Development of a Software Application for Solving of Problems of Chemical Kinetics and its Implementation in a C

M.R.Manafov

***Abstract*— In this paper the authors described the software package for solution of wide range of tasks of the chemical and petrochemical industry. The existing programs are analyzed and their advantages and shortcomings are specified. The shortcomings of these works has been taken into account at creation of the software package. Along with numerical methods for the solution of various tasks (calculation of integral, numerical methods for solving equations etc.), class for the solution of direct and the inverse problem of kinetics, calculation and a choice of the equipment from the Access database has been defined . The generated package can be used by schoolchildren, students, engineers and scientists.**

***Index Terms*— software package, numerical methods, direct and the inverse problem of kinetics, C #**

I. INTRODUCTION

One of the main directions of scientific activities of the Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan is the study of the kinetics and mechanism of chemical processes, their modeling and optimization. In the Department "Modeling and technology of chemical and ecological processes" of the Institute of complex chemical reactions are studied using a software package OptimME, including methods of constructing mathematical models of chemical reactions [1], as well as methods for solving direct and inverse kinetic problems.

The development of information technology has opened up access to a huge, ever-increasing amounts of information about the catalytic reactions, technology processes and reactors. The emergence of the multiprocessor computers made possible to simulate the tasks which are not subject to direct experimental solution, such as, for example, research problems of the fast and limiting processes.

The need for the numerical solution of problems of chemical kinetics for reactions with a large number of steps is caused by modern requirements of the industry. Solution of tasks on improvement of oil and gas processing, improvement of chemical reactors are actual.

For each of these tasks should be carried out mathematical modeling and before changing production processes, it is necessary to improve chemical schemes at various stages of production. However, analytically solve such problems practically do not work out because of the huge size of the systems of ordinary nonlinear differential equations corresponding to schemes of chemical reactions.

The efficiency of the use of modern computer technology is an important criterion for the competitiveness of modern software application. Thus, the application software is relevant if it meets the requirements of the task and and as much as possible uses the available computing resources [2]. In this regard the problem of search of kinetic constants of a chemical reaction - a complex multi-parameter computing task, which decision is directly dependent on the performance of the computing environment, and on the used algorithms.

Creating a computer system [1], including the parameters of natural and computational experiments, mathematical modeling of reactions, processes and information and computer system with an ever-growing database of kinetic studies, would reduce the development time of kinetic models of complex reactions that, in turn, lead to acceleration of research and development of the new processes.

The objectives of this work are:

1) a description of mathematical models for problems of chemical kinetics;

2) analysis of existing software systems for the determination of kinetic parameters;

3) Development of the universal software for realization of kinetic studies and also calculation and a choice of some processing equipment on the basis of a database.

II. THE MATHEMATICAL FORMULATION OF THE PROBLEM

The equations of chemical kinetics is a system of ordinary differential equations [3]

$$\frac{dx}{dt} = f(x,k), x(0) = x_0, t \in [0, t_k]$$

where x, x_0 - current vectors and the initial concentrations of the reactants, f - vector function of the kinetic dependences which are built in accordance with the mechanism of chemical reactions, k - vector of the rate constants of elementary reactions.

2.1. Statement of the inverse and direct problems of chemical kinetics

2.1.1. Inverse task of chemical kinetics. As part of constants and often the entire vector k is unknown, there is a problem of identification of the mathematical model and the inverse kinetic problem, which is a problem of minimizing the functional deviations between the calculated and experimental data:

$$F = max \frac{x_j^e - x_j^c}{x_j^e} \rightarrow min, j = \overline{1,N}$$

Manafov Manaf Rizvan oglu, Department of "Modeling and technology of chemical and ecological processes, Laboratory "Modeling of chemical-technological processes", Institute of Catalysis and Inorganic Chemistry named after academician M.F.Nagiyev, Baku, Azerbaijan, (+994)502222927.

where x_j^c - the calculated values of the observed concentrations of substances (mole fractions); x_j^e - Experimental values of the observed concentrations of substances (mole fractions); *N* - the number of points of the experiment. In other words, the task is to determine the kinetic parameters corresponding to the minimum value of the difference calculated (the direct problem solution) and natural chemical (lab) data.

