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Multiobjective Optimization of a Metal Complex Catalytic Reaction Based on a Detailed Kinetic Model with Parallelization of Calculations

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Abstract: The solution of the multiobjective optimization problem was performed with the help of the Pareto approximation algorithm. The problem of multiobjective optimization of the reaction process conditions for the olefin hydroalumination catalytic reaction, with the presence of organoaluminum compounds diisobutylaluminumchloride, diisobutylaluminumhydrate, and triisobutylaluminum, was solved. The optimality criteria are the yield of the reaction resultants. The largest yield of the high-order organoaluminum compound Bu₂AIR was observed for the reactions with diisobutylaluminumhydrate and triisobutylaluminum. Such results were obtained due to the fact that in the case of diisobutylaluminumchloride, Bu₂AIR was used for the formation of ClBuAIR. The yield of the Schwartz reagent Cp₂ZrHCl was higher by a third in the reaction in the presence of diisobutylaluminumchloride. Unlike the experimental isothermal conditions, the temperature optimal control showed the sufficiency of the gradual growth temperature for achieving the same or higher values of optimality criteria. For computational experiments, the algorithm for solving the multi-criteria optimization problem was parallelized using an island model.

Keywords: multiobjective optimization; optimal control; detailed kinetic model; Pareto approximation; olefins hydroalumination with organoaluminum compounds; parallelization of calculations

MSC: 34H05; 34G20



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1. Introduction

The examination of new metal complex catalytic reaction laboratory conditions suggests their future introduction into the industry. For this purpose, the optimal conditions for process operations must be defined. Such optimization and optimal control become possible if they are based on the detailed kinetic model, which reflects the fundamental regularities of the course of a chemical process.

A detailed kinetic model is an increase in the number of steps of known sequences of chemical transformations in the process based on new experimental data, quantum-chemical calculation data, and new calculation experiments on resolving the inverse problem of chemical kinetics. The detailed kinetic model (DKM) includes an expanded step-by-step sequence of chemical transformations, corresponding chemical equations, the regularities of time-dependent changes in substances' concentration, values of kinetic parameters (both known and newly introduced ones), and physical-chemical conclusions on the reactions. Based on the DKM and the criteria of optimality, the problem of optimization and optimum control of the chemical process conditions can be set. A simultaneous existence of several optimality criteria defines the problem of multiobjective optimization.

2. Literature Review

The development of mathematical optimization methods in chemical technology has been carried out and is being carried out by many authors: M. G. Slinko [1], V. I. Bykov [2], R. Aris [3], V. V. Kafarov [4], etc. These researchers use the following optimization methods: (1) classical analysis of the study of functions; (2) calculus of variations; (3) Pontryagin's maximum principle; (4) dynamic programming and linear programming; (5) nonlinear programming; (6) methods of global optimization, etc. Optimization methods in chemical technology are mainly devoted to single-criteria optimization according to the criterion of the product yield. In the study of multi-criteria optimization, the problem of compromise of the values of the optimality criteria arises. The authors of such methods are A. P. Karpenko [5], R. Wang [6], D. E. Goldberg [7], A. Abraham [8], K. Deb [9], D. Corne [10], and S. Chowdhury [11]. However, for problems of chemical kinetics, methods of multi-criteria optimization with simultaneous analysis of several criteria were not used earlier.

The object of this research is a metal complex catalytic (MCC) reaction—olefin hydroalumination with organoaluminum compounds. The application of metal complex catalysts in this reaction provided for basic changes in the strategy of organoaluminum synthesis: olefin hydroalumination was performed in soft conditions with high regio- and stereoselectivity [12]. Catalytic olefin hydroalumination allows researchers to obtain important cyclic and acyclic organoaluminum compounds with set structures and has great industrial significance [12–15]. Based on the available manufacturing data, it is necessary to elaborate on the DKM to calculate process optimal conditions, both stationary and dynamic. The reaction products are high-order organoaluminum compounds $\text{Bu}_2\text{Al}(\text{CH}_2\text{CH}_2\text{R})$, $\text{ClBuAl}(\text{CH}_2\text{CH}_2\text{R})$, and the Schwartz reagent Cp_2ZrHCl . It is essential to solve the multi-objective optimization task as the Pareto approximation and optimal control.

In connection with the above-described topical research in this paper is the development of a methodology for multi-criteria optimization using the simultaneous optimization of the output of competing products in the reaction of hydroaluminating olefins with organo-aluminum compounds and determining the totality of non-improved solutions in the form of a Pareto front.

3. The Problem of Multiobjective Optimal Control of a Chemical Reaction and Solution Algorithms

The problem of the multiobjective optimal control of the chemical reaction conditions represents a system of nonlinear ordinary differential, Equation (1):

$$\begin{cases} \dot{y}_1(t) = \phi_1(y_1, y_2, \dots, y_n, u_1, u_2, \dots, u_m) \\ \dot{y}_2(t) = \phi_2(y_1, y_2, \dots, y_n, u_1, u_2, \dots, u_m) \\ \dots \\ \dot{y}_n(t) = \phi_n(y_1, y_2, \dots, y_n, u_1, u_2, \dots, u_m) \\ t \in [0; t^*]; y_i(0) = y_i^0. \end{cases} \quad (1)$$

where $Y_0 = (y_1^0, y_2^0, \dots, y_n^0)$ —the vector of the initial conditions; $Y(t) = (y_1(t), y_2(t), \dots, y_n(t))$ —the vector of the state variables; $U(t) = (u_1, u_2, \dots, u_m)$ —the vector of the control; $\Phi(Y, U) = (\phi_1, \phi_2, \dots, \phi_n)$ —the vector of the right parts; t^* —the reaction time in min.

The limitations for the vector of the control can be written as (2), where D_U represents a function space.

$$U(t) \in D_U. \quad (2)$$

The control quality criteria (control optimality criteria) in the problems on the optimal control of the chemical reaction conditions depend on the values of the phase variables, including the concentration of the reagents and controlling parameters (3).

$$J = J(Y, U) \quad (3)$$

Thus, the problem of optimal control for chemical kinetics is to find the vector control, $U(t)$, satisfying condition (2), in which a system of nonlinear ordinary differential equation (SNODE) solutions provides the optimality criterion extremum (3).

The solution for the problem of the optimal control of catalytic reactions will provide the determination of not only initial optimal conditions but also the optimal variability of the parameters during the process, aimed at the achievement of the optimality criteria that have been set [16].

In order to solve the problem of the dynamic system's optimal control, in general, and chemical reaction of the metal complex catalysis in particular, researchers use the R. Bellman method of dynamic programming [17], the L. S. Pontryagin maximum principle [18], the methods of dynamic systems controlling developed in the works [19,20], and the methods based on resolving the problem of optimal control to the problem of nonlinear programming and other [21–24].

