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Computer simulation of direct chemical kinetics tasks*

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Abstract. A new technology for the simulation of physico-chemical processes in a reactive medium is proposed, which allows optimizing and adjusting kinetic schemes of chemical reactions. To implement the technology, a ChemPAK software tool, which is used to solve the primal problems of chemical kinetics, was developed. The proposed technological solution has proved to be efficient in a series of studies. The schemes presented in the literature for the gas-phase pyrolysis of ethane and the Butlerov reaction of organic synthesis of sugars were considered along with their modifications. A high precision solver gives the possibility to the user to simulate kinetics schemes with a high stiff value of ODE.

1. Introduction

The update of chemical processes and reactors is an interdisciplinary problem, which requires the involvement of experts in physics, chemistry and mathematical modeling [1–3]. Determination of a kinetic scheme of chemical reactions is the key stage in devising a mathematical model of a reactor. Such a scheme includes the proposed reaction mechanism and the rate constants values for individual reaction steps. As was shown elsewhere [7], different kinetic schemes used to describe a certain reactive flow with the same gas-dynamic parameters lead to radically different simulation results. In the literature, such a process can be described by alternative schemes due to the prevalence of semi-empirical models of chemical kinetics, with stoichiometric equations being used instead of elementary steps. Although semi-empirical representations are of limited application, the development of such kinetic schemes is of a topical character, as they provide a model of a reactive medium, which is adequate in a specified range of conditions. The development of semi-empirical models and determination of the rate constants for individual reaction steps are based on the full-scale and computational experiments.

The computational experiment aimed at the determination of a kinetic scheme is an iterative process including the following stages: advancement of a postulated reaction scheme; generation and solution of a stiff nonlinear set

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of ordinary differential equations that describes chemical transformations of substances within the scheme proposed; and the comparison of numerical and experimental data on the reaction kinetics.

Note that a correct comparison of the calculated and experimental data is not a trivial task, since each time it is necessary to evaluate the accuracy of a numerical model and that of measurements. Thus, to determine the parameters of elementary steps in relatively simple kinetic schemes, it is reasonable to use a detailed two-dimensional model taking into account the diffusion, heat conduction and heterogeneous reactions on the reactor walls in combination with the in situ spectral diagnostics [6]. The development of semi-empirical schemes for more complicated processes (e.g., pyrolysis of hydrocarbons) makes possible to use rougher models due to technical limitations of experimental diagnostics.

Analysis and selection of kinetic schemes can be performed with any software package that solves the primal problem of chemical kinetics, i.e., determines changes in the composition of a reacting mixture that occurs with time. There are several types of the software available at market: multifunctional modeling software packages — FLUENT, CHEMKIN, HYSYS, STARCD, etc.; single-purpose packages — CKS, Kintekus, Acuchem, etc.; and chemical data libraries — NAG, Numerical Recipes, etc. However, most of them are not intended for the search for kinetic schemes. In addition, in many cases, the proposed scheme can be evaluated only in the context of its energy effects or design features of the reactor where experiments are carried out [5]. Such an analysis should be based on spatial models of a reactive medium. Thus, program packages intended for the research and engineering (ReactOp, CARAT [9, 10], etc.) were offered for the reactor optimization and kinetic model development. The use of these packages is arranged as follows. Employing the library of reactor models, the user can make computations with these models using different kinetic schemes entered via the package interface. For instance, the ReactOp library comprises 30 types of single reactors with liquid and gaseous reactants, and seven types of cascade reactors. Fortran codes implementing numerical models of these reactors are extensible, which allows the user to modify them. This approach is convenient when working with the reactor designs that are in most common use, since all the stages of the chemical process simulation and optimization can be performed within a single software product. However, this approach has some limitations: the development of mathematical models for the new type reactors will require a considerable extension of each library; the search problem using a full model of a reactor will be time-consuming. There are several problems featured to software available at the market that need to be solved: a limited number of chemical reactions in a chemical reactions system, a limited possibility of the usage of chemical data from different chemical databases such as Grimech, NIST, a limited possibility of reuse

chemical reactions from other chemical reactions systems from database, a limited possibility of using results of modeling in gas-dynamics software, independence of the reactors geometry that gives a possibility of modeling chemical kinetics before starting the reactor modeling.

