Development of a program for optimizing chemical reactions

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Abstract. A program is designed to optimize chemical reactions, allowing to carry out modeling and optimization of catalytic reactions has been developed. Implemented export and import of the reaction model and calculation of the direct kinetic problem. As an object of study, the catalytic reaction of the synthesis of benzyl butyl ether is considered. A mathematical reaction model is given and the concentrations of all reaction components are calculated.

1. Introduction

A comprehensive analysis of the chemical reaction involves modeling and subsequent optimization of the conditions. The goal of optimization is to introduce a process into production or to intensify an existing industrial process. The basis for optimizing the conditions is a kinetic model that describes the speed of the stages and the rate of change in the concentration of reagents. For each chemical reaction, optimality criteria are characteristic. It is relevant to develop a database of kinetic models of chemical reactions, optimality criteria, and a program that implements optimization algorithms.

The object of study in this work is the catalytic reaction of the synthesis of benzylalkyl ethers (figure 1). The product is benzylbutyl ether, which is widely used for flavoring perfumery, cosmetics and food products. [1].

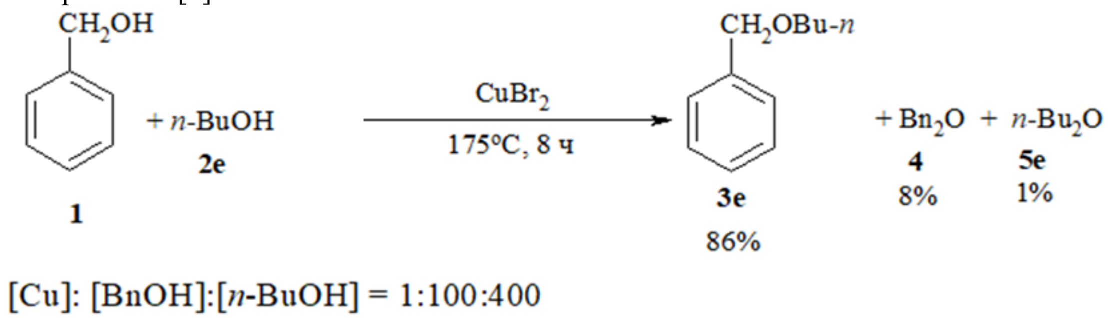

Figure 1. Reaction of the synthesis of benzylalkyl ethers.

A kinetic model of the reaction was developed in the work [2]. Physical experimental setup for the chemical reaction limits the minimum and maximum temperature values 140°C≤T≤200°C, time up to 800 min.

2. Structure of the chemical reaction optimization program

To optimize the conditions for the catalytic reaction, information on the mathematical model of the reaction is needed. Data on the mathematical model is stored in a database. Optimization criteria are also determined from the database. Variable parameters and restrictions on variable parameters are set. In the case of dynamic parameters, the optimal control problem is reduced to the problem of multicriteria optimization (MCO) by decomposition of a given time interval into equal intervals. For each interval, the optimal value is determined[3]. The obtained MCO problem is solved by the NSGA-II algorithm or the mesh algorithm In the event that the solution does not meet the specified characteristics, optimization criteria, variable parameters and restrictions on variable parameters are reviewed.