The application of the Pontryagin maximum principle provides the most exact results for solving the problem of optimal control from the point of view of computation. However, for the problems of the optimal control of a large-scale chemical kinetics, especially industrial reactions, the complicated formula of maximum principle makes it more difficult to obtain the solution.

That is why it is important for chemical kinetics to examine the effectiveness of numerical methods of the chemical reaction optimal control. One of the peculiarities of the problem of the MCC chemical reaction optimal control is its multiobjective character [25]. Modern approaches to the solution of the problem of multiobjective optimization use preliminary elaboration of an approximation of all or part of the Pareto front of this problem, usually with the help of evolutionary or, more often, genetic algorithms. The most known Pareto approximation algorithms are the algorithm of switching objective functions, VEGA (Vector Evaluated Genetic Algorithm); the algorithm of weighted sums SWO (Sum of Weighted Objectives); the algorithm of non-dominated sorting NDS (non-dominated sorting), the SPEA (Strength Pareto Evolutionary Algorithm) and its extension SPEA-2 [26,27], the non-dominated sorting genetic algorithm NSGA, and its extension NSGA-II [9,28] and other algorithms [29,30].

The decentralized approach with the application of decomposition and discrete methods is a separate section in solving the problems of optimal control. The approach provides for avoiding some computational complications and makes the methodology of the solution of a large class of problems easier [26]. One such method is the method of resolving the problem of optimal control to the problem of nonlinear programming [27]. It can be outlined as follows: the interval $[0, t^*]$ is covered by a uniform or non-uniform grid with nodes $t_i, i \in [0, N]$, where N is the number of grid nodes depending on the interval; the optimal control, $u^*(t)$, is defined in the class of piecewise constant functions. In this case, there is a problem of nonlinear programming with the vector of the control, U (Figure 1), where u_{jmin} and u_{jmax} are the preset minimum and maximum values of the control, defining the area D_U .

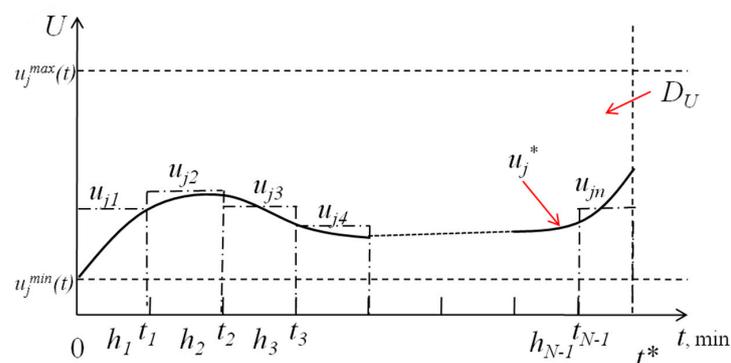


Figure 1. Resolving the problem of the optimal control to the problem of nonlinear programming.

The SNODE (1) can be replaced with a finite difference equation.

$$Y_k = Y_{k-1} + h_k \Phi(Y_{k-1}, U_k), Y_0 = Y^0, Y_N = Y^{t*}, U_k \in D_U, k \in [0, t*]. \quad (4)$$

The control quality criterion (3) $J = J(Y, U)$, where $U = (u_1, u_2, \dots, u_m)$ is the $(m \times N)$ matrix. Then, the discrete problem of optimal control is represented as a problem of nonlinear programming.

$$\max_{U \in D_U} J_0(U) = J_0(U^*) = J_0^*. \quad (5)$$

In this case, not the vector of the variable parameters, but the matrix U of the variable parameters is the object of research.

The calculation algorithm of the control quality criterion values can be written as:

The setting of the first approximation of the U matrix elements values.

With the U matrix elements being set, one performs a consequential calculation of values $Y_k, k \in [1, t*]$ according to (4).

With the U matrix elements being set and $y_k, k \in [1, t*]$ values being calculated, one performs a calculation of the control quality criterion value $J(U)$ according to (3).

Then, it follows a nonlinear programming problem calculation with the use of methods of conditional minimization according to (5).

The described methods and algorithms will be applied for the optimization of the metal complex catalytic homogeneous reaction, olefin hydroalumination with organoaluminum compounds, according to the detailed kinetic model.

4. Kinetic Model of a Metal Complex Catalytic Reaction

An experimental examination of the mechanism of olefin hydroalumination by organoaluminum compounds $XAlBu^i_2$ (where $X = H, Cl, Bu^i$) with the presence of Cp_2ZrCl_2 made it possible to define the structure of intermediate Zr, Al-hydride complexes, which form during the process, and to reveal the key intermediate of the reaction $[Cp_2ZrH_2 \cdot ClAlBu^i_2]_2$ that is responsible for olefin coordination. The isolation of this key complex in the pure form provided for the examination of its structure and reactivity in relation to terminal olefins.

It turned out that the isolated intermediate can be reckoned as a new class of Zr, Al-hydride complexes that possess high hydroaluminating ability in comparison with well-known traditional hydrozirconating and hydroaluminating reagents.

Thus, obtaining a detailed scheme of this reaction may, in the future, allow the researchers to control this process and understand the impact of various factors (temperature, pressure, solvent, the origin of reagents, etc.) on the reaction course.

In [31–33], the authors elaborated a detailed kinetic model of olefin hydroalumination Cp_2ZrCl_2 -catalyzed reaction with organoaluminum compounds $ClAlBu^i_2$ (DIBAC), $HAlBu^i_2$ (DIBAH), and $AlBu^i_3$ (TIBA). For the general olefin hydroalumination reaction, the following olefins were experimentally tested: heptene, octene, nonene, and decene. The kinetic model was elaborated with the use of a methodology of examination of particularly isolated reactions for key complexes.

Table 1 represents the sequence of chemical transformations of general olefin hydroalumination reactions with DIBAC, DIBAH, and TIBA.

For the general olefin hydroalumination reaction, the following olefins were examined experimentally: heptane, octene, nonene, and decene. These chemical experiments were conducted for several temperatures and several values of the catalyst's initial amount. Thus, it is necessary to introduce the initial amount of the catalyst into the mathematical description [34]. For homogeneous reactions and in the case when a reaction was carried out at low pressure and temperatures, it was allowed to describe the process by the Arrhenius kinetics [35–37]:

$$\frac{dy_i}{dt} = \frac{y_{kt}}{V_p} \sum_{j=1}^l v_{ij} w_j, i = 1, \dots, n; t \in [0, t*]; y_i(0) = y_i^0; \quad (6)$$

$$w_j = k_j \cdot \prod_{i=1}^n (y_i)^{\alpha_{ij}} - k_{-j} \cdot \prod_{i=1}^n (y_i)^{\beta_{ij}}; k_j = A_j \cdot \exp\left(-\frac{E_j}{RT}\right); \tag{7}$$

where ν_{ij} is the matrix stoichiometric coefficients; w_j is the rate's j-th stage, 1/h; k_j is the constant velocity stage (reduced), 1/h; T is the temperature, K; α_{ij} is the negative elements ν_{ij} ; β_{ij} is the positive elements ν_{ij} ; A_j is the preexponential factors, 1/h; E_j is the activation energy of the reactions, ccal/mol; R is the universal gas constant; y_{kt} is the amount of catalyst, mol; V_p is the reaction volume, l.

