Algorithms for optimizing conditions complex catalytic reactions

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Abstract. The paper developed a method for studying complex catalytic reactions using optimization algorithms. At the first stage, an inverse kinetic problem of recovering the values of unknown parameters is solved using single-purpose optimization algorithms. At the second stage, on the basis of a kinetic model, a problem of determining the optimal conditions for the reaction using multi-purpose optimization algorithms is solved.

1. Introduction

In the study of complex catalytic reactions, optimization problems arise. For develop a mathematical model of a chemical process, it is necessary to solve the problem of restoring kinetic parameters, based on the correspondence of the calculated values concentrations of reagents to experimental data. Based on the developed mathematical model, the problem of optimizing conditions of the process, in accordance with the specified objective functions is solved.

2. Study of complex catalytic reactions by mathematical methods

In Fig. 1 shows the scheme for the study of complex catalytic reactions by mathematical methods. For homogeneous catalytic reactions and reactions taking place at low pressures, it is assumed that the process belongs to the Arrhenius kinetics [1]. When considering closed systems, the state at stationary points obeys the law of effective masses [2]. Then for the components of the system (chemical reaction reagents) the equations (1) are correct.

$$\frac{dx_i}{dt} = \sum_{j=1}^{J} \nu_{ij} w_j(k_j, x_i), i = 1, ...I; \qquad k_j = k_j(k_j^0, E_j, T); \tag{1}$$

With initial conditions: $t = 0, x_i(0) = x_i^0$;
where t reaction time, min; ν_{ij} stoichiometric coefficients; J number of stages, x_i concentrations of substances involved in the reaction, mol/L; I number of substances; w_j j-th rate, 1/min; k_j stage rate constants (normalized), 1/min; E_j activation energy of the stages, kcal/mol; T temperature, K; k_j^0 preexponential factor, 1/min.System (1) is a Cauchy problem [3]. Then under the direct problem should be considered the determination of unknown concentrations of substances as a function of time at given rate

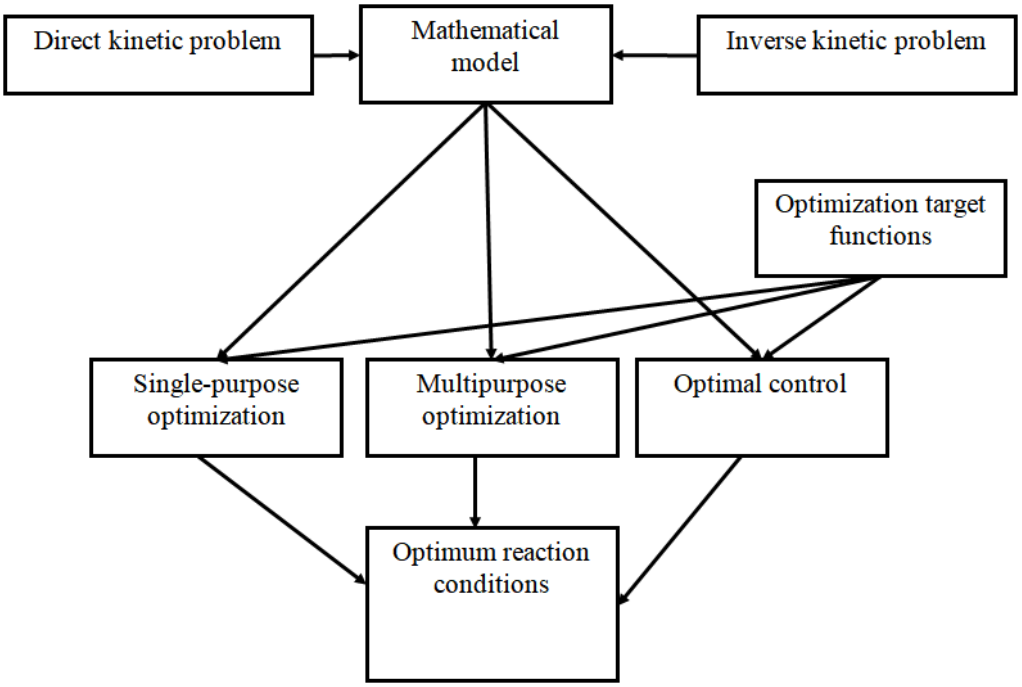

Figure 1. Scheme for the study of complex catalytic reactions by mathematical methods.

constants (k_j). Under the inverse problem is the determination of such rate constants, the solution of system (1), with which it leads to xi values as close as possible to the experimental data. Each inverse problem is a set of direct problems with given rate constants [4, 5, 6]. The parameters of kinetic equations are rate constants and activation energies; it is necessary to determine the condition for minimizing the functional (2) [7].

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

where x_{pi}^e, x_{pi}^r experimental and calculated values of component concentrations, γ_i weight coefficient, I number of substances, P number of measurement points in time of the observed substances during reaction.

Thus, to build a mathematical model of a chemical reaction, the problem of optimizing kinetic parameters is solved (Fig. 1).

Based on a developed mathematical model, it is possible to determine an optimal conditions for the process. Depending on a specified optimization target functions, one of the optimization tasks is solved (Fig. 1):

a) If a single objective function is defined, then the problem of single-purpose optimization is solved.

b) If there is more than one mutually independent objective optimization function, then the multi-purpose optimization problem (MPO) is solved.

c) If it is possible to control the process under study in time with an influence on the criteria under consideration, then the optimal control problem is solved.

3. Single-purpose optimization algorithms

When solving optimization problems, the following single-purpose optimization algorithms are used: global search (globalsearch) and multistart; Hook-Jeeves method (patternsearch); genetic algorithm; simulated annealing (simulatedannealing) and others [8]. These algorithms are both local and global. The global search is based on gradient calculation methods. The genetic algorithm imitates the principles of biological evolution. The simulation algorithm imitates the physical annealing process, seeking to improve the current minimum by slowly reducing the search volume.

When solving an optimization problem in chemistry, the main problem is that all theoretical optimization work investigated each criterion separately (product yield). Then, the next criterion was optimized (for example, the amount of reagents spent), etc. There were two different conditions for a chemical reaction (or more, if there were more than two optimized indicators). These states were the answer to the optimization question [9, 10]. It is worth noting that conditions for carrying out a reaction in these states were different, and in a sense, in themselves extreme, which indicated the impossibility of carrying out a chemical reaction in industry. Thus, in the future, when designing the reactor and chemical production as a whole, these conditions were not taken into account. An average was chosen that was a compromise for the quality criteria. The situation was even more complicated during the practical implementation, when the conditions for the purity of the experiment under laboratory conditions were practically unattainable. Thus, the value of an optimization itself in the laboratory tended to zero.

4. Algorithms for multipurpose optimization

But over the past decades, many effective evolutionary algorithms for multipurpose optimization have been proposed, which take into account all scientific developments in the field of Pareto-dominance, genetic algorithms, and significantly increased the power of computing resources, which allows high-performance computing to be carried out in a reasonable time [11].

It should be noted that when talk about multipurpose optimization, it means a range of solutions, the values of which lie among Pareto solutions [12]. The decision maker (DM) is interested in a compromise solution, but it must be the best, based on mathematical calculations. That is, the points satisfying the solution must be unimprovable, in other words, nondominated [11].

The essence of the solution of the MPO by probing algorithms (for example, the grid algorithm) is to split the domain into small cells, then find the solution of the objective functions in each, then determine the non-dominated points (Pareto front) and the corresponding Pareto set [13]. The downside of the algorithm is that it will require large computing power and time-consuming. With an increase in the number of parameters, the grid algorithm is hardly applicable, since the costs increase significantly. The solution to the problem is the evolutionary algorithms for multicriteria optimization.

Vector estimation is one of the earliest evolutionary algorithms for solving multipurpose optimization problems. Here it is proposed to use a vector fitness function to select decision points (individuals). In this case, the step of selecting individuals is realized in the form of a cycle, where each time e corresponding part (the proportion of the population or subpopulations) is selected on the basis of each q criteria. Then an entire population is completely mixed up and crossing and mutation operators are applied. In the process of evolution, non-dominated individuals are identified in population, but this information is not used directly in the genetic algorithm. The vector method shown in Fig. 2 ensures the survival of best individuals in relation to each criterion and at same time increases the probability of multiple choice of individuals that are by criteria.

One of the earliest algorithms for multicriteria optimization is the Vector Evaluated Genetic Algorithm (VEGA) method (Schaffer D., 1985). This method is based on a fact that at each

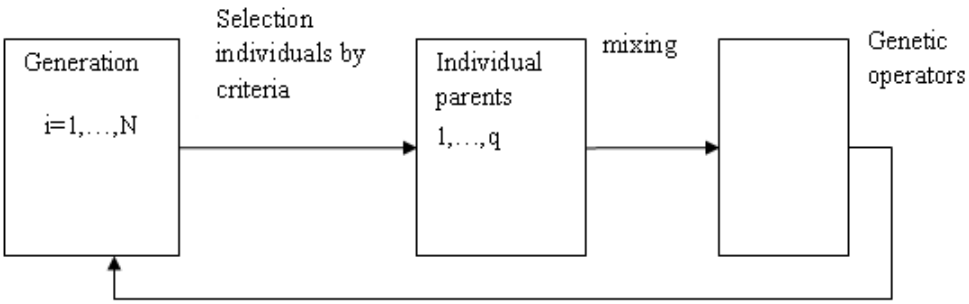

Figure 2. Vector selection of solutions in multipurpose optimization problem.

generation several subsets of individual parents are formed that participate in the reproduction of descendants. Each set is selected based on the suitability of individuals according to one criterion. Further, selected individuals are combined together to obtain a population of descendants using crossing and mutation operators. The main disadvantage of this method lies in a fact that obtained solutions accidentally fell into the Pareto-optimal solution, since the selection of individuals is oriented to the optimum by only one criterion.
The solution to the problem was suggested by Goldberg - ranking individuals [14, 15] it is ranked is 1 for all non-dominated individuals, which are removed from further consideration. Further, among the remaining individuals are non-dominated, which are assigned rank 2. This process continues until the entire population is ranked. The most effective method of the end of ., Based on ranking, is considered to be Non-dominated Sorting Genetic Algorithm (NSGA)(Srinivas and Deb, 1994) [16, 17]. The first non-dominated points (front) are considered, with which some value of the fitness function is assigned. Then these points are decomposed according to the given values and excluded from the subsequent similar procedures. And after each stage, the value less than the minimum decomposed value of the fitness function is assigned to all current non-dominated points (Fig. 3).

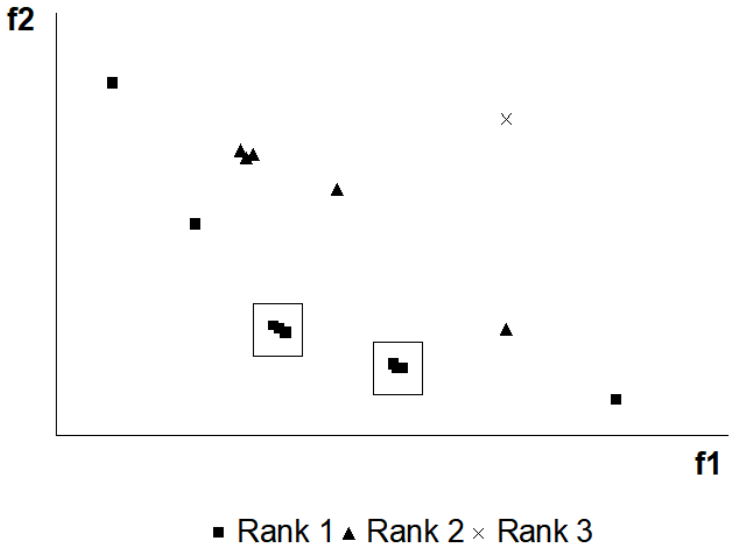

Figure 3. Ranking in NSGA method.

A priori algorithms reduce the multipurpose task to a single-purpose optimization problem by assigning the weights of the partial objective functions

$$F(X) = \sum_{l=1}^{|F|} \eta_l f_l(X); \tag{3}$$

where η_l - assigned weight coefficient, f_l local objective functions, F objective functions vector, X control parameter vector.

Further development of multi-purpose optimization algorithms followed the path of improving algorithms that were developed earlier. Algorithms SPEA2 [18], PESA-II [19], and Non-dominated Sorting Genetic Algorithm II (NSGA-II) [20] were created. The main development followed the path of increasing diversity of individuals and using elitism to preserve the best decisions. The NSGA-II method proved to be the most accurate in determining Pareto-dominant points compared to others, although it also has drawbacks with an increase in a number of criteria.

At the beginning of the algorithm, according to the principles of ranking, each individual is assigned its own rank. Non-dominated points have the first rank, points that are dominated only by points of the first rank have the second rank, etc. The crowding of the individuals obtained is also estimated, the greater distance - the greater diversity of population. At each iteration, the selection of descendants is based on the rank and crowding (proximity) of individuals. Later in the iteration, the best points are chosen based on crossing, as well as mutations, which ensures diversity of a next population. Parents and descendants are combined into one population with best solutions, etc.

Also, undoubted advantage is high citation of the NSGA-II algorithm and its implementation in many programming environments, in particular in Matlab software system (MATrix LABoratore), which has found wide application for modeling chemical reactions, as well as optimization. It includes expansion packages necessary for solving a wide variety of tasks that require mathematical calculations and modeling [21].

For solving multipurpose problems in Matlab, the gamultiobj function was developed. It creates many Pareto-optimal solutions. To find the optimum, a controlled genetic algorithm is used (based on the NSGA-II algorithm). Both individuals with the best rank value (elitism) and individuals are used to improve diversity of the fitness function (even if they have a lower rank). It also uses a distance between individuals, displaying a distance for the Pareto border. It is possible to set the number of populations, the number of individuals, the parameters of crossing and mutations. There is also possibility of parallelization of calculations. All these advantages, as well as some logical assumptions necessary when setting the starting conditions (for example, the number of individuals may tend to infinity, but in applied problems, as a rule, there is no task of finding the Pareto front with an accuracy of more than two decimal places) computing and the need for computing power compared to non-population (grid) algorithms.

Thus, in the study of complex catalytic reactions by mathematical methods, optimization problems arise that require the use of appropriate optimization algorithms [22, 23, 24]. The optimization problem arises both when solving the inverse kinetic problem of recovering values of unknown parameters, and when solving the problem of determining an optimal reaction conditions based on a kinetic model. The application of optimization algorithms is also relevant for chemical kinetics problems. It is especially advisable to use optimization for the analysis of new chemical reactions.

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