Kinetic parameters are the values of the kinetic rate constants and activation energies of stages. To determine the kinetic parameters To find the kinetic parameters should be put and solve direct and inverse kinetic problem.

2.1.2. Direct problems of chemical kinetics - is to calculate the composition of a multicomponent reaction mixture (concentration) and the reaction rate based on the mathematical description of the known kinetic parameters. At the same time solve the system of ordinary differential equations with given initial conditions with fixed and unknown, that is, the Cauchy problem. The solution of such systems is carried out by methods of Euler, Euler-Cauchy, Runge-Kutta, Kutta-Merson et al., depending on the required accuracy.

III. SOFTWARE FOR DETERMINATION OF KINETIC PARAMETERS.

The problem of finding the kinetic constants of a chemical reaction - a complex computing task, which is directly dependent on the performance of the computing environment, and the used algorithms.

The analysis of the existing programs for the calculation of the kinetic constants of chemical reactions is carried out. As the closest analogues are the following system (in parentheses indicate the software company): 1). ChemCAD; 2) .Chemical Kinetics Simulator (IBM); 3). (Chempak); 4) MATLAB (MathWorks); 5). Dynafit (BioKin); 6). Freefem Freefem3d and 7). Other programs.

3.1. ChemCAD [4] - Chemical Process Simulation Software - Includes database of chemical components, thermodynamic methods, and unit operations to allow steady state simulation of continuous chemical processes from lab scale to full scale. ChemCAD allows to create, analyze and optimize various options for technological design of production processes, evaluate their effectiveness and to choose the best of them.

The complex research using ChemCAD makes it possible to achieve a satisfactory agreement of the results of calculations with the data of industrial experiments that can solve the problem of automatic process control and improve the efficiency of existing production, determination of optimum operating and structural parameters of the processes in the individual devices from a position of total production as a whole.

3.2. Chemical Kinetics Simulator (CKS) [5], Chemical Kinetics Simulator (CKS) [5], was created by IBM in 1996 г. (PC) CKS is, on the one hand, quite limited means for modeling of chemical reactions, and on the other hand, the program including a intuitive input system of stages of chemical reactions. The main purpose of PC CKS - mathematical modeling of chemical reaction, the solution of the direct problem of chemical kinetics. The rate constants of reaction steps can be dependent or independent of the temperature, and stage-direct and inverse, but in any case the kinetic constants are set manually. However, despite the convenient input and visualization of solving the direct problem by using a PC CKS, can not solve the inverse problem of chemical kinetics. In addition, parallelization of a direct task that which affects the time of construction of the kinetic model isn't provided. The absence of the possibility of solving the inverse kinetic problem limits the use of CKS PC in combination with other software products (including in the framework of a unified information-analytical system solutions of multiparameter inverse problems of chemical kinetics, described in this paper).

3.3. Chempak [6]. Software package for the optimization of kinetic schemes of chemical reactions.

The algorithm - the system of ordinary differential equations (ODE) is generated from the system of chemical reactions. To solve the obtained ODE systems are used third-party software codes freely-distributable formats, adapted to work in the software package.

Functionality - The generation of systems of ODE of the systems of chemical reactions, in a unified storage network database systems of chemical reactions and initial data, decision of the ODE systems using the proposed solvers, obtaining of the output data (changing concentrations of chemicals in the time) in a form convenient for drawing freely distributed graphic packages.

Creation tools - DBMS Interbase, Borland C ++ Builder.

To install the software package and database of chemical reactions necessary configuration author solvers ODE systems under existing user Fortran compiler.

3.4.MatLab [7,8] of the company MathWorks - one of the oldest, well-developed and proven automation of mathematical calculations, based on the extended presentation and use of matrix operations.

Among the shortcomings of the system MatLab can be noted a low integration environment (lots of windows, which is better to work on two monitors), is not very coherent reference system (and yet the amount of firm documentation is big, which makes it difficult foreseeable) and specific MatLab-code editor programs (M-file). Today the system MatLab widely used in engineering, science and education, but all the same it is more suitable for data analysis and algorithms, rather than for purely mathematical calculations.

As a simple, but ideologically close alternatives MatLab program packages can be noted such as Octave (www.octave.org), KOctave (bubben.homelinux.net/~matti/koctave/) and Genius (www.jirka.org/genius .html). The advantages of MATLAB compared with the packages MathCAD, MAPLE, SciLab, FreeMath. these are extensive help system, a large number of reference books, including the Russian-speaking, relatively comfortable programming environment, the availability of versions for the operating systems Linux and Windows, and means for the effective parallelism.

Ready-made modules for the calculation of the inverse problem of chemical kinetics in MATLAB does not exist yet. At the same time there is the possibility of using ready-made libraries, among which there are algorithms for solving systems of differential equations, finding the minimum criterion of conformity of calculated and observed data, and others. The main disadvantage of MATLAB is its high cost.

3.5. Dynafit [9] - the program for the calculation of kinetic constants -designed by BioKin. The interface is divided into two parts: Input and Output. In the Input tab is made entering the reaction scheme, the designation of the kinetic constants and the building of the time axis with the experimental data. The main objective of Dynafit - is the search for the initial values of kinetic constants of the least squares method. As the format of input data using a symbolic notation, while the circuit parameters and not conversions are given graphically in a tabular format, according to certain rules. Such a scheme may be inconvenient input inexperienced user, but in the future can be used as a means of quick editing of new schemes. Result of the work programs can be output characteristics of the used algorithm and concentration changes in time. The program has a good help system.

3.6. In order to solve partial differential equations by finite element method and visualization solutions have freeware packages Freefem and Freefem3d [10], which in its capabilities are not inferior to the module solutions of the equations of mathematical physics package Matlab.

3.7. To solve problems of chemical kinetics with a large dimension requires advanced software that meets certain requirements. Among them should indicate the presence of an ergonomic interface and extensible library of computational methods, the ability to work with modern database physico-chemical data (GRIMECH, NIST, NASA, and others.) and the ability to work in conjunction PC - supercomputers. Recently a number of the software products focused on the tasks described above were developed. There are major software products for a wide range of modeling tasks FLUENT, CHEMKIN, StarCD, HYSYS and others. There are small software packages (CKS, Kintecus, AcuChem, ChemMathS et al.). In addition to these commercially distributed software packages, there is also a number of specialized libraries of subroutine NAG, Numerical recipes developed over the years. The disadvantages of specialized libraries routines are the high complexity of the data structure, the lack of an ergonomic interface, as well as difficulties associated with the library architecture.

Thus, today there are software products, specializing not only in solving a wide range of problems of the chemical industry (ChemOffice, Chemkin, Khimera, MATLAB), but also specialized programs for the calculation of kinetic constants (Dynafit, CKS, KINET). These programs are generally easy to solve a specific range of tasks. The main drawback of the programs is that they do not use existing information technology fully, which in turn affects the speed of calculation, reliability and ease of visualization.

IV. THE STRUCTURE OF THE SOFTWARE PACKAGE OPTIMME FOR SOLUTION OF KINETIC PROBLEMS

4.1. General characteristics of SP OptimME

The developed software package OptimME differs: 1. The presence of readily expandable database of chemical reactions and chemical auxiliary data. The presence of an open architecture for replenishment of package with uniprocessor and multiprocessor computing modules. 3. Availability of software interface for searching of chemical reactions in the database on a template with the possibility of entering of retrieval system in a new system of chemical reactions within the common programming interface of package. 4. Availability of the software interface of interaction with databases of third-party developers. 5. The presence of various formats input and output files of the package for working with different types of computing modules 6. The presence of parallel code generator for the numerical solution of direct problems of chemical kinetics on a parallel supercomputer. The main interface of the package shown in Fig.1.

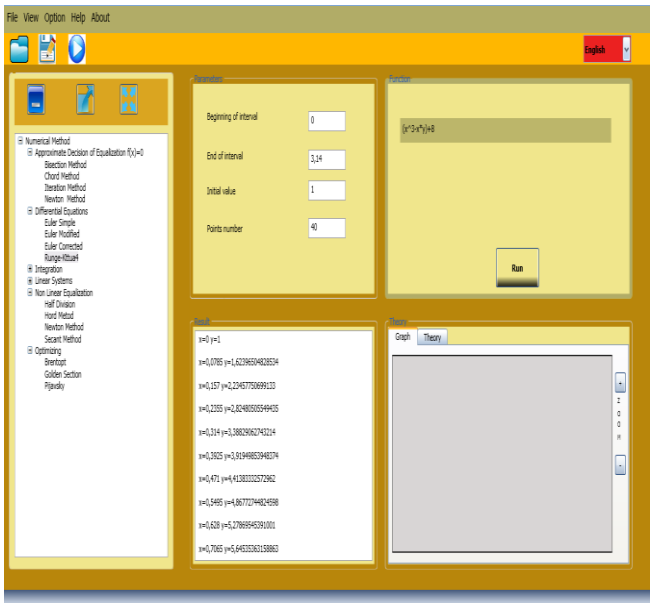

Fig. 1. The main interface of the software package .

4.2. Classes of solved tasks. As you can see from the picture all solved tasks are distributed on classes. So class codes in short form are as shown below.

4.2.1. Class "Methods of approximate solutions of equations F (x) = 0 ". In this class implemented methods: bisection method, method of chords, iteration method, Newton's method

4.2.2. Class "Differential equations". In this class implemented methods: Euler method (simple), Improved Euler method, The specified Euler's method, Runge-Kutta method.

Below is the code for this class.

```
using System;
using System.Collections.Generic;
using System.Linq;
using System.Text;
namespace riyazi
{
   // metod diferensiyal
   public class EulerSimple
   {
      public double[,] result { get; protected set; }
      public delegate double Function(double x, double y);
      public delegate double FunctionOne(double x);
      public EulerSimple(Function function, double begin,
double end, double y0, int pointsNum)
      {
         double y;
         double y1;
         double x = 0;
         double h;
         result = new double[2, pointsNum];
```

```
            h = (end - begin) / pointsNum;
            y1 = y0;
            y = 0;
            for (int i = 0; i < pointsNum; i++)
            {
               y = y1 + h * function(x, y);
               y1 = y;
               x = x + h;
               result[0, i] = x;
               result[1, i] = y;
            }
         }
      }
      public class EulerModified
      {
         public double[,] result { get; protected set; }
         public delegate double Function(double x, double y);
         public delegate double FunctionOne(double x);
         public EulerModified(Function function, double begin,
double end, double y0, int pointsNum)
         {
            double y = 0;
            double y1;
            double f1;
            double x = 0;
            double h;
            result = new double[2, pointsNum + 1];
            h = (end - begin) / pointsNum;
            y1 = y0;
            x = 0;
            result[0, 0] = x;
            result[1, 0] = y1;
            for (int i = 1; i <= pointsNum; i++)
            {
               f1 = function(x, y);
               x = x + h;
               y = y + f1 * h;
               y = y1 + h * (f1 + function(x, y)) / 2;
               y1 = y;
               result[0, i] = x;
               result[1, i] = y1;
            }
         }
      }
      public class EulerCorrected
      {
         public double[,] result { get; protected set; }
         public delegate double Function(double x, double y);
         public delegate double FunctionOne(double x);

         public EulerCorrected(Function function, double begin,
double end, double y0, int pointsNum)
         {
            double y = 0;
            double y1;
            double f1;
            double x = 0;
            double h;
            result = new double[2, pointsNum + 1];
            h = (end - begin) / pointsNum;
            y1 = y0;
            for (int i = 0; i <= pointsNum; i++)
            {
               f1 = function(x, y);
               y = y1 + (h / 2) * (function(x, y) + function(x + h, y
+ h * f1));
               result[0, i] = x;
               result[1, i] = y1;
               y1 = y;
               x = x + h;
            }
         }
      }
      public class RungeKutta4
      {
         public double[,] result { get; protected set; }
         public delegate double Function(double x, double y);
         public delegate double FunctionOne(double x);
         public RungeKutta4(Function function, double begin,
double end, double y0, int pointsNum)
         {
            result = new double[2, pointsNum + 1];
            double k1;
            double k2;
            double k3;
            double h = (end - begin) / pointsNum;
            double y1;
            double x = 0;
            double y = 0;
            y1 = y0;
            result[0, 0] = x;
            result[1, 0] = y1;
            for (int i = 1; i <= pointsNum; i++)
            {
               k1 = h * function(x, y);
               x = x + h / 2;
               y = y1 + k1 / 2;
               k2 = function(x, y) * h;
               y = y1 + k2 / 2;
               k3 = function(x, y) * h;
               x = x + h / 2;
               y = y1 + (k1 + 2 * k2 + 2 * k3 + function(x, y) * h)
/ 6;
               y1 = y;
               result[0, i] = x;
               result[1, i] = y1;
            }
         }
      }
   }
```

1) *4.2.3. Class "Calculations of the integral." Within this class implemented methods: Chebyshev's method, Simpson's Rule , the midpoint rule, the trapezoidal rule .*

2) *4.2.4. Class "Nonlinear equations". Within this class implemented methods: bisection method , chord method, Newton's method, secant method.*

4.2.5. Class "Optimization Techniques". Within this class implemented methods: golden section, Brentopt's method.

4.2.6. Class "Kinetics of chemical reactions" includes modules for determining the order and constant individual reaction, the temperature dependence of the reaction rate constant and the activation energy, and numerical methods for solving direct and inverse task of kinetics.

For definition of the activation energy of elementary stages traditionally find the rate constants by separate solution of the of inverse problems of chemical kinetics for different experimental temperatures, with further approximation of the integral form of the Arrhenius equation, method of least squares (OLS). This approach leads to additional error under experimental and calculated values observed concentrations of substances and does not always determine the kinetic parameters of the reaction stages, but it is the express method [11].

4.2.7. Class "Calculation and selection of equipments" includes a module for the heat exchanger and absorber with the Access database.

V. DISCUSSION OF THE RESULTS OF DEVELOPMENT OF " SP OPTIMME" .

As a result of the analysis of the differential equations in the solution of the major classes of problems of chemical and petrochemical industry , it was decided to realize the Runge-Kutta method, golden section, Brentopt, Pizhavski methods and others. The reason for this is that these methods are universal to the main tasks of chemistry and petrochemistry[12]. Advantages of the method of golden section and Brentopt's method lies in the fact that they are quite simple, do not require large computing resources, and do not require the derivative of the objective function. Use the *Piyavsky method*, is justified by the fact he has a simple convergence condition and can be applied to a broad class of functions. Runge-Kutta method shows high accuracy compared to study methods. Good results are obtained when applying the4-th order of this method.

Analysis of programming languages and computer industry and the current state of computer resources of the country, confirm the benefits in C #. This language does not impose a limitation when choosing an operating system.

A large number of implemented mathematical methods allows depending on required accuracy to choose one or the other method and reduce the calculation time.

The practical significance of the work

Designed PP for the solution of inverse problems of chemical kinetics tested for solvent extraction separation of contaminated water, the study of the kinetics of vapor phase ammoxidation al., And is used to improve the efficiency of numerical experiments [1],[13]-[17].

VI. CONCLUSION

Within the carried-out work the following results were received:

• The analysis of existing software systems for the determination of kinetic parameters.

• developed a software package for solving problems of chemical and petrochemical industries, which increases the efficiency of computing experiments.

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