Since the detailed mechanism of the reaction is extracted based on the isolated steps, then the sequences include common steps (Table 1, e.g., steps 4 and 8). Furthermore, three reactions with organoaluminum compounds (OACs) have identical steps themselves. That is why for the solution of an inverse problem, it is necessary to take into account the fact that the values of the kinetic parameters at these steps must be identical [38,39].

The inverse kinetic problem of the stage parameters' identification was resolved with the help of a genetic optimization algorithm with the minimization of the deviation of the calculated values functional from the experimental data for concentrations of the examined reagents. Such examined reagents of the olefin hydroalumination (HA) reaction with OACs were CH₂CHR and Bu₂Al(CH₂CH₂R). To solve the direct and inverse problems, parallelization methods were applied [40,41]. The values of the kinetic parameters of the steps of the chemical transformations of the olefin HA reactions with the OACs were calculated (Table 2).

Table 1. Sequences of chemical transformations of general olefin HA reactions with OACs.

DIBAH	TIBA	DIBAC
(1) Y ₁₅ +Y ₅ ↔Y ₁₀ : k ₁₇ , k ₋₁₇	(1) Y ₁₅ +Y ₁₄ ↔Y ₁₈ +Y ₉ : k ₁₈ , k ₋₁₈	(1) Y ₁₅ +Y ₉ ↔Y ₁₈ +Y ₁₁ : k ₁₃ , k ₋₁₃
(2) Y ₁₀ +Y ₅ ↔Y ₂ +Y ₉ : k ₇ , k ₋₇	(2) Y ₁₈ +Y ₉ →Y ₁₀ +Y ₁₃ : k ₁₄	(2) Y ₁₈ +Y ₉ →Y ₁₀ +Y ₁₃ : k ₁₄
(3) Y ₂ +Y ₅ →Y ₈ : k ₃	(3) Y ₁₀ +Y ₉ →Y ₂ +Y ₁₃ +Y ₁₁ : k ₈	(3) Y ₁₀ +Y ₉ →Y ₂ +Y ₁₃ +Y ₁₁ : k ₈
(4) 2Y ₂ ↔Y ₁ : k ₁ , k ₋₁	(4) 2Y ₂ ↔Y ₁ : k ₁ , k ₋₁	(4) 2Y ₂ ↔Y ₁ : k ₁ , k ₋₁
(5) Y ₁ +Y ₅ →Y ₈ +Y ₂ : k ₂	(5) Y ₂ +Y ₃ →Y ₄ +Y ₅ : k ₉	(5) Y ₂ +Y ₃ →Y ₄ +Y ₅ : k ₉
(6) Y ₂ +Y ₃ →Y ₄ +Y ₅ : k ₉	(6) Y ₁ +Y ₅ →Y ₈ +Y ₂ : k ₂	(6) Y ₁ +Y ₅ →Y ₈ +Y ₂ : k ₂
(7) Y ₄ +Y ₅ →Y ₇ +Y ₆ : k ₁₀	(7) Y ₂ +Y ₅ →Y ₈ : k ₂	(7) Y ₂ +Y ₅ →Y ₈ : k ₂
(8) Y ₈ +Y ₃ →Y ₄ +2Y ₅ : k ₁₂	(8) Y ₈ +Y ₃ →Y ₄ +2Y ₅ : k ₁₂	(8) Y ₈ +Y ₃ →Y ₄ +2Y ₅ : k ₁₂
(9) Y ₇ +Y ₅ →Y ₂ : k ₁₁	(9) Y ₄ +Y ₅ →Y ₇ +Y ₆ : k ₁₀	(9) Y ₄ +Y ₅ →Y ₇ +Y ₆ : k ₁₀
(10) Y ₇ +Y ₉ →Y ₁₀ : k ₁₅	(10) Y ₁ +Y ₁₄ →Y ₈ +Y ₂ +Y ₁₃ : k ₄	(10) Y ₁ +Y ₉ →Y ₈ +Y ₁₀ : k ₆
(11) Y ₁ +Y ₉ →Y ₈ +Y ₁₀ : k ₆	(11) Y ₇ +Y ₅ →Y ₂ : k ₁₁	(11) Y ₇ +Y ₅ →Y ₂ : k ₁₁
	(12) Y ₇ +Y ₉ →Y ₁₀ : k ₁₅	(12) Y ₇ +Y ₉ →Y ₁₀ : k ₁₅
	(13) Y ₁₅ +Y ₅ ↔Y ₁₀ : k ₁₇ , k ₋₁₇	(13) Y ₆ +Y ₁₁ ↔Y ₁₉ +Y ₉ : k ₁₆ , k ₋₁₆
	(14) Y ₂ +Y ₁₄ →Y ₈ +Y ₁₃ : k ₅	(14) Y ₁₅ +Y ₅ ↔Y ₁₀ : k ₁₇ , k ₋₁₇
		(15) Y ₁₀ +Y ₅ ↔Y ₂ +Y ₉ : k ₇ , k ₋₇

where Y₁ = [Cp₂ZrH₂·ClAlBu₂]₂, Y₂ = [Cp₂ZrH₂·ClAlBu₂], Y₃ = CH₂CHR, Y₄ = Cp₂ZrCl(CH₂CH₂R), Y₅ = HAlBu₂-DIBAH, Y₆ = Bu₂Al(CH₂CH₂R), Y₇ = Cp₂ZrHCl, Y₈ = [Cp₂ZrH₂·HAlBu₂·ClAlBu₂], Y₉ = ClAlBu₂-DIBAC, Y₁₀ = [Cp₂ZrHCl·ClAlBu₂], Y₁₁ = Cl₂AlBu, Y₁₂ = [Cp₂ZrHBU·ClAlBu₂], Y₁₃ = C₄H₈, Y₁₄ = AlBu₃, Y₁₅ = Cp₂ZrCl₂, Y₁₆ = [Cp₂ZrH₂·HAlBu₂·2(ClAlBu₂)], Y₁₇ = [Cp₂ZrH₂·HAlBu₂·ClAlBu₂], Y₁₈ = Cp₂ZrClBu, Y₁₉ = ClBuAl(CH₂CH₂R), Y₂₀ = Cp₂ZrHBU·ClAlBu₂, R = C₅H₁₁, C₆H₁₃, C₇H₁₅, C₈H₁₇, Bu = C₄H₉, and Cp = C₅H₅.

Table 2. The values of kinetic parameters of the steps of chemical transformations of olefin HA reactions with OACs.

k _j	lnA _j ; min ⁻¹	E _j , ccal/mol	k _j	lnA _j ; min ⁻¹	E _j , ccal/mol
k ₋₁ , k ₁	16.62; 9.37	7.02; 4.50	k ₁₀	19.52	7.04
k ₂	12.70	6.07	k ₁₁	24.21	14.20
k ₃	18.53	7.00	k ₁₂	42.32	26.00
k ₄	5.49	4.40	k ₁₃ , k ₋₁₃	46.70; -13.10	31.0; 1.10
k ₅	40.45	22.40	k ₁₄	20.15	12.40
k ₆	22.67	12.3	k ₁₅	45.42	12.40
k ₋₇ , k ₇	25.71; 14.97	11.10; 8.00	k ₁₆ , k ₋₁₆	36.43; 16.40	18.20; 19.00
k ₈	24.28	10.60	k ₁₇ , k ₋₁₇	9.39; 12.67	13.60; 10.10
k ₉	33.74	16.20	k ₁₈ , k ₋₁₈	24.64; 26.62	12.20; 13.20

The resultants of olefin HA reactions with OACs were the high-order organoaluminum compounds Bu₂AlR (Y₆) and ClBuAlR (Y₁₉) (in the case with DIBAC) and the Schwartz reagent Cp₂ZrHCl (Y₇). During the analysis of the catalytic reactions examined in the laboratory, optimization problems arose, which required us to determine the reaction conditions necessary for obtaining particular resultants. It is only possible to determine such conditions on the basis of a detailed kinetic model of the process [42,43]. Thus, the process conditions' optimization problem will be formulated and solved based on the elaborated detailed kinetic model of the metal complex catalytic reaction.

5. Multiobjective Optimization of the Metal Complex Catalytic Reaction Conditions

The chemical experiments were executed under several different temperatures and with various initial amounts of catalyst. Then, the variable parameters were the reaction temperature, the initial amount of catalyst, and the reaction time (the dependence was defined according to (6) and (7)), with corresponding physical–chemical constraints.

The problem of multiobjective optimization (MCO) of the olefin HA catalytic reaction conditions with DIBAC can be written as:

- The vector of the variable parameters, $U = (u_1, u_2, u_3)$, where u_1 is the reaction temperature, T ; u_2 is the initial amount of catalyst, y_{kt} ; u_3 is the reaction time, t^* ; the dimension of the vector of the variable parameters is $|U| = 3$;
- The vector function of the optimality criteria, $J(U) = (J_1(U), J_2(U), J_3(U))$: J_1 is the yield of the resultant Bu₂AlR (Y₆); J_2 is the yield of the resultant ClBuAlR (Y₁₉); J_3 is the yield of the resultant Cp₂ZrHCl (Y₇);
- $J(U)$, with values in the target space $\{J\} = R^{(l)} = R^2$, is determined in the area $D_U \subset \{U\} = R^{|U|} = R^3$: $T \in [T_{\min}; T_{\max}]$, $y_{kt} \in [y_{kt \min}; y_{kt \max}]$, $t^* \in [t^*_{\min}; t^*_{\max}]$.

For the olefin HA reactions with DIBAC: $T_{\min} = 0$ °C; $T_{\max} = 30$ °C; $y_{kt \min} = 0.18$ mmol; $y_{kt \max} = 1$ mmol; $t^*_{\min} = 1$ min; $t^*_{\max} = 300$ min. For the olefin HA reactions with DIBAH: $T_{\min} = 1$ °C; $T_{\max} = 50$ °C; $y_{kt \min} = 0.18$ mmol; $y_{kt \max} = 1$ mmol; $t^*_{\min} = 1$ min; $t^*_{\max} = 700$ min. For the olefin HA reactions with TIBA: $T_{\min} = 1$ °C; $T_{\max} = 20$ °C; $y_{kt \min} = 0.18$ mmol; $y_{kt \max} = 1$ mmol; $t^*_{\min} = 1$ min; $t^*_{\max} = 700$ min.

Then, it was necessary to maximize the optimality criteria in the area D_U according to (5).

The multiobjective optimization task assumes there is a set of solutions that are Pareto solutions [44]. The decision-maker (DM) acquires a totality of compromise solutions based on mathematical calculations. Paper [20] shows, by the example of known tests and practically significant multiobjective optimization tasks, the effectiveness of the Pareto approximation with the help of evolutionary algorithm classes. The Pareto approximation algorithm's non-dominated sorting genetic algorithm (NSGA-II) provides acceptable solution accuracy for complicated tasks. The authors applied the elitism of solutions, i.e., the best "specimens" were preserved for further "crossing". The algorithm NSGA-II allows one to determine non-dominated points faster than SPEA2 and PESA-II [10].

The solution of the problem of multiobjective optimization was performed with the use of the Pareto approximation algorithm NSGA-II [28,29] (cl. 1.4.) in MATLAB with the help of parallelizing [45,46] in the automated system of identification of homogeneous and heterogeneous reaction conditions in the problems of the multiobject optimization elaborated earlier [47]. The algorithm's exit condition was the minimum change of the value of the optimality criterion (less than 10^{-6}) in accordance with experimental values. The algorithm hyperparameter values were 'PopulationSize' = 1000, 'Generations' = 300, and 'ParetoFraction' = 0.5).

Figures 2 and 3 demonstrate the results of the solution to the problem of multiobjective optimization of the olefin (octen-1) HA reaction conditions with DIBAC.

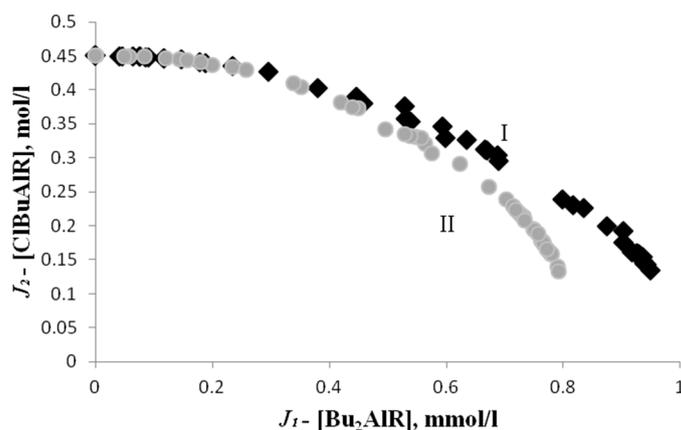


Figure 2. Approximation of the Pareto front of the MCO problem of the olefin HA reaction in the presence of DIBAC. I—variable parameters: reaction temperature, initial amount of catalyst, reaction time, II—variable parameters: reaction temperature, initial amount of catalyst.