In this connection, the simulation technology for the reactive media dynamics should be improved as follows. When searching for an adequate kinetic scheme, the simplest (one-dimensional) reactor models will be used, and simulation will be performed for a wide range of temperatures and pressures. Then a chosen kinetic scheme can be included into computations by the three-dimensional models implemented in commercial or special-purpose CFD (Computational Fluid Dynamic) packages. The results of modeling can be obtained quite rapidly due to a rational use of computational tools at the stage of kinetic scheme development and through an equal distribution of labor among specialists involved in the simulation process and computations. Here we present the ChemPAK software package [8]. The ChemPAK has been improved for the operation within the proposed technology. The package makes possible to generate a set of ordinary differential equations corresponding to the introduced scheme of chemical reactions; this set with relevant kinetic and heat parameters is automatically included in the model computations. The new possibilities of the program package and operational procedures are presented in Section 2. The problems that can be solved with the ChemPak and the main results obtained are briefly reported in Section 3.

2. The ChemPAK software package

Figure 1 shows the three main stages necessary for the development of a numerical model of a reactive medium. At the first stage, the basic numerical models of a reactive medium are bilt and codes for evaluation of kinetic schemes are chosen. This can be done by specialists in mathematical modeling and chemical kinetics. The second stage consists in the evaluation of a kinetic scheme during the iterative process. This can be done by specialists

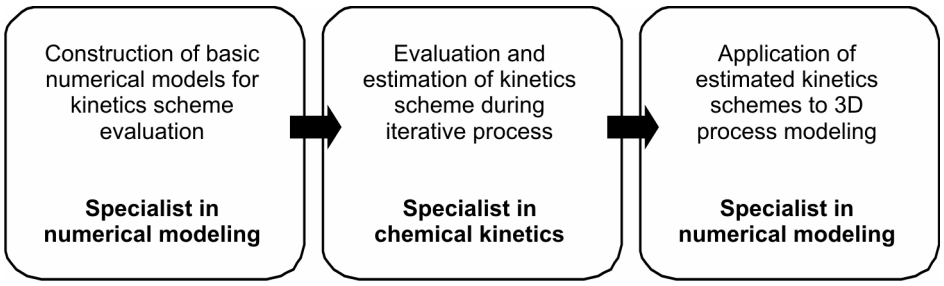

Figure 1. The main stages in the development of a numerical model of a reactive medium

in chemical kinetics using an efficient chemical kinetics software. At the third stage, the estimated kinetic schemes are applied to the 3D simulation of a reactive medium (CFD + chemical reactions, etc.). This can be done by specialists in mathematical modeling. For the first two stages, a new software package ChemPAK was devised by the authors. The ChemPAK can be operated by a specialist in chemical kinetics without any knowledge of mathematical modeling. The ChemPAK can operate on the chemical reactions system stored in the network database or obtained via the package interface. Then the program automatically generates a numerical model of the chemical reaction system and makes computations. Thus, the user of the ChemPAK can obtain results of numerical modeling, adjust a chemical kinetic scheme, and promptly evaluate the resulting scheme.

The main features of the ChemPAK software package are an easy-to-use interface adapted to modification and evaluation of kinetic scheme of a chemical process, an automatic solver of chemical kinetic tasks, a network chemical database for storing chemical reaction systems and other chemical data, the possibility of using the reactor models with chemical reaction models. The ChemPAK architecture is schematically shown in Figure 2.

The ChemPAK can solve a wide range of problems, in particular: input and editing of large chemical reaction systems (the ChemPAK can import data from Microsoft Excel), evaluation of a system of chemical reactions, translation of a reaction system written in a standard chemical notation into the internal notation of the mathematical model, numerical solution of stiff and big sets of ordinary differential equations, automatic export of a mathematical model written in internal ChemPAK notation to a Fortran programme that can be used in different PC and supercomputer software for modeling multistep physical processes. The ChemPAK has two operating

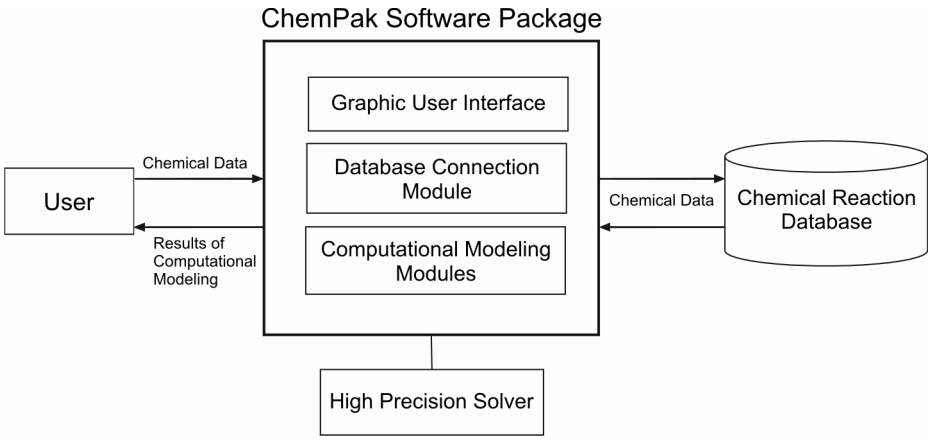

Figure 2. The architecture of ChemPAK

modes — simple and advanced. In the simple mode, the user can automatically solve a task, all computations being without any manual steps. User may employ a system of chemical reactions from the database or introduce his own system and add some needful chemical data. In the advanced mode, the user can operate with his own computational module. This feature will be useful for modeling multistep physical processes. The user has to add some labels to his own computational code written in Fortran language notation. This feature gives an additional possibility for optimization of a kinetic scheme under specific physical conditions. For example, modeling chemical processes in chemical reactors. The user can control the reactor geometry, energy input parameters, etc., and then optimize a chemical kinetic scheme using physical parameters. A more detailed description of the simple operation mode is given in the next subsection.

Step-by-step usage of ChemPAK by specialists on chemical kinetics. Any task for the ChemPAK can be decomposed and solved in 5 steps: creation and placing chemical reactions system into a chemical database, placing additional chemical data into the database, translation of a chemical reactions system into ordinary differential equations (ODE), computation of additional data needed for solving an ODE system, and computation of chemical species concentration changes.

A chemical reactions system can be placed to the ChemPAK database by the import from different table formats like Microsoft Excel or by the manual input using the ChemPAK interface. Additional chemical data can be added to database in a similar manner.

The ChemPAK has a translation module that compiles and translates a chemical reactions system to ordinary differential equations system. Also, the translation module prepares additional chemical data for solving an ODE system.

The ChemPAK has different ODE solvers based on implicit and explicit one-step methods. Solving the ODE systems that are based on chemical reactions systems has some distinguishing features. For example, most of the ODE systems translated from chemical reactions systems are stiff because the values of constants of reactions velocities can differ by many orders. This is typical of chemical processes with slow and fast chemical reactions during one process. The ChemPAK has its own diagnostics module for choosing and activating the best solver for an ODE system.

3. Application of the ChemPAK package

The ChemPAK software package was designed as environment for prompt obtaining the results of numerical simulations within specially developed numerical models of reactors with different kinetic schemes. The first step of

the usage implies creating the basic Fortran codes for numerical models, with allowance for the key features of a reactor or a process under investigation. The codes should include a special system of labels. These labels will be substituted by parts of the code generated by the ChemPAK after specifying a kinetic scheme. These codes should be added to the ChemPAK library. The second step implies specifying a kinetic scheme and possible reaction rate constants through the ChemPAK interface. The third step is obtaining the results of numerical simulation within ChemPAK, their visualization and estimation. If the user decides that numerical results with a kinetic scheme are not in a proper agreement with experimental data, he improves the scheme or reaction rate constants and goes back to the second step. Here is an example of ChemPAK usage.

Pyrolysis of ethane in a wall-less reactor with laser energy input. The present version of the ChemPAK software package is in the pilot-plant operation at the Boreskov Institute of Catalysis, SB RAS. The package was used to analyze several schemes of ethane pyrolysis leading to ethylene [13, 14]. A model of a stationary reaction mixture in an infinite volume was used in the study. This model represents the Cauchy problem for a set of ordinary differential equations written down according the mass action law:

$$\begin{cases} \dfrac{dc_l}{dt} = \displaystyle\sum_{i=1}^{I} \tau_i k_i \prod_{j=1}^{J} c_j^{\nu_j}, \\ c_l|_{t=0} = c_l^0, \end{cases}$$

where c_l is the concentration of the substance l, k_i are reaction velocity constants, I is the number of reactions, J is the number of reactants in the system, ν_j is an exponent equal to the number of substance j, particles involved in the reaction i, and

$$\tau_i = \begin{cases} 1, & \text{if substance } l \text{ is synthesized in the reaction } i, \\ -1, & \text{if substance } l \text{ is decomposed in the reaction } i, \\ 0, & \text{if substance } l \text{ is not involved in the reaction } i. \end{cases}$$

This model is of considerable current use for the search for semi-empirical kinetic schemes. To provide numerical integration of the model, the ChemPAK library includes a code implementing the RADAU5 method, which is among the most efficient modern techniques for solving stiff systems [16].

Figure 3 shows the results of computation for changes in the reaction mixture composition at ethane pyrolysis; the computation is based on the radical-chain mechanism at 1000 K and the constants [13]. One may see that the representative reaction time is ca. 100 s.

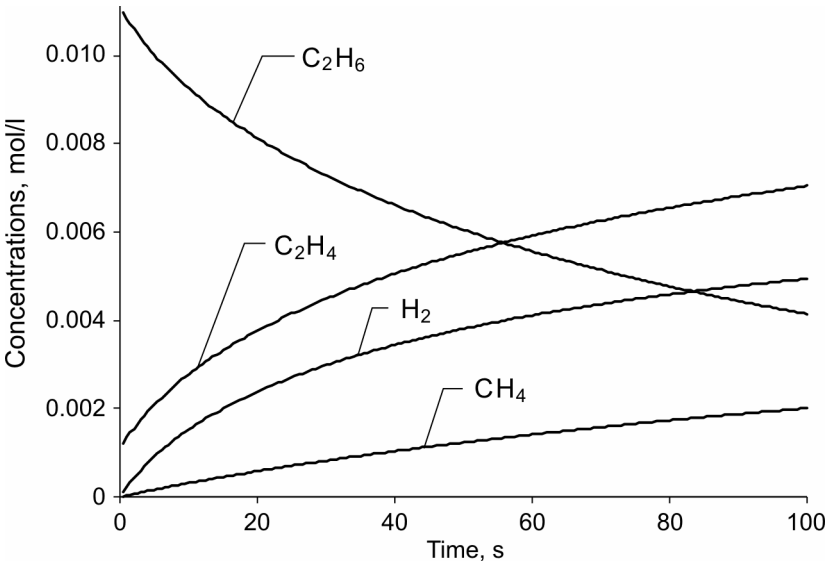

Figure 3. Computation of changes in the reaction mixture composition during ethane pyrolysis

The thermophysical evaluation of the schemes was performed by modeling the gas mixture temperature with the use of a boundary-value problem for the one-dimensional heat transfer equation with allowance for the thermal effect of chemical reactions and heating of a mixture by laser radiation:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\kappa\left(\frac{T}{T_0}\right)^{\beta}\frac{\partial T}{\partial r}\right)+\frac{\lambda}{T}e^{-r^2/\sigma^2}-Q=0,\quad Q=\sum_i q_i w_i,\ \ \lambda=\alpha I;$$

$$\frac{\partial T}{\partial r}|_{r=0}=0,\qquad T|_{r=r_0}=T_0.$$

Here T is the gas temperature, T_0 is the wall temperature, κ is the gas heat capacity coefficient, α is the radiation absorption coefficient, β is the exponent, I is the radiation power, σ is the wave beam radius, q_i is the heat of decomposition (synthesis) of the ith reactant in the mixture, and w_i is the decomposition rate (synthesis) of the ith reactant in the mixture.

Figure 4 shows the radial distribution of temperature in the reactor at $\sigma = 4$ mm according to the scheme [13] for $I = 60$ and 90 W. It is seen that the reaction zone with the gas temperature above 800 is separated from the walls of a reactor chamber. This evidences the gas-phase nature of the reactions that occur in the chamber.

The computational and experimental data on the reaction kinetics obtained at the Boreskov Institute of Catalysis were compared to the data in literature [15], primarily in terms of representative reaction time. It was found that the schemes under consideration are applicable in quite a narrow

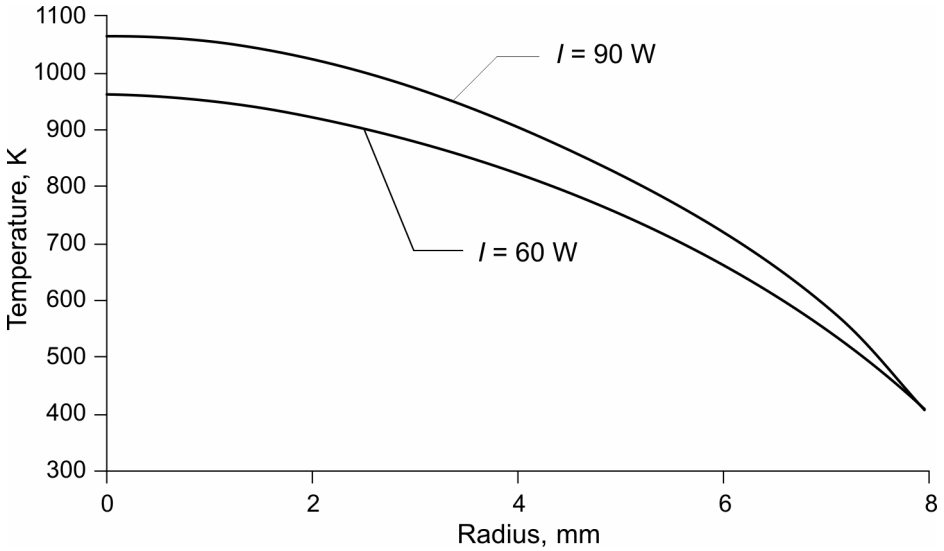

Figure 4. The calculated temperature distribution in the reactor

temperature interval under the atmospheric pressure. Some modifications of the schemes aimed at extending their range of use were also studied (description of experiments and theoretical estimations are presented in [17]). The simulation results for a wall-less reactor including the modification obtained were used to estimate the efficiency of the energy input to a reaction mixture and the possibilities of conducting the reaction control [18].

4. Conclusion

This paper presents the ChemPAK software package allowing the optimization of the kinetic scheme search and adjustment for the construction of a reaction mixture model. The package makes possible to evaluate the kinetic schemes using different models of a reaction mixture, which may include spatial models of reactors; it also provides specialists in the chemical kinetics and mathematical modeling with an efficient tool for simulating the physico-chemical processes in reactive media. Benefits of the ChemPAK are in the unlimited number of chemical reactions in a chemical reactions system, the possibility of chemical data from different chemical databases such as a Grimech, NIST, the possibility of re-using chemical reactions from other chemical reactions systems from database, possibility of using results of modeling in the FLUENT software, the network access to the ChemPAK chemical database, independence from the reactors geometry that gives the possibility of modeling the chemical kinetics before starting the reactor modeling. The ChemPAK was successfully tested on different chemical processes such as pyrolysis of hydrocarbons and sugar synthesis.

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