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From Experimental Data Via Kinetic Model to Predicting Reactivity and Assessing Reaction Hazards

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ABSTRACT

There is no other way to get original data regarding chemical reaction but experimental study. What kind of experimental technique to use depends on the aim of a study. Nevertheless, there is one almost universal method that is particularly applicable in such areas as predicting reactivity, assessment of reaction hazards, thermal stability of chemicals, etc. This is calorimetry of various types (DSC, isothermal, reaction, adiabatic etc.). Very often calorimetry is used for direct experimental determination of necessary characteristics. At the same time, introduction of mathematical simulation can provide obtaining much more versatile and reliable results in combination with more complete use of information contained in experimental data. The approach to investigating chemical reaction and predicting its behavior under various conditions, which systematically uses kinetics-based simulation, is the subject of the paper.

At first, several examples are shown that demonstrate efficiency of the approach. The following cases are discussed:

- Predicting adiabatic course of a reaction using DSC and adiabatic data
- Analyzing thermal stability of a product, influence of product's composition and presence of contaminants
- Determining reactivity rating number of a chemical product
- Determining critical parameters of thermal explosion
- Simulating runaway in a BATCH and vent sizing
- Designing an inherently safer process

All these examples are based on real experimental data and regard some typical practical problems.

Then the general scheme of the simulation-based approach is discussed which consists of three basic steps:

- Carrying out the necessary set of calorimetric experiments and proper processing of data for kinetics evaluation;
- Creating the mathematical model of a reaction – evaluating kinetics;
- Solving practical problem using mathematical (numerical) simulation.

The main merits of the approach are as follows

- possibility to apply more adequate complex mathematical models of processes;
- possibility to simulate and analyze various scenarios of process proceeding;
- possibility to model thermal explosions and runaways without essential simplifications;
- principal solution of the scale-up problem.

Some problems dealing with practical application of the proposed method are examined.

In conclusion, the composition of a problem-oriented software series is discussed that simplifies introduction of simulation-based methods into research practice. The programs of this series form three groups intended for initial processing of calorimetric data, creation of mathematical model of a reaction, and for simulation of processes' proceeding.

FROM EXPERIMENTAL DATA VIA KINETIC MODEL
TO PREDICTING REACTIVITY AND ASSESSING REACTION HAZARDS
(Methodology and Software)

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Abstract.

The objective of this paper is to discuss the features of the approach to investigating chemical reactions and predicting their behavior under various conditions, which systematically uses kinetics-based simulation. Several practical examples demonstrate the efficiency of this approach when it is applied for assessment of reaction hazards, reactivity analysis, design of inherently safer processes. Being very promising and versatile, simulation based methods turn out to be rather difficult for introduction into research practice because they involve knowledge from various areas – experiment's technique, chemical kinetics, thermal physics, mathematics, numerical methods, etc. This problem can be resolved by applying some problem-oriented tools that are convenient for researchers and include relevant methods and corresponding software. The Thermal Safety Software (TSS) series developed by CISP may serve as an example of such tool. An overview of TSS is presented in the last part of the paper.

Introduction.

There is no other way to get original data regarding chemical reaction but experimental study. Specific kind of experimental technique, which is to be used, depends on the aim of a study. Nevertheless there is one almost universal method that is particularly applicable in such areas as predicting reactivity, assessment of reaction hazards, thermal stability of chemicals, etc. This is calorimetry of various types (DSC, isothermal, reaction, adiabatic calorimetry etc.). Very often calorimetry is used for direct experimental determination of necessary characteristics. At the same time introduction of mathematical simulation can provide obtaining much more versatile and reliable results in combination with more complete use of information contained in experimental data. The approach to investigating chemical reactions and predicting their behavior under various conditions, which systematically uses kinetics-based simulation, is the subject of the paper.

At first several practical examples demonstrate the potential of simulation-based method for solving such problems as analyzing reactivity of a substance, determining critical parameters of thermal explosion, designing inherently safer process, etc.

Then the general scheme of the simulation-based approach is considered and its merits and related problems are discussed.

