n_R \), \( T^* \in [T_{\text{min}},T_{\text{max}}] \), which for given input parameters \( X \) ensure maximum output concentration of the target product \( A_{n_R+1} \) while meeting requirements to the conversion of the raw substances and meeting limits for the concentrations of the byproducts \( A_l \), \( l = n_R + 2 \ldots n \) in outlet flow:

\[
C_{l,\text{out}}(X,V^*) = \max_{\text{var } F(\{X,V,x,t\})} C_{l,\text{out}}(X,V), \quad \chi_l(X,V^*) \geq \chi_l^{\text{min}}, \quad C_{l,\text{out}}(X,V^*) \leq C_{l,\text{out}}^{\text{max}}
\]

where \( V^* = \{C_{i,\text{in}},l = 1 \ldots n_R\} \) are the best values of the variable technological parameters; \( V^{\text{min}} = \{C_{i,\text{in}}^{\text{min}},l = 1 \ldots n_R\} \) are minimum allowable procedural values of variable technological parameters; \( V^{\text{max}} = \{C_{i,\text{in}}^{\text{max}},l = 1 \ldots n_R\} \) are maximum permissible procedural values of variable parameters; \( \chi_l^{\text{min}} \) is the minimum allowable conversion degree of \( l \)-th raw substance \((l = 1 \ldots n_R)\) (%); \( C_{l,\text{out}}^{\text{max}} \) is the maximum permissible output concentration of \( l \)-th byproduct \((l = n_R + 2 \ldots n)\), ensuring that there is no toxic release (mol l\(^{-1}\)).

3. Functional structure and mathematical ware of the computer modeling system

The investigation problem is solved using the developed computer modeling system of chemical processes in tubular reactors. The functional structure of the modeling system is shown in figure 2.
Figure 2. Functional structure of computer modeling system (examples of researcher interface elements are shown in Russian, since the Russian version of the system has so far been developed).
The modeling system includes a subsystem for structural and parametric synthesis and numerical analysis of mathematical models of chemical processes in tubular reactors, an information subsystem for adjustment of the modeling system according to geometric and technological parameters of the object and saving modeling results, an interface of the chemical process researcher, an interface of the modeling system administrator. Each factual database included in the information subsystem is based on a relational data model. Databases have been developed with use of the SQLite database management system. Modeling system software has been developed with use of the Visual Studio visual object-oriented programming environment in C# language. The modeling system allows us to fill up the databases and the solution method library using the system administrator interface.

For the brand of the reactor \( M \), chosen by researcher, values of length \( L \) and diameter \( D \) of the reactor are determined using a database of geometric parameters of reactors. Procedural restrictions for reactor flow rate \( Q \), \( Q \) are determined using a database of procedural ranges of technological parameters. The researcher sets the mechanism of the chemical process by entering a number \( n \) of raw substances and symbols \( A \), \( l = 1 \ldots n \) of raw substances, number \( n \) of products (number of components in the system is \( n = n + n \)), schemes of \( m \) chemical reactions. Amounts of raw substances and products \( \nu \) are entered. If a reversible chemical reaction is present in the chemical process, it is introduced as two simultaneous reactions – direct reaction and reverse reaction. Procedural restrictions for input concentrations of raw substances and reactor temperature \( V \), \( V \) are determined using a database of procedural ranges of technological parameters. Researcher enters input concentrations \( C \), \( l = 1 \ldots n \) and reactor temperature \( T \), belonging to the created ranges. The chemical process is modeled at these values.

Structural (topological) model of the chemical process is formed according to the specified mechanism of the chemical process. The topological model includes a matrix of stoichiometric coefficients of chemical reactions \( \alpha \) and matrix of partial orders of chemical reactions \( p \). These matrices are formed by the following rules:

- \( \alpha = -\nu \), \( p = \left| \alpha \right| \) if substance \( A \) is a raw substance for the \( s \)-th chemical reaction;
- \( \alpha = \nu \), \( p = 0 \) if substance \( A \) is a product of the \( s \)-th chemical reaction;
- \( \alpha = p = 0 \) if substance \( A \) does not participate in the \( s \)-th chemical reaction.

The formed topological model is the basis for the structural synthesis of a functional mathematical model describing the chemical process in a tubular reactor. The following assumptions have been taken in the modeling:

- the flow structure in the reactor is described by a hydrodynamic model of plug flow reactor (the plug mode of the reactionary mixture movement without mixing along the flow is modeled, the components of the mixture are uniformly distributed in each cross-section of the flow);
- each chemical reaction is an elementary act of chemical conversion \( s = 1 \ldots m \), formal kinetics laws are applied to describe the kinetics of such reaction; reaction rate constants depend on temperature according to the Arrhenius law;
- the density of the reactionary mixture does not vary along the length of the reactor (volumetric flow rate of the mixture in each cross-section of the reactor is the same);
- chemical process takes place under isothermal conditions (temperature is maintained by temperature control system of tubular reactor at constant value) [8].

Mathematical model of chemical process in tubular reactor describing various mechanisms of chemical processes has been developed using the block principle of mathematical models construction and taking into account the above assumptions. The mathematical model includes the equations of mass balances on each of components of reactionary mixture, the kinetic equations, and the equations of dependence of rate constants of chemical reactions on temperature. The system of equations is supplemented by appropriate initial and boundary conditions. Equations of mass balances have been
written based on the law of mass conservation and the principle of independence of chemical reaction rates, kinetic equations have been written based on the law of mass action:

$$\frac{\partial C_l}{\partial t} = -u \frac{\partial C_l}{\partial x} + \sum_{i=1}^{n} (\alpha_{s,i} \cdot r_s), \quad l = 1...n, \quad 0 < x \leq L, \quad 0 < t \leq \Theta$$

(2)

$$r_s = k_s \prod_{i=1}^{L} C_{p,i}^{\alpha_{s,i}}, \quad s = 1...m$$

(3)

$$k_s = k_{s,0} \exp \left[-\frac{E_{As}}{8.31(T + 273.15)}\right], \quad s = 1...m$$

(4)

$$u = 10^{-3} QS^{-1}, \quad \tau = Lu^{-1}, \quad \Theta = f(\tau)$$

(5)

$$C_{l,0} = C_{l,0}, \quad l = 1...n, \quad 0 \leq x \leq L; \quad C_{l,0} = \begin{cases} C_{l,\in}, & l = 1...n_R, \quad 0 < t \leq \Theta \\ 0, & l = n_R + 1...n, \quad 0 < t \leq \Theta \end{cases}$$

(6)

$$C_{l,\in} = C_{l,\in}^0, \quad l = 1...n, \quad C_{l,\in} = \left(C_{l,\in} - C_{l,\in}^0\right)C_{l,\in}^{-1}100, \quad l = 1...n_R$$

(7)

where \( \Theta \) is the time for modeling (min); \( r_s \) is the rate of \( s \)-th chemical reaction (mol l\(^{-1}\) min\(^{-1}\)); \( \tau \) is the residence time of the mixture in the tubular reactor (displacement time) (min).

The structural synthesis of the mathematical model of the chemical process carried out by given mechanism includes:

- determining the structural parameter values of a generalized model (2)–(6) \( n, m, \alpha_{s,i}, p_{s,i} \);
- formation of a corresponding system of balance and kinetic equations.

This system consists of \( n \) component mass balance equations (2), \( m \) kinetic equations (3), \( m \) Arrhenius equations (4), \( n \) initial conditions \( u \) \( n \) boundary conditions (6). No more \( m \) source members present in each mass balance equation.

Adjustment of parameters of mathematical model consists in determination of coefficient values of equations (2)–(5) and right parts of initial and boundary conditions (6) on the basis of vector of input parameters \( X \) and vector of variable parameters \( V \).

The synthesized mathematical model of chemical process in tubular reactor is a system of evolutionary one-dimensional non-uniform partial differential equations with constant coefficients \( u, \alpha_{s,i}, k_s \). Equations have hyperbolic type, first order by spatial coordinate \( x \) and time \( t \). The system is closed by uniform or non-uniform initial conditions and non-uniform Dirichlet boundary conditions. The nonlinearity of the mathematical model (in the presence of second and/or third order chemical reactions in the chemical process) is its main feature. Nonlinearity is due to power dependence of reaction rates \( r_s \) on the current concentrations of components \( C_l \) (nonlinearity of right parts of kinetic equations). Therefore, the solution of this mixed boundary value problem can be obtained only by numerical methods. The finite difference method has been used for numerical integration of the partial differential equations in computer modeling. The method is characterized by simplicity, versatility, well-developed theory (in particular, theory of stability of finite-difference schemes), and flexibility with regard to boundary conditions of the problem. Multiple finite-difference schemes are available for partial differential equations that differ in types and characteristics.

Uniform grid \( \Omega_{\Delta x, \Delta t} = \{ x_i = i\Delta x, i = 0...M, t^j = j\Delta t, j = 0...N \} \), approximating computing area \( \Omega(x, t) = \{ 0 \leq x \leq L, 0 \leq t \leq \Theta \} \), is shown in figure 3. Here \( x_i, t^j \) are coordinates of the grid node \((i, j)\) over reactor length and time, which are discrete analogues of continuous independent variables \( x \) and \( t \); \( \Delta x \) is the grid step along the length of the reactor (m); \( \Delta t \) is the time grid step (min); \( M = \frac{L}{\Delta x} \) is the number of grid steps along the length of the reactor; \( N = \frac{\Theta}{\Delta t} \) is the number of time grid steps;
\[
C_{li}^{j} = C_{lj}(x, t), \quad C_{li}^{j+1} = C_{lj}(x, t + \Delta t), \quad C_{li}^{j+1} = C_{lj}(x, t + \Delta x, t + \Delta t) \quad \text{are concentrations of } l\text{-th component in grid nodes } (i,j), (i \pm 1, j), (i, j+1), (i \pm 1, j+1) \quad \text{accordingly (grid functions introduced by projecting continuous functions onto the grid).}
\]

Figure 3. Grid approximating computing area and generalized grid stencil for two-layered in time finite-difference schemes.

The partial differential equations (2) are the equations of convective transfer of substances involved in chemical reactions. Therefore, the library of methods for solving the convective transfer equation of substance has been developed for computer modeling of different mechanisms of chemical processes and compositions of material flows in tubular reactors with different geometric and technological parameters. The library includes 8 explicit and implicit finite-difference methods.

Explicit methods are:
- the ‘explicit left corner’ method with forward-time finite difference and up-flow finite difference (the method has the first order of approximation error over both the time and the reactor length);
- the Lax method with forward-time finite difference and centered-space finite difference, and spatial averaging of the value of the grid function in the central grid node on the current time layer of the grid (the method has the first order of approximation error);
- the ‘cross’ method with centered-time and centered-space finite differences (the method has the second order of approximation error over both the time and the reactor length);
- the two-step Lax–Wendroff method, which is a combination of the Lax method and the ‘cross’ method (the method has the second order of approximation error) [9, 10].

Stability analysis of explicit finite-difference schemes using the Fourier–Neumann method (spectral criterion of stability) has been performed. It has showed that explicit finite-difference schemes are stable when the enhanced (strict) Courant–Friedrichs–Lewy condition \(Ku < 1\) is met, if convective transfer equations with source members including desired functions (component concentrations) are solved [10]. Here \(Ku = u\Delta t\Delta x^{-1}\) is the Courant number dependent on grid steps.

Implicit methods are:
- the ‘implicit left corner’ method with backward-time finite difference and up-flow finite difference (the method has the first order of approximation error);
- the ‘implicit right corner’ method with backward-time finite difference and down-flow finite
difference (the method has the first order of approximation error);  
- the Euler method with backward-time finite difference and centered-space finite difference (the method has the first order of approximation error over the time and the second order of approximation error over the reactor length);  
- the Crank–Nicholson method with backward-time finite difference and semi-sum of centered-space finite differences on the current and previous time grid layer (the method has the second order of approximation error) [9, 10].

Stability analysis of implicit finite-difference schemes using the Fourier–Neumann method has showed that the ‘implicit left corner’ method, the Euler method, and the Crank–Nicholson method are unconditionally stable (at any values of the Courant number). The ‘implicit right corner’ method is stable if the condition $Ku > 1$ is met.

Mathematical models of chemical processes in tubular reactors are in most cases nonlinear and always include boundary conditions. Therefore, the stability of finite-difference schemes implemented in the modeling system is, by the Lax equivalence theorem, a necessary (but not sufficient) condition for convergence of the resulting numerical solutions (concentration fields). The numerical solution accuracy order is equal to the approximation error order of the finite-difference method.

The computational algorithm is generated by the modeling system for the finite-difference method chosen by the researcher. The algorithm includes the following steps. Parameters $u$, $\tau$, $\Theta$, $k_s$, $s = 1, \ldots, m$ are calculated by equations (4) and (5). Initial and boundary (at the reactor inlet) values of reactionary mixture component concentrations are formed in accordance with finite-difference approximations of initial and boundary conditions (6). Component concentration distributions along the reactor length and during time are calculated. Component concentrations at the reactor outlet and conversion degrees of raw substances are determined by equations (7). Ratio $C_l^0 = 0.5(C_l^i + C_l^j)$, $l = 1, \ldots, n_x$ is used in approximation of initial conditions for concentrations of raw substances in grid node with coordinates $(0, 0)$. This increases the accuracy of the calculation [9]. The procedure for calculating component concentration fields depends on the solution method you select. Thus, the generalized recurrence equation for two-layered in time one-step explicit and implicit finite-difference schemes is as follows:

$$
\frac{C_{ji}^{i+1} - \delta C_{ij}^j}{\Delta t} - (1 - \delta)0.5(C_{ji+1}^{i+1} + C_{ji}^j) = 0.5u \left( \beta \left[ C_{ji+1}^{i+1} + C_{ji}^j \right] (2 - \gamma) \left[ C_{ji+1}^{i+1} + C_{ji}^j \right] \right) + (1 - \beta) \times \left[ \left( \frac{C_{ji+1}^j + C_{ji}^j}{\Delta \alpha} + (2 - \gamma) \left( C_{ji+1}^{i+1} + C_{ji}^j \right) \right) + \sum_{s=1}^n \sum_{k=1}^n \left[ \beta \left( C_{ji+1}^{i+1} + (1 - \beta) C_{ji}^j \right) \right] \right],
$$

$$
i = 1, \ldots, M - 1, \quad j = 0, \ldots, N - 1.
$$

Adjusting coefficients $\delta, \beta, \gamma$ allow us to obtain from the generalized equation (8) finite-difference equations for various finite-difference methods, as shown in table 1.

Table 1. Finite-difference methods and corresponding adjusting coefficients.

| Method number | Method name                        | Adjusting coefficients of the equation (8) |
|---------------|------------------------------------|------------------------------------------|
| 1             | ‘Explicit left corner’ method       | $\delta = 1$, $\beta = 0$, $\gamma = 0$ |
| 2             | Lax method                         | $\delta = 0$, $\beta = 0$, $\gamma = 1$ |
| 3             | ‘Implicit left corner’ method       | $\delta = 1$, $\beta = 1$, $\gamma = 0$ |
| 4             | ‘Implicit right corner’ method      | $\delta = 1$, $\beta = 1$, $\gamma = 1$ |
| 5             | Euler method                       | $\delta = 1$, $\beta = 1$, $\gamma = 1$ |
| 6             | Crank–Nicholson method             | $\delta = 0.5$, $\beta = 0$, $\gamma = 1$ |
Equation (8) is converted into a formula for explicit methods. This formula calculates the concentration value \( C_{ij}^{n+1} \) of \( i \)-th component in \( j \)-th reactor cross-section in \( (j+1) \)-th time moment by known concentrations of this component and other components in \( j \)-th time moment. Equation (8) is a system of algebraic equations for implicit methods. The solution of this system allows calculating concentration values of \( i \)-th component in all reactor cross-sections in \( (j+1) \)-th time moment. Each equation of the system of algebraic equations in the case of the ‘implicit right corner’ method, as in the case of explicit methods, is converted into a formula for calculating the concentration value \( C_{ij}^{n+1} \). The non-linearity of the discrete analog of the total source term in equation (8) does not cause computational difficulties when calculating using explicit methods and the ‘implicit right corner’ method. This nonlinearity results in nonlinearity of the system of algebraic equations solved at each time step using the Euler method and the Crank–Nicholson method. The two-step technique is implemented in the modeling system for this case. The technique involves the following steps: linearization of the system of algebraic equations using the Newton–Raphson method; solving the obtained linearized system for concentration corrections at each iteration using the Thomas algorithm. The Thomas algorithm ensures high computation efficiency (the number of arithmetic operations on each time layer of the grid is proportional to the number of parameters sought). The Thomas algorithm is applicable because the linearized system coefficient matrix for concentration corrections is tridiagonal.

The Lax method, the ‘cross’ method, the Lax–Wendroff method, the Euler method, and the Crank–Nicholson method use centered-space (three-point) finite differences to approximate derivatives in convective members of balance equations. Therefore, these methods allow us to calculate concentrations of components only in internal nodes \((i = 1 \ldots M - 1)\) of each time layer of the grid. In this case, difference schemes with up-flow finite differences are used to calculate the concentrations of components in boundary nodes \((i = M)\) on each time layer of the grid. These are the ‘explicit left corner’ and ‘implicit left corner’ methods when calculated by explicit methods and implicit methods, respectively.

Modeling system generates computational algorithm and sets its parameter limits

\[
P_{\text{sol}} = \{ \Delta x_0, \text{Ku}, \varepsilon_{\text{max}}, q_{\text{max}} \}.
\]

Here \( \Delta x_0 \) is initial grid step along the reactor length, determined depending on the reactor length \( L \) (m); \( \varepsilon_{\text{max}} \) is a maximum permissible error in calculating the concentration of the target product (\%); \( q_{\text{max}} \) is the maximum number of iterations when checking convergence and ensuring the specified accuracy of the solution. The Courant number is determined depending on the chosen solution method taking into account the stability condition. Initial time grid step \( \Delta t_0 \) (min) is calculated by the formula:

\[
\Delta t_0 = \Delta x_0 \mu^{-1} \text{Ku}.
\]

The stability of finite-difference schemes is only a necessary condition for convergence of numerical solutions according to the Lax theorem. Therefore, the iterative procedure of checking the convergence of calculations and obtaining a numerical solution with error \( \varepsilon \leq \varepsilon_{\text{max}} \) has been implemented in the modeling system [8]. This procedure is based on the Runge method. The procedure is to grid the system sequentially (by dividing its steps \( \Delta x \) and \( \Delta t \) in half on each iteration) and comparing the target product concentration distributions along the reactor length and during time calculated on grids with steps \( \Delta x \), \( \Delta t \) and \( 0.5 \Delta x \), \( 0.5 \Delta t \). Comparison is performed by calculation of reduced error of target product concentration calculation \( \varepsilon \). This error is calculated as the ratio of the absolute error calculated by the Runge–Romberg formula in the root-mean-square norm to the maximum product concentration \( C_{ni+1}^{\text{max}} \)

\[
\varepsilon = \frac{1}{2^{n-1}} \left[ \frac{1}{N^M} \sum_{j=1}^{M} \sum_{k=1}^{N} \left( | C_{j, k}^{n+2} - C_{j, k}^{n+1} | \right)^{1/2} \right]^{1/2} \frac{100}{C_{ni+1}^{\text{max}}} \tag{9}
\]

where \( v \) is the order of accuracy of the method, chosen as the smallest order from the orders of accuracy in time and spatial coordinate (coordinate along the reactor length); \( M^*, N^*, C_{ni+1}^{*} \) are number of grid steps along the reactor length, number of time grid steps and array of target product concentration values
at grid steps $\Delta x, \Delta t$; $C_{n+1}$ is an array of target product concentration values at steps $0.5\Delta x, 0.5\Delta t$.

Iterative loop ends when condition $\varepsilon \leq \varepsilon_{\text{max}}$ is completed. Modeling system generates solution method parameters $P_{\text{sol}}$, including calculated grid step values $\Delta x'$, $\Delta t'$, calculated error $\varepsilon$ at these steps, and the number of step divisions in half $q^*$, at which the specified calculation accuracy is ensured. Also computer calculation time $\tau_{\text{calc}}$ evaluating computation efficiency is determined. If the specified calculation accuracy is not reached by $q_{\text{max}}^*$ grid step divisions in half, the corresponding message is displayed to the researcher, and he can choose a different solution method.

The modeling results are displayed on the researcher interface in the form of tables, 2D and 3D graphs of the concentration distributions of raw substances, target product and byproducts along the reactor length and/or during time. Input data $X, V$ and results of calculations $P = \{P_{\text{react}}, P_{\text{func}}, P_{\text{sol}}\}$, $Y$ are saved as a modeling report in the modeling results database.

4. Results and discussion

Adequacy check of mathematical models of chemical processes in tubular reactors has been performed. Data from the process of thermal decomposition of ethylene into carbon and hydrogen, the process of benzene oxidation (to produce maleic anhydride), the process of pyrolyzing a mixture of ethane, butane and propane (to produce ethylene and propylene), the process of producing vinyl acetate (from acetylene and acetic acid) have been used [11]. The output concentrations of the target products of the chemical processes have been calculated by varying the input concentrations of the raw substances and the temperatures in the reactors within the procedural ranges. The calculated values of the output concentrations of the target products have been compared with the measured values. The results of the check have confirmed the adequacy of mathematical models by the Fisher criterion and standard deviation (not more than 8%).

The modeling system is adjusted according to the mechanism of the chemical process (number of reactionary mixture components, chemical reaction schemes) and the tubular reactor brand.

System testing has been performed for various mechanisms and kinetic parameters of chemical processes, geometric and technological parameters of tubular reactors. Computer modeling results of the chemical process carried out by mechanism: $A_1 + A_2 \rightarrow A_3$, $A_3 \rightarrow A_4 + A_5$ are shown in figure 4. Input data for modeling: $L = 300 \text{ m}$, $D = 1 \text{ m}$, $Q = 1000 \text{ l min}^{-1}$, $C_{A_{1,0}} = C_{A_{2,0}} = 2 \text{ mol l}^{-1}$, $T = 200 \text{ °C}$, $C_{A_{3,0}} = C_{A_{4,0}} = 0$; $k_{A_{1}} = 5530 \text{ l mol}^{-1} \text{ min}^{-1}$, $E_{A_{1}} = 48650 \text{ J mol}^{-1}$, $k_{A_{2}} = 2 \cdot 10^{13} \text{ min}^{-1}$, $E_{A_{2}} = 137000 \text{ J mol}^{-1}$.

The Lax method has been used to calculate concentration distributions of components $A_1$, $A_2$, $A_3$ along the reactor length and during time ($\Delta x_0 = 2 \text{ m}$, $Ku = 0.95$, $\Delta t_0 = 1.49 \text{ min}$, $\varepsilon_{\text{max}} = 0.4 \%$, $q_{\text{max}}^* = 10$). Calculation has been executed for $q' = 2$ iterations ($\Delta x' = 0.5 \text{ m}$, $\Delta t' = 0.372 \text{ min}$). Error of concentration calculation of product $A_3$ is $\varepsilon = 0.24 \%$. Calculation time $\tau_{\text{calc}} = 125 \text{ ms}$ for a PC with CPU speed 3.6 GHz.

Figure 4 shows that changes of the output concentrations of the raw substance $A_1$ and product $A_3$ in time start from the moment of time $t = 235.5 \text{ min}$. This time is equal to the residence time of the mixture in the reactor. Graphs of dependences of output concentrations on time are stepped. The shape of the graphs repeats the step disturbance of the input concentration of the substance $A_1$. Thus, the tubular reactor is a transport lag element. But the output concentration of the substance $A_3$ reaches the maximum value $0.168 \text{ mol l}^{-1}$ (conversion degree is equal 92%). This value is less than the input concentration of the substance $A_1$, as it is consumed in the first chemical reaction. Maximum output concentration of the product $A_3$ $0.145 \text{ mol l}^{-1}$ does not reach the maximum possible value $1.83 \text{ mol l}^{-1}$ (if $r_2 = 0$). This is because the product $A_3$ is consumed in the second reaction. Concentration of the raw
substance $A_2$ at the end of the modeling time ($t = \Theta = 472$ min) is reduced along the reactor length due to consumption in the first reaction. Graph of concentration dependence of the product $A_3$ on the reactor length at each modeling time moment has a parabolic shape. Maximum value of concentration 0.891 mol l$^{-1}$ is achieved in the reactor cross-section with coordinate $x = 45.5$ m. The parabolic shape of dependence of concentration on the reactor length is due to the following. Rate of formation of the product $A_3$ in the first reaction exceeds the rate of its consumption in the second reaction in the reactor section with length $x = 45.5$ m. Then the consumption rate of the product $A_3$ becomes greater than the rate of its formation, as a sufficient amount of the product $A_3$ is present in the reactor to substantially accelerate the second reaction. Dependence of maximum output concentration of the product $A_3$ on temperature in the reactor is also parabolic. Concentration increases from 0.569 mol l$^{-1}$ (at temperature $T = 100$ °C) till 1.41 mol l$^{-1}$ (at temperature $T = 157$ °C). Concentration decreases at temperature $T > 157$ °C. It is necessary to carry out the simulated chemical process at the reactor temperature $T^* = 157$ °C, to maximize the yield of the product $A_3$.

![Figure 4. Example of computer modeling results of chemical process.](image)

Thus, the results are consistent with the theory of chemical processes in isothermal plug flow tubular reactors and expert assessments. This confirms the operability of the created software solution for this
class of modeling objects.

5. Conclusion
The computer modeling system of chemical processes in tubular reactors has been developed. The system implements methods of structural and parametric synthesis and numerical analysis of deterministic dynamic mathematical models for investigation of chemical processes carried out by various mechanisms in continuous reactors described by plug flow reactor model. The system is adjusted for the number of components (raw substances, products) of processes, schemes and kinetic parameters of chemical reactions, geometric and technological parameters of reactors. Synthesized computer models allow the calculation of component concentration distributions along the reactor length and during time and efficiency indices (conversion degree of raw substances, output concentrations of products) depending on input concentrations of raw substances and temperature conditions of the process. Modeling results are rendered as tables, 2D and 3D graphs, and written (with input data) to Excel files.

The results of the modeling system testing based on the data of industrial chemical processes have confirmed the operability of the software solution. The system can be used as a flexible, effective tool to analyze causal relationships in chemical processes and to choose rational modes of chemical processes to meet requirements to their efficiency indices. Developed solution method library has been integrated into the computer modeling system of hardware flexible extrusion processes for quality control of multi-assortment polymeric materials [12]. The library is used to numerically solve the equations of the plug flow reactor models that are elements of cell-type hydrodynamic models with recycles for calculating the residence time of polymers in extruders of various types and configurations [13].

The system is used to train technologies of numerical modeling of chemical technological objects with distributed parameters.

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