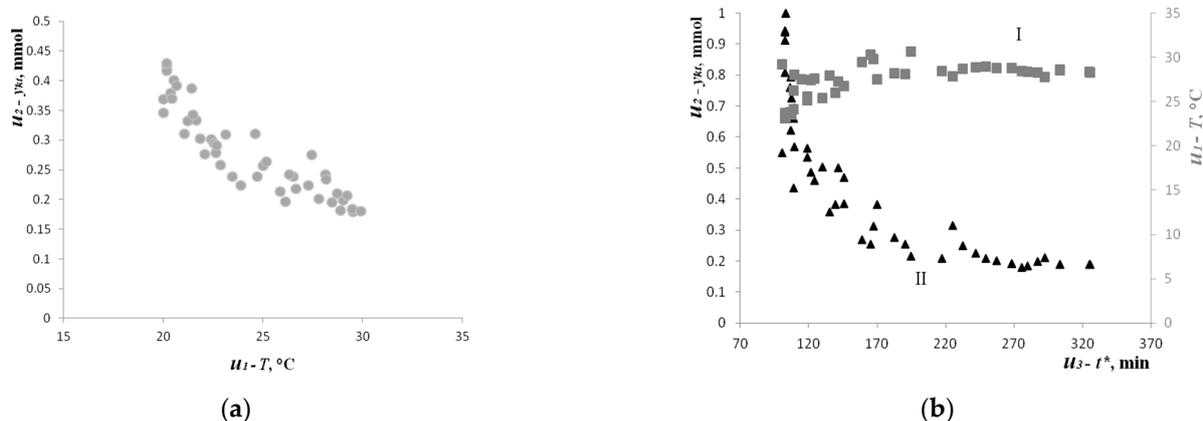


Figure 3. Approximation of the Pareto set of the MCO problem of the olefin HA reaction in the presence of DIBAC: (a) variable parameters—reaction temperature, initial amount of catalyst; (b) variable parameters—reaction temperature, initial amount of catalyst, reaction time.

At a fixed reaction time (250 min, according to the chemical experiment) and varying temperatures and the initial amount of catalyst, the values of the reaction resultants' concentration are represented in Figure 2, curve II. Additional varying of the reaction time provided an increase in the amount of the resultant Bu_2AIR (Y_6), but it did not affect the yield of CIBuAIR (Y_{19}), as shown in Figure 2, curve I. Corresponding values of the variable parameters, i.e., the Pareto set, are presented in Figure 3.

Figure 3a demonstrates the values of the variable parameters, and the reaction temperature and the initial amount of catalyst that make it possible to reach the extreme points of optimality criteria are shown according to Figure 2, II. The introduction of the third variable parameter to the optimization allows one to obtain the values of the reaction conditions stated in Figure 3b. Set I, Figure 3b demonstrates the dependence between the reaction time and temperature, while set II demonstrates the dependence between the reaction time and the initial amount of catalyst. Prolongation of the reaction duration allows one to decrease the initial amount of catalyst from 1 mmol to 0.2 mmol. The optimal temperature for the process is 25–30 °C. The adequacy of the calculated values is supported by the experimental data [47].

The examination of a three-criterion optimization problem with three variable parameters makes it possible to obtain the values of optimality criteria shown in Figure 4.

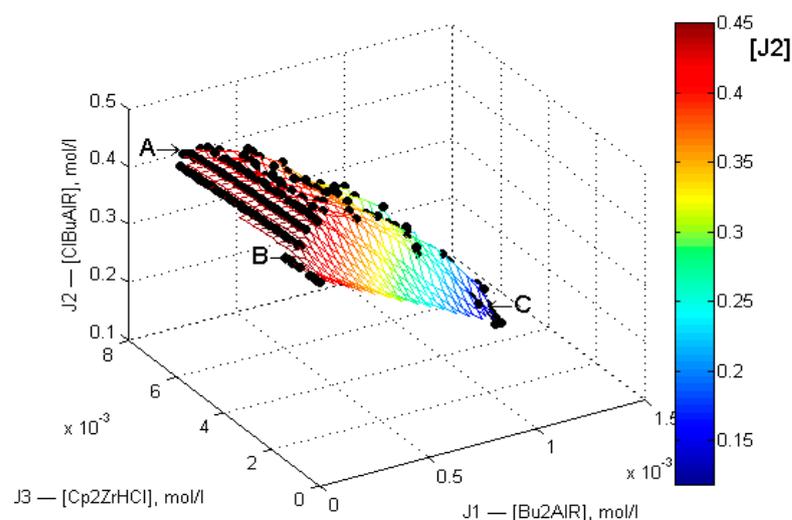


Figure 4. Approximation of the Pareto front of the MCO problem of the olefin HA reaction in the presence of DIBAC for three optimization criteria: J_1 —the yield of the resultant Bu_2AIR ; J_2 —the yield of the resultant CIBuAIR ; J_3 —the yield of the resultant Cp_2ZrHCl .

A graphic representation of the Pareto front for three-criterion optimizations is shown in Figure 4. The calculated set of points is a fragment of some surface convex from the direction of the original since all the criteria are maximized. The points with extreme values for one of the criteria are marked A, B, and C. Point A corresponds to the maximum concentration of the Schwartz reagent Cp_2ZrHCl (Y_7). CIBuAIR (Y_{19}) has the maximum value in point B at a minimum of Y_6 and Y_7 . Point C is the maximum value of Bu_2AIR (Y_6) at the minimum Y_{19} . In accordance with Figure 4, Table 3 provides the values of the variable parameters and optimality criteria for the isolated points A, B, and C. As the temperature increases, the yield of Y_{19} prevails, and the amount of catalyst is at its minimum (Table 3, line 3). The maximum amount of catalyst and reaction time provides for the maximum yield of Y_7 . A shorter reaction duration provides for a larger yield of Y_6 , in comparison with that of Y_{19} , since, according to step 13 of the sequence of chemical transformations of the olefin HA reaction with DIBAH (Table 1), the Y_6 complex transforms into Y_{19} .

Table 3. Approximation of the Pareto set and front of MCO problems of the olefin HA reaction in the presence of DIBAC.

Points	$u_1 - T, \text{ } ^\circ\text{C}$	$u_2 - y_{kt}, \text{ mmol}$	$u_3 - t^*, \text{ min}$	$J_1 - \text{Bu}_2\text{AIR} \text{ (} Y_6 \text{) Yield, mmol/l}$	$J_2 - \text{CIBuAIR} \text{ (} Y_{19} \text{) Yield, mol/l}$	$J_3 - \text{Cp}_2\text{ZrHCl} \text{ Yield (} Y_7 \text{), mmol/l}$
A	23	0.94	277	0.14	0.43	6.50
B	33	0.18	159	0.00	0.45	0.10
C	22	0.69	106	0.95	0.11	3.60

The resultant Bu_2AIR (Y_6) and Schwartz's reagent Cp_2ZrHCl (Y_7) are yielded during the reaction of the olefin hydroalumination in the presence of DIBAH and TIBA. Thus, for the problem of multiobjective optimization of the olefins HA catalytic reaction conditions in the presence of DIBAH and TIBA, the vector function of the optimality criteria can be written as follows: $J(U) = (J_1(U), J_2(U))$: J_1 —the Bu_2AIR (Y_6) resultant yield; J_2 —the Cp_2ZrHCl (Y_7) resultant yield.

Figures 5–8 represent the results of the solution of the problem of multiobjective optimization of the olefins (octen-1) HA reaction conditions in presence of DIBAH and TIBA.

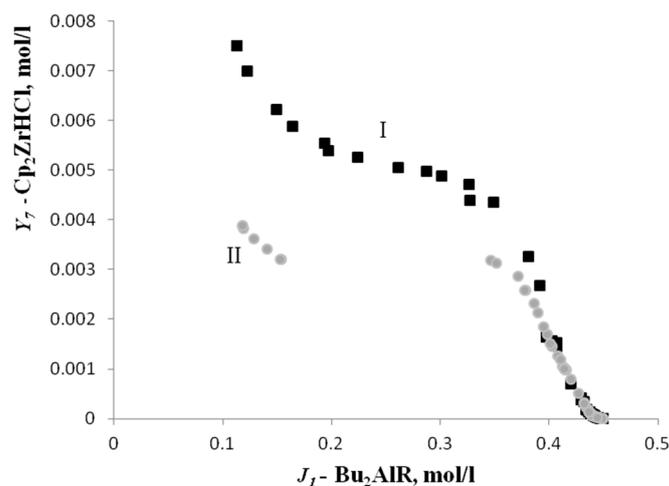


Figure 5. Approximation of the Pareto front of the MCO problem of the olefin HA reaction in the presence of DIBAH. I—variable parameters: reaction temperature, initial amount of catalyst, reaction time, II—variable parameters: reaction temperature, initial amount of catalyst.

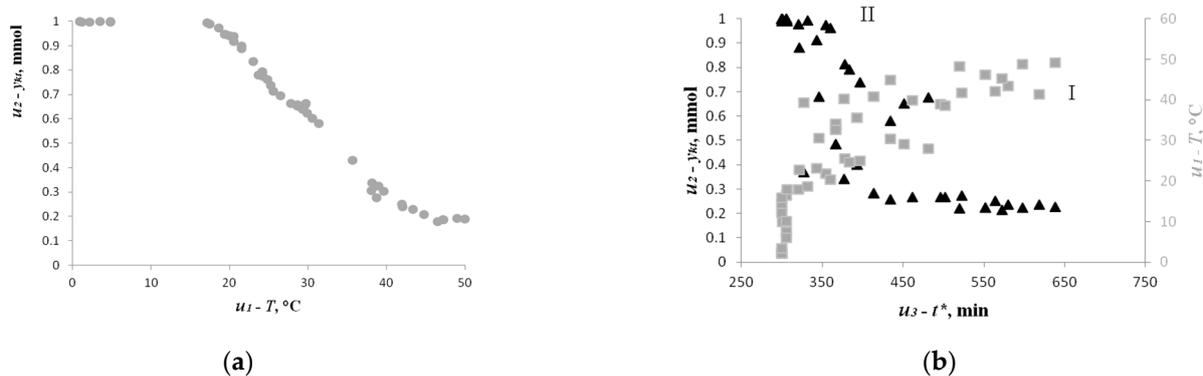


Figure 6. Approximation of the Pareto set of the MCO problem of the olefin HA reaction in the presence of DIBAH: (a) variable parameters—reaction temperature, initial amount of catalyst; (b) variable parameters—reaction temperature, initial amount of catalyst, reaction time.

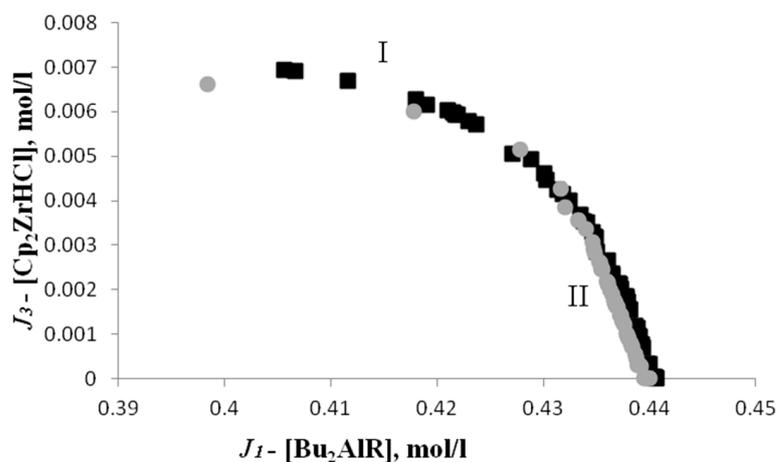


Figure 7. Approximation of the Pareto front of the MCO problem of the olefin HA reaction in the presence of TIBA: I—variable parameters: reaction temperature, initial amount of catalyst, reaction time, II—variable parameters: reaction temperature, initial amount of catalyst.

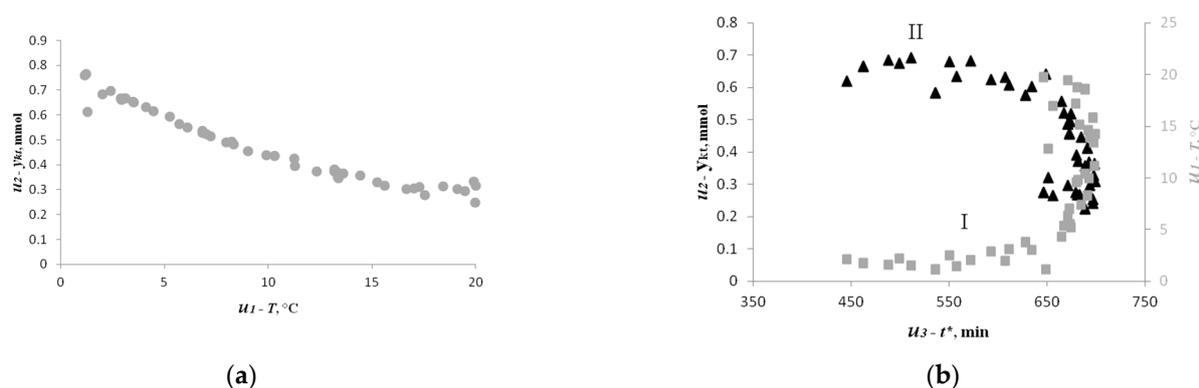


Figure 8. Approximation of the Pareto set of the MCO problem of the olefin HA reaction in the presence of TIBA: **(a)** variable parameters—reaction temperature, initial amount of catalyst; **(b)** variable parameters—reaction temperature, initial amount of catalyst, reaction time.

The Pareto front of the MCO problem of the olefin HA reaction in the presence of DIBAH with three variable parameters is of the convex–concave type (Figure 5I). In the case when there are two variable parameters, the Pareto front is of a discontinuous type (Figure 5II). The discontinuity of the Pareto front can be explained by the presence of the area that contains no solutions that might be improved, i.e., other solutions predominate over these points in another place within the range of this front. Additional varying of the reaction time helps to increase the yield of Cp_2ZrHCl , and the yield of Bu_2AlR is not affected by such varying.

From the point of view of studying the temperature and the amount of catalyst, the Pareto set in the area of variable parameters shows the same discontinuity as the front (Figure 6a). The increase in the reaction temperature results in a decrease in the amount of catalyst necessary for the process. The Pareto set under the additional varying of the reaction time is represented in Figure 6b. Set I, Figure 6b, displays the dependence between the reaction temperature and duration, and set II—the dependence between the reaction duration and the initial amount of the catalyst. Unlike the reaction with DIBAC, here, a wider range of optimal temperature values can be observed, from 0 to 50 °C, depending on the reaction duration and the amount of catalyst.

Figure 7 demonstrates the approximation of the Pareto front of the MCO problem of olefins HA reaction in the presence of TIBA. Unlike the reactions with DIBAC and DIBAH, here the varying reaction time almost does not affect the yield of resultants. This means that the fixed time of 500 min in the case of TIBA is optimal. However, shortening of the reaction duration can be compensated by the increase in the initial amount of catalyst (Figure 8b, I).

Figure 8a represents the values of variable parameters—the reaction temperature and initial amount of catalyst that allow one to reach the extreme point of optimality criteria according to Figure 7, II. The introduction of the third variable parameter to the optimization allows one to obtain the values of reaction conditions stated in Figure 8b. Set I, Figure 8b, demonstrates the dependence between the reaction time and temperature, and set II—the dependence between the reaction time and the initial amount of catalyst. The reaction whose duration is less than 600 min requires an increase in temperature and the initial amount of the catalyst up to 0.6–0.7 mmol to achieve the maximum yield of resultants. The increase in the reaction time to 650–700 min allows one to lower the temperature and initial amount of the catalyst to 0.2 mmol.

The adequacy of the obtained solutions for the multiobjective optimization of the metal complex catalytic reaction is based on its correspondence to the experimental data and on the estimation of the Pareto approximation quality [28,48]. The values of the criteria of the Pareto approximation quality estimation are shown in Table 4. These values correspond to the error in computational data and the capacity of the calculated solution provides for defining the optimal values on the whole interval of variable values.

Table 4. Evaluation of the quality of Pareto approximations.

	Phenotype	Genotype
Average distance between solutions	0.002	0.003
Average scattering	0.182	0.165

The problem of multiobjective optimization of the reaction process conditions for the olefins hydroalumination catalytic reaction with the presence of organoaluminum compounds DIBAC, DIBAH, and TIBA was solved. The optimality criteria are the yield of reaction resultants. The largest yield of high-order OAC Bu₂AlR was observed for the reactions with DIBAH and TIBA. Such a result was obtained due to the fact that in the case with DIBAC Bu₂AlR is used for the formation of ClBuAlR. The yield of the Schwartz reagent Cp₂ZrHCl is insignificantly higher in the reaction in the presence of DIBAH. However, for the reaction with DIBAH, it is necessary to maintain a higher temperature than for the reactions with TIBA and DIBAC.

6. Optimal Control of the Metal Complex Catalysis Reaction Conditions

Experimental studies of the olefins hydroalumination reaction are performed at constant temperatures. However, the elaborated kinetic model allows one to account for the temperature changes according to the Arrhenius equation. In the olefins hydroalumination catalytic reaction in the presence of DIBAC in the optimal control task (1)–(5), the control parameter $u(t) = T(t)$ for the control quality criterion $J(Y, U) = y_{Bu_2AlR}(Y_6)(T(t)) \rightarrow \max$ at $t^* = 250$ min. The solution of the optimal control task is performed based on the kinetic model. The limitation for the reaction conditions is $0\text{ }^\circ\text{C} \leq T(t) \leq 30\text{ }^\circ\text{C}$.

The solution method is the method of reduction to a nonlinear programming task (Figure 1). The interval of integration $[0; 250]$ is discretized in such a way that the length of one section $[t_i; t_{i+1}]$ corresponded to the limitations imposed on the temperature $T(t)$ change speed. Maximization of the yield Y_6 at $t = 250$ min with limitations of the temperature change speed—not more than one degree per minute—was realized. The results represented in Figure 9 shows that the obtained maximum ($Y_6(250) = 0.94$ mmol/L) corresponds to the values found earlier at constant temperature (Figure 2). A solid curve in Figure 9 demonstrates the changes in Y_6 concentration depending on time (principal axis), and a dotted curve—the changes of temperature depending on time (auxiliary axis).

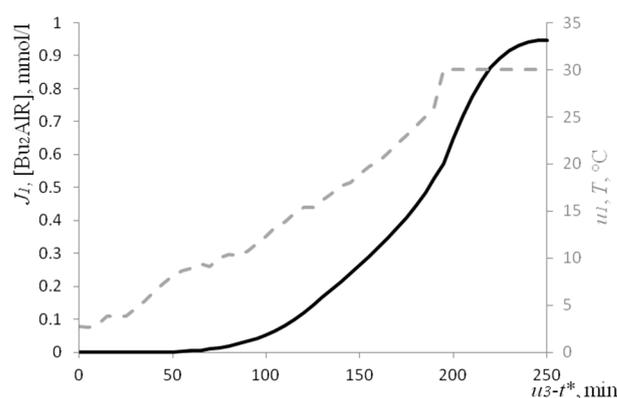


Figure 9. Change of concentration of Bu₂AlR at non-isothermal conditions for the olefin HA reaction in the presence of DIBAC (with limitations).

The next series of calculation experiments had no temperature change limitations. As a result, a new maximum value was obtained ($Y_6(250) = 1.0$ mmol/l) (Figure 10). According to Figure 11, controlled temperature has significant fluctuations. Such control is hard to implement in the real life. This fluctuation of the temperature level's optimal control can be caused by the multi-stage character of the metal complex catalysis with

multiple intermediate complexes (Table 1). Thus, local fluctuations of temperature affect the concentration of intermediate compounds (either stable or unstable), which determine the end product yield.

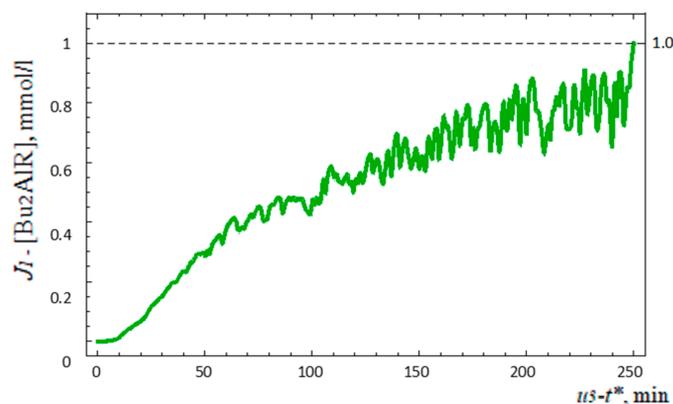


Figure 10. Change of concentration of Bu₂AlR at non-isothermal conditions for the olefins HA reaction in presence of DIBAC (without limitations).

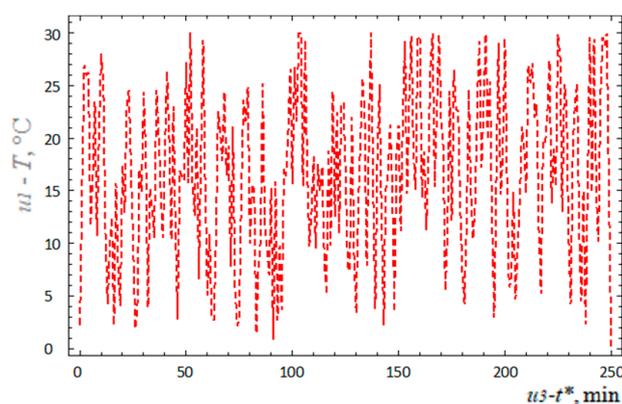


Figure 11. Obtained optimal control $T(t)$ for the olefins HA reaction in presence of DIBAC (without limitations).

Unlike the experimental isothermal conditions, the temperature optimal control shows the sufficiency of the gradual growth of temperature (Figure 9) for achieving the same or higher values of optimality criteria. The optimal control of temperature during the olefin HA reaction in the presence of DIBAC provides for less power consumption in comparison to isothermal conditions.

7. Parallelization of Calculations in a Multi-Criteria Optimization Problem

The basis of parallelization of multi-criteria optimization algorithms is the decomposition and structuring of a population (a set of possible solutions). That is, splitting the original population into several subsets (subpopulations). Decomposition can be implemented in various ways. Partitioning methods define parallelization models. The most popular parallelization models are [49,50]: the island parallelization model and global client/server model, cellular model.

The most common model for parallelization of the computational process is the island parallelization model (Figure 12).

$$S = \bigcup_{i=1}^{|P|} S_i$$

where S —multipopulation, S_i —subpopulations (islands), and $|P|$ —number of processors.

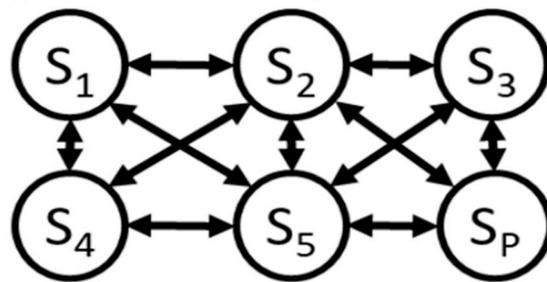


Figure 12. Island parallelization model for solving the problem of multiobjective optimization.

From a multi-population of values of variable parameters (desired conditions for carrying out a catalytic reaction), subpopulations are created according to the number of available processors. According to Figure 1, individuals settle on several isolated islands. These subpopulations will develop independently, with subsequent synchronization of results.

To solve the problem of multi-criteria optimization of catalytic reactions, the genetic algorithm NSGA-II was applied with an island model of parallelization of the computational process. The processor receives a local interval of varying parameters at the input. At the output, the processor produces the optimal values of the variable parameters from the indicated interval. Based on these values, the system of differential equations is solved with the determination of the values of the optimality criteria. The corresponding values of the variable parameters are optimal for this interval (Figure 13).

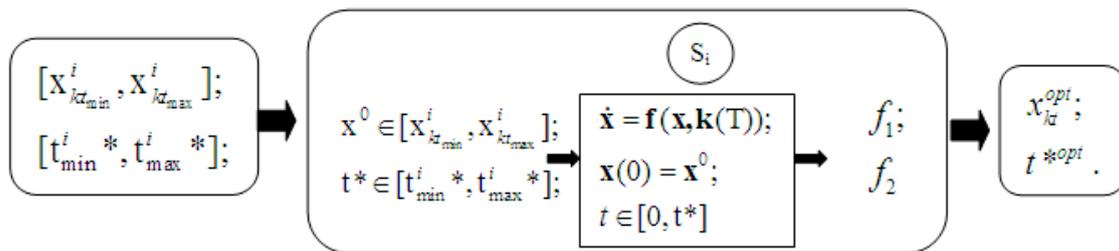


Figure 13. Calculation with the island parallelization model.

When calculating the considered process of olefin hydroalumination, the efficiency of the computational experiment depending on the number of processors is shown in Figure 14. In this case, the difference in time was sequential calculation—420 min.; calculation on two processors—262 min.; on three—200 min.; on four—162 min. For the calculations, a 4-core PC Intel Core I5 7th Gen was used.

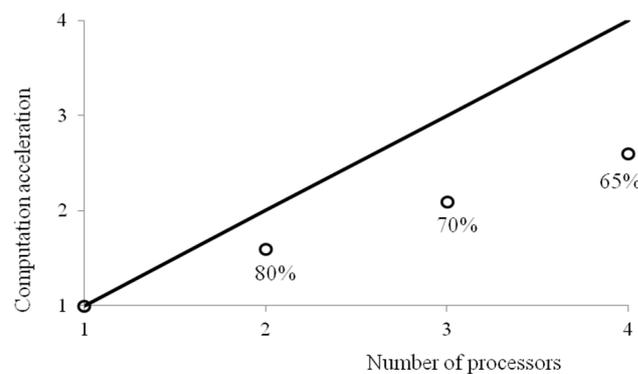


Figure 14. Efficiency of parallel program execution for NSGA-II algorithm.

With an increase in the number of processors, the efficiency decreases due to the time spent on data synchronization between subpopulations.

8. Conclusions

This paper provides the solution algorithm for the MCO task and optimal control over homogeneous catalytic reactions according to the detailed kinetic model. For the olefin hydroalumination catalytic reaction in the presence of organoaluminum compounds DIBAC, DIBAH, and TIBA, the task of the reaction conditions multiobjective optimization was solved.

Based on the calculated set of optimum values of variable parameters (the Pareto set) and corresponding values of optimality criteria (the Pareto front) the decision-maker has a choice of optimum conditions for the olefins hydroalumination reaction with the presence of metal complex catalysts for various organoaluminum compounds. The task of the process temperature optimal control was resolved. Unlike the experimental isothermal conditions, temperature optimal control shows the sufficiency of gradual growth of temperature for achieving the same or higher values of optimality criteria.

The development of this study will be the analysis of the stability of the optimal solution with a small change in the values of the variable parameters. That will allow determining the allowable interval for changing the process conditions to maintain the best values of the optimality criteria.

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