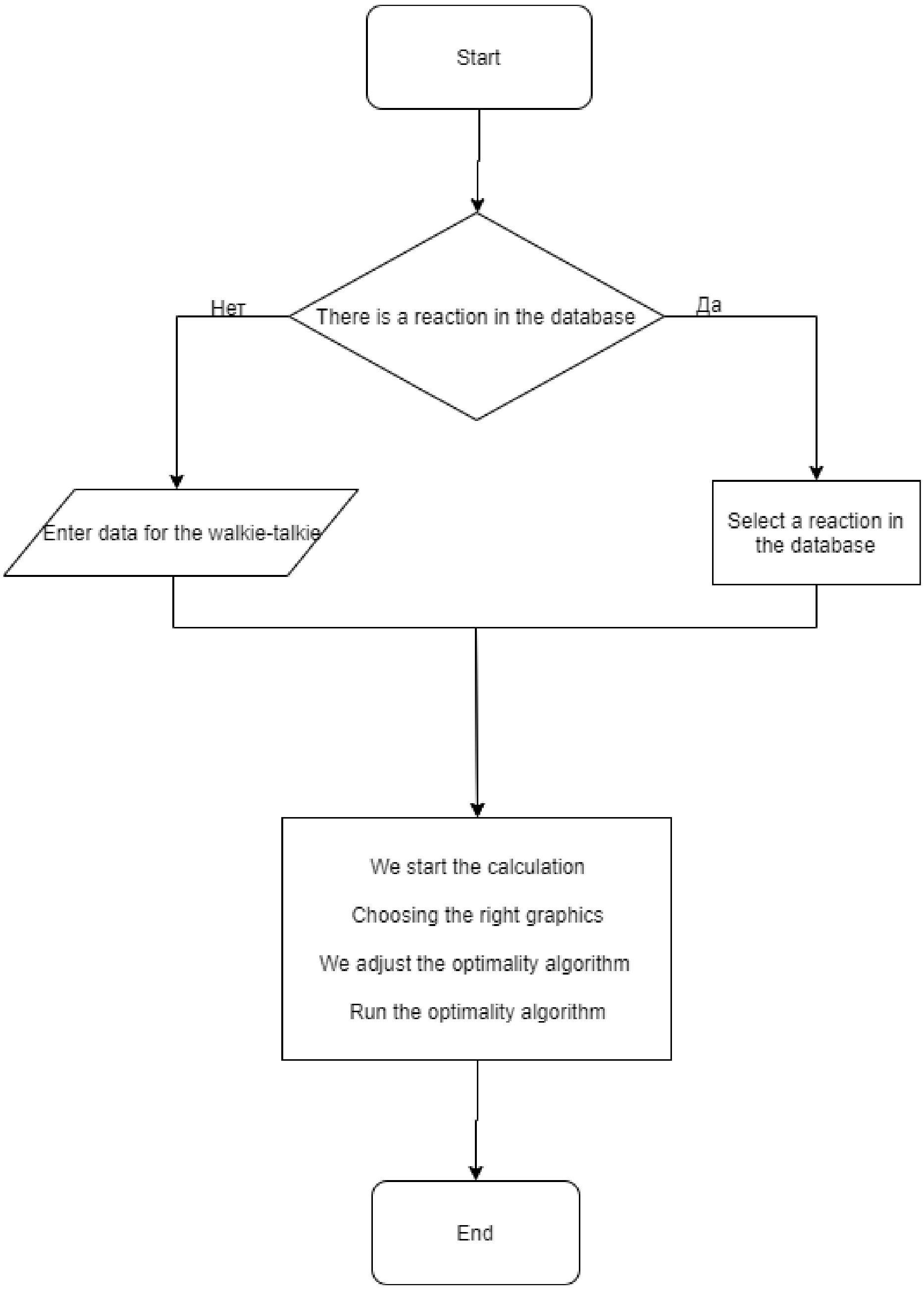

Figure 2. Block diagram of the chemical reactions optimization program.

The operation of the program is presented in figure 2. User can select a reaction from the database for analysis. The reaction is selected in the form of its kinetic model: a scheme of chemical transformations, a mathematical model in the form of a system of differential equations for the change in the concentration of components over time, values of kinetic parameters, and initial data. The test reaction can be selected from existing or create a new one. According to the selected or introduced reaction, calculation and selection of the display of graphs of changes in the concentration of substances over time is carried out. For this reaction, it is possible to calculate single-criterion-multicriteria optimality in time or temperature in given ranges. As a result of program calculations, we obtain the extremum of optimality criteria.

The program is written in Python in the PyCharm development environment [4-6]. To solve the system of differential equations used Runge-Kutta method of scipy library [7, 8].

In figure 3 shows the ER diagram of the database of the chemical reaction optimization program. As the DBMS, MySql, a relational storage model, was used [9, 10]. Implemented 5 tables in a one to many relationship (figure 1). The main table is reaction. On which the rest depend on secondary keys. The table **reaction**, contains attributes: id reaction identifier (integer), name reaction name (text), type_of reaction type (integer), begin_data initial data (text). The table **math_model** contains attributes: id_react identifier from the reaction table (integer), diff_system system of differential equations (text), preexp_factors data for each substance (text), speed_factors equations for reaction rate (text). Storage of the mathematical reaction model is implemented in the form of text attributes diff_system and speed_factors. Differential equations containing changes in the concentration of reagents over time and kinetic equations of stage velocities, respectively. The table **reaction_optimality** contains attributes: id_react identifier from the reaction table (integer), name optimality name (text), formula formula (text), optime optimality direction (int). The table **general_reaction_optimality** contains attributes: id_react identifier from the reaction table (integer), name of the optimality criterion (text), formula (text). The table **variable_parameters** contains attributes: id_react identifier from the reaction table (integer), name parameter name (text), variables designation (text), type_of parameter type (int).

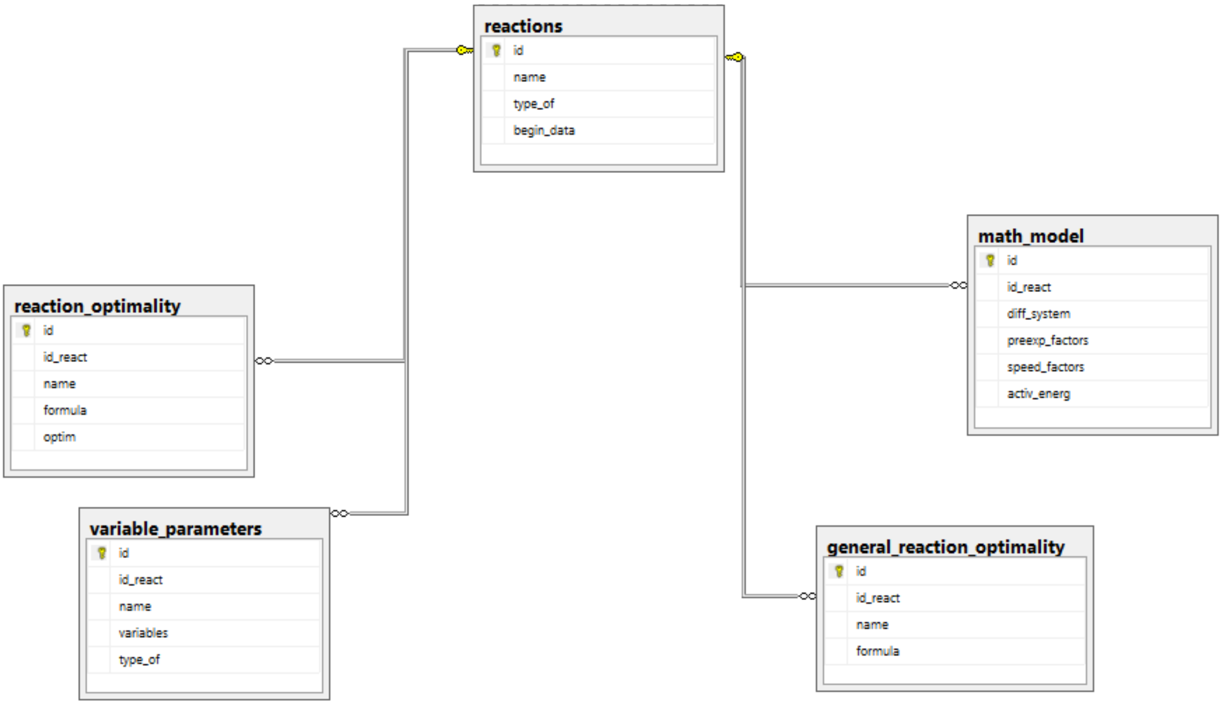

Figure 3. ER-diagram of a database program for optimization of chemical reactions.

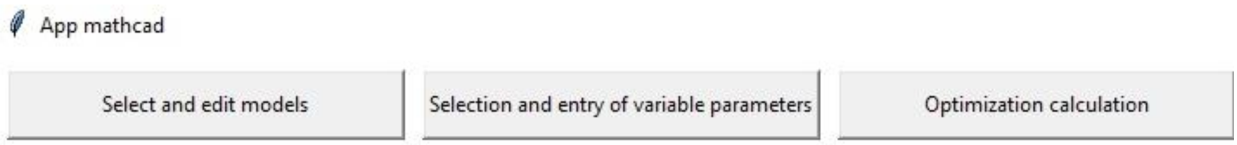

Figure 4. The main menu.

In figure 4 shows the main menu of the chemical reaction optimization program. It is represented by three modules: selection and editing of models, selection and input of variable parameters, calculation of optimization [11, 12].

3. Results

At the first stage, it is necessary to choose a reaction and its mathematical model (Figure 4). The mathematical model is represented by a system of differential equations for the change in the concentration of substances over time, depending on the kinetic equations of the reaction stages (1).

$$\frac{dy_i}{dt} = \sum_{j=1}^{J} \nu_{ij} w_j (k_j, k_j^0, E_j, T, y_i), \quad i = 1,...,I \tag{1}$$

with initial conditions: at $t=0,\ y_i(0)=y_i^0$; where t is time, min; ν_{ij} is the stoichiometric coefficient; J is the number of stages; y_i is the concentration of substance, involved in the reaction, mol/l; I is the number of substances; w_j is the speed of the j-th stage, 1/min; k_j is the rate constant for the stages, 1/min; E_j, is the activation energy of the stages, kcal/mol; T is temperature, K; k_j^0 is pre-exponential factor, 1/min.

The determined kinetic parameters of the system of differential equations (1) are k_j^0, E_j and, k_j accordingly to the Arrhenius equation. Unknown parameters are determined from the condition of minimization of the functional (2) [13, 14].

$$\sum_{p=1}^{P} \sum_{i=1}^{I} \gamma_i (y_{pi}^e - y_{pi}^r) \to \min, \tag{2}$$

where y_{pi}^e and y_{pi}^r – experimental and calculated values of the concentrations of the components, γi – the weight coefficient, I – the number of substances, P – the number of measurement points in time for the observed substances during the reaction.

For the process under consideration, a scheme of chemical reactions was proposed (Table 1).

Table 1. Scheme of the reaction of benzyl butyl ether synthesis.

№	**Scheme**
1	$PhCH_2OH(\mathbf{Y_1}) + CuBr_2(\mathbf{Y_2}) \to [PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{Y_3})$
2	$[PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{Y_3}) + BuOH(\mathbf{Y_4}) \to [PhCH_2OBu]H^+ [CuBr_2(OH)]^-(\mathbf{Y_5})$
3	$[PhCH_2OBu]H^+ [CuBr_2(OH)]^-(\mathbf{Y_5}) \to PhCH_2OBu(\mathbf{Y_6}) + H_2O(\mathbf{Y_7}) + CuBr_2(\mathbf{Y_2})$
4	$[PhCH_2]^+[CuBr_2(OH)]^-(\mathbf{Y_3}) + PhCH_2OH(\mathbf{Y_1}) \to [PhCH_2OHCH_2Ph]^+ [CuBr_2(OH)]^-(\mathbf{Y_8})$
5	$[PhCH_2OHCH_2Ph]^+ [CuBr_2(OH)]^-(\mathbf{Y_8}) \to PhCH_2OCH_2Ph (\mathbf{Y_9}) + H_2O(\mathbf{Y_7}) + CuBr_2(\mathbf{Y_2})$
6	$BuOH(\mathbf{Y_4}) + CuBr_2(\mathbf{Y_2}) \to [Bu]^+[CuBr_2(OH)]^- (\mathbf{Y_{10}})$
7	$[Bu]^+[CuBr_2(OH)]^- (\mathbf{Y_{10}}) + BuOH(\mathbf{Y_4}) \to [BuOHBu]^+[CuBr_2(OH)]^- (\mathbf{Y_{11}})$
8	$[BuOHBu]^+[CuBr_2(OH)]^- (\mathbf{Y_{11}}) \to BuOBu(\mathbf{Y_{12}}) + H_2O(\mathbf{Y_7}) + CuBr_2(\mathbf{Y_2})$
9	$[Bu]^+[CuBr_2(OH)]^- (\mathbf{Y_{10}}) + PhCH_2OH(\mathbf{Y_1}) \to [PhCH_2OBu]H^+ [CuBr_2(OH)]^-(\mathbf{Y_5})$

It has been established that the intermolecular dehydration of benzyl alcohol X_1 with n-butyl alcohol X_4 with the formation of ethers is catalyzed by copper compounds, the best for this reaction is $CuBr_2$. Benzyl butyl ether X_6 is the target product of the reaction.

Experimental study of the reaction was carried out at temperatures 140°C, 160°C, 175°C. The reaction time was 8-10 hours.

Minimizing the functional (2), the kinetic parameters were calculated – the rate constants of the stages and the activation energy of the stages – table 2.

Using the “Export Model” button (Figure 4), a file is created for transferring one or several models in json format. The “Import Models” button loads all models from a file into the program. The action "Export to database" generates a script for transfer to the shared database located on the server in sql format. By the “Add” action, a field is created for the new model.

In figure 5 shows the data of a mathematical model for the catalytic reaction of the synthesis of benzylalkyl ethers: kinetic equations, values of kinetic parameters, initial data and differential equations for changing concentrations of substances.

Selection and entry of the initial values of the varied parameters is presented in Figure 6. For the reaction under consideration for the synthesis of benzylalkyl ethers, the variable parameters are temperature, the ratio of the starting reagents, and the reaction time.

Table 2. The values of the kinetic parameters of the reaction of the synthesis of benzyl butyl ether.

N stage	E_j, kcal/mol
1	5.36
2	12.18
3	10.31
4	13.96
5	21.69
6	15.029
7	18.46
8	35.10
9	11.94

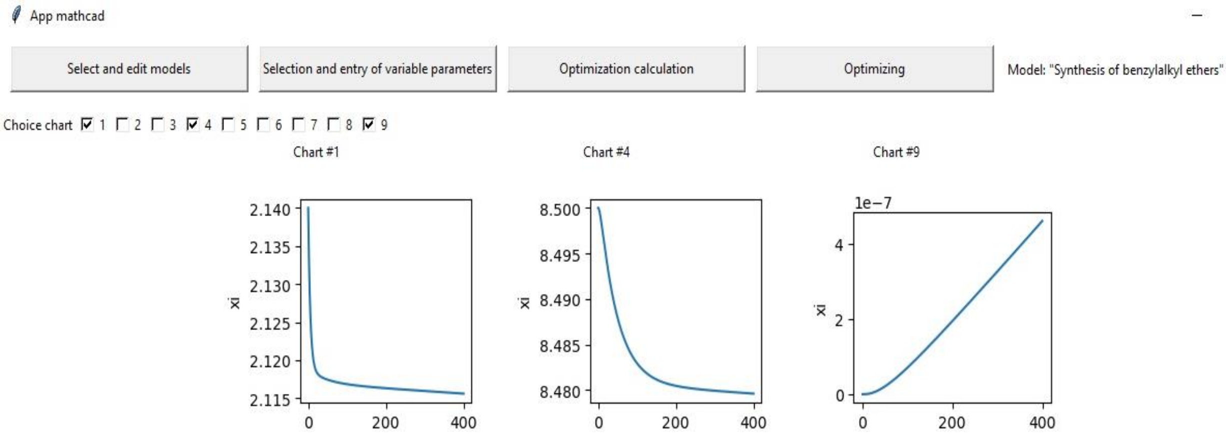

Figure 5. Reaction selection.

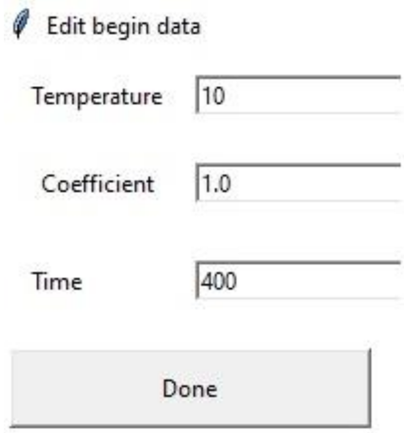

Figure 6. Selection and entry of variable parameters.

After calculation, the user has the opportunity to select the displayed graphs of changes in concentration over time. For each reagent of the chemical reaction, a graph of the concentration change on demand is displayed (ticked) (Figure 7).

In figure 7 shows the results of a chemical reaction simulation program. The conclusion of changes in reagent concentrations is given Y_1, Y_6, Y_8. In the investigated reaction Y_1 is the original alcohol and its concentration during the reaction decreases. Y_6 – target benzylbutyl ether, the concentration of which increases during the reaction.

In figure 8 is a view of a module of a program for calculating optimal reaction conditions. The output of a substance is considered as a criterion. The criterion can be maximized to account for the output of the target products or minimized for by-products or non-productive reaction products. In the same window of the program, the output graph of the substance output is implemented (figure 8).

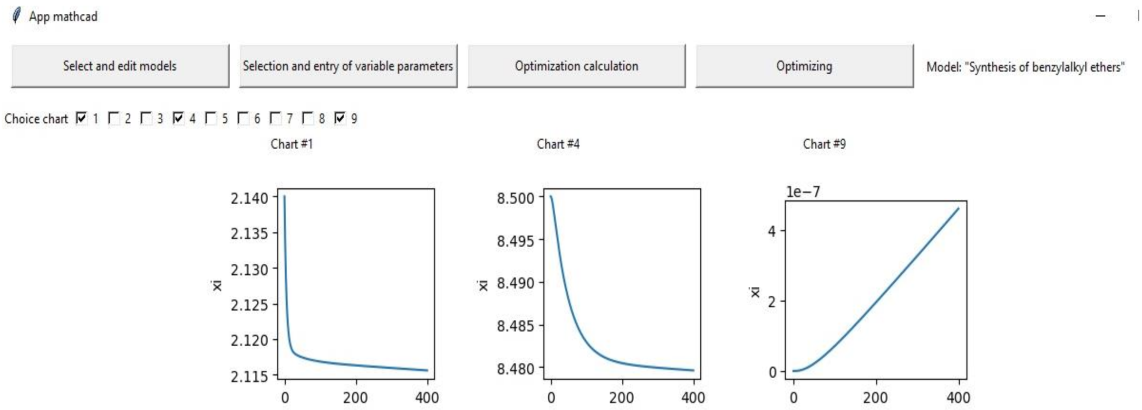

Figure 7. Charts after calculation.

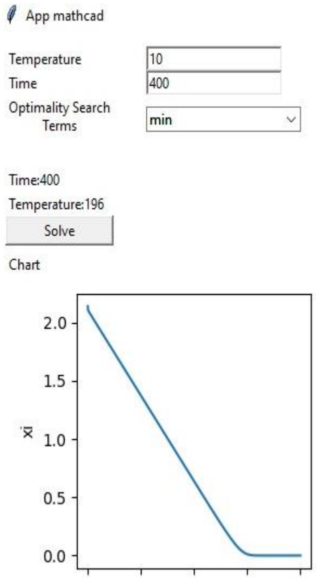

Figure 8. Chart after optimality.

The main function of the program is to solve the problem of determining the optimal reaction conditions . For the catalytic reaction of the synthesis of benzylalkyl ethers, the variable parameters are the temperature and reaction time. The optimality criterion is the maximum conversion (or minimum output) of the first reagent. The solution to the optimization problem is based on the genetic algorithm.

4. Conclusion

Thus, the program is designed to optimize chemical reactions, allowing to carry out modeling and optimization of catalytic reactions. Implemented export and import of the reaction model and calculation of the direct kinetic problem. As an object of study, the catalytic reaction of the synthesis of benzyl butyl ether is considered. A mathematical reaction model is given and the concentrations of all reaction components are calculated.

5. Acknowledgments

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6. References

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