In conclusion the composition of the problem-oriented software is presented that simplifies introduction of simulation-based methods into research practice

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Examples of Applying the Approach

1. Predicting Reaction Course under pure adiabatic Conditions

Predicting reaction course under pure adiabatic conditions ensures close approximation of the runaway in an industrial reactor. It can be done on the basis of available calorimetric data. How can simulation help to make such prediction? Let us consider two cases.

Case 1. Correcting Adiabatic Data on Thermal Inertia

Phenol + Formaldehyde runaway reaction has been studied by using the accelerating rate calorimeter (ARC) at $\phi = 1.33$. The primary analysis of data reveals pronounced two-stage mechanism. (Fig. 1).

The data processing is aimed at correcting adiabatic data on thermal inertia. There are several well-known simplified methods (for instance, proposed by D. Townsend [1]), but all of them are based, explicitly or implicitly, on the assumption that a reaction has the simplest single-stage zero order mechanism. Therefore they are inapplicable in our case.

Let us suppose that the reaction kinetics consists of two consecutive stages:



The corresponding mathematical model is

$$\frac{d\alpha}{dt} = r_1 = k_{01}(1-\alpha)^{n1} e^{-\frac{E_1}{RT}}; \quad \frac{d\gamma}{dt} = r_2 = k_{02}(\alpha-\gamma)^{n2} e^{-\frac{E_2}{RT}}; \quad \frac{dQ}{dt} = Q_1^\infty r_1 + Q_2^\infty r_2 \quad (2)$$

After estimating kinetic parameters of the model the appropriate data fitting has been obtained. Then the model was used for simulation of pure adiabatic conditions ($\phi = 1$). Fig. 1 depicts both fitting of experimental data and results of simulation of pure adiabaticity. These results allow assessing all the necessary characteristics of adiabatic runaway.

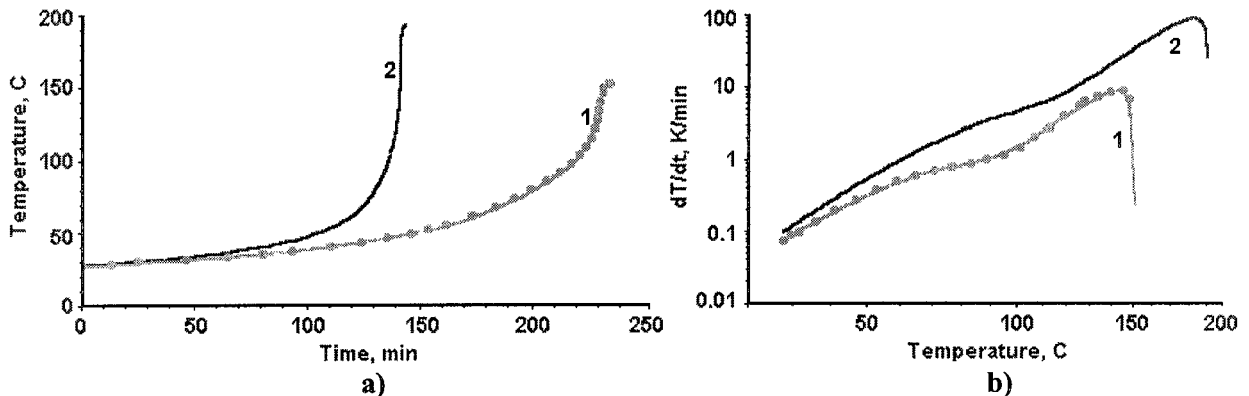


Fig. 1 Kinetics-based fitting of adiabatic data and simulation of pure adiabaticity.

a) – temperature profile; b) – self heating rate

1 – experimental conditions ($\phi=1.33$); 2 – prediction of pure adiabaticity ($\phi=1$);

**** - experiment; — - simulation.

As we can see the method is applicable to a reaction of any complexity (more examples can be found in [2]).

Case 2. Using DSC data for predicting adiabatic profile of a reaction.

Consider now the decomposition of di-tert-butyl peroxide (20% solution in toluene), which is often used as a benchmark. Two data sets are available. One of them was obtained by using capillary DSC. The other one is the result of adiabatic (ARC) experiment. The substance is decomposed in accordance with the simple N-order reaction. The question is whether DSC data can be used for reliable prediction of an adiabatic process. Therefore ARC data will be used for validation of the simulated results.

The model of the N-order reaction:

$$\frac{d\alpha}{dt} = r = k_0(1-\alpha)^n e^{-\frac{E}{RT}}; \quad \frac{dQ}{dt} = Q^\infty r \quad (3)$$

with the parameters estimated on the basis of DSC data provides good data fitting (Fig. 2a). Then the reaction course under conditions of the ARC experiment was simulated using the created model. The appropriate correspondence between calculated and experimental curves (see Fig. 2b) confirms correctness of the simulated results. Apparently the reaction profile under pure adiabatic conditions can also be predicted reliably.

Again the method is applicable to a reaction of any complexity

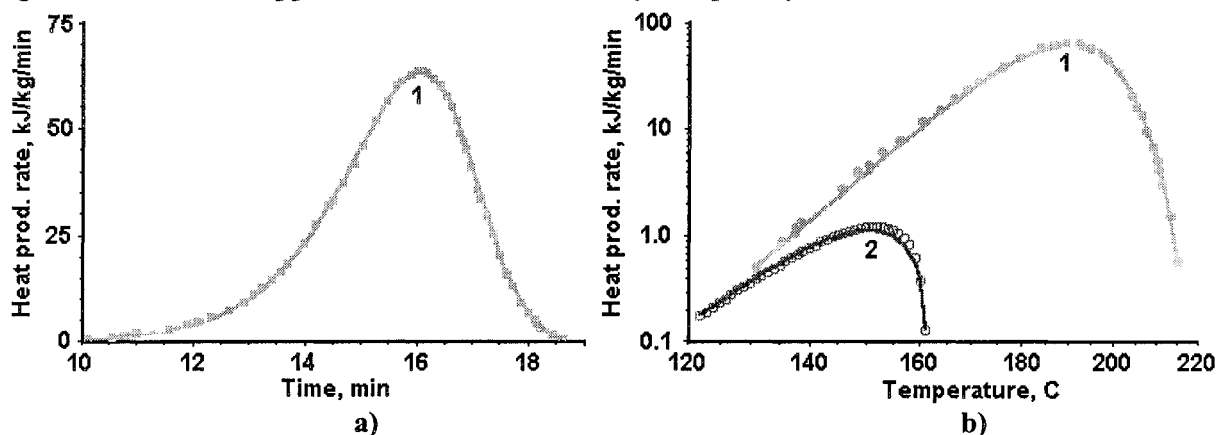


Fig. 2. Decomposition of DTBP. Kinetics-based simulation of adiabatic mode.

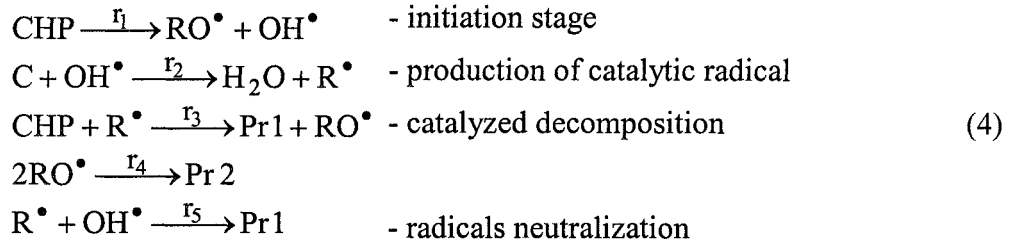
a) – Fitting of original DSC data; b) – Comparison of ARC data with simulated results.

1 – DSC data; 2 – ARC data; ■■■□ - experiment; — - simulation.

2. Reactivity Analysis

One of very important practical problems is prediction of how such factors as mixture composition, presence of contaminants, etc., affect the reaction proceeding. Consider as an example the decomposition of Cumene Hydroperoxide (80% solution in Cumene), which has been investigated by using heat flux calorimetry under isothermal conditions [3].

Experimental results (Fig. 3a) demonstrate pronounced self-acceleration of the decomposition. As is well known the origin of self-acceleration of this reaction is production of some intermediate radicals. Following this idea we will use for further analysis the hypothetical reaction scheme:



where the following notation was used: CHP - cumene hydroperoxide; C - cumene; R, RO and OH - radicals, Pr1 and Pr2 - reaction products.

All 23 kinetic parameters of the model have been estimated using four available data sets simultaneously, which resulted in good data fitting shown in Fig. 3a.

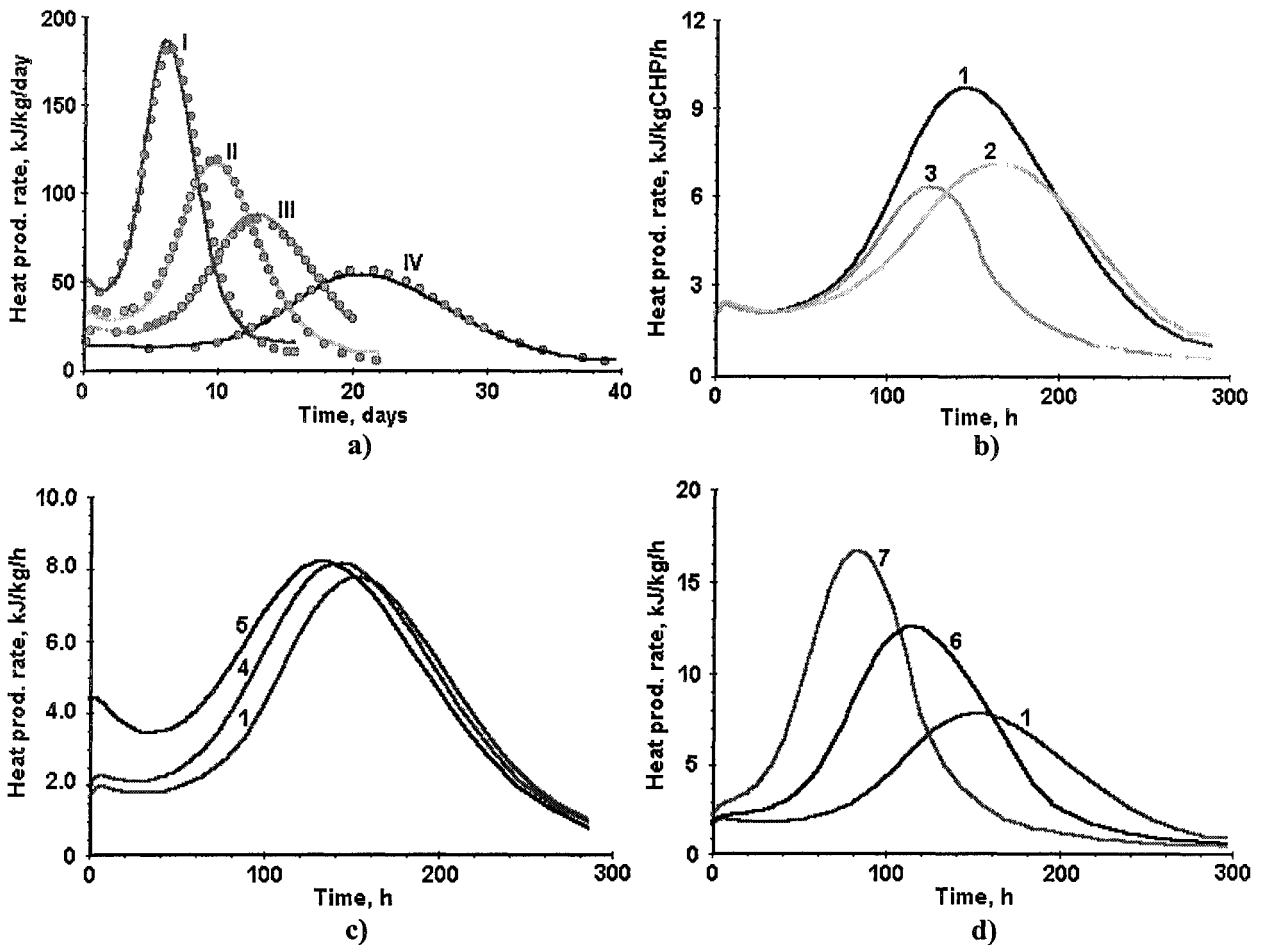


Fig. 3. Decomposition of Cumene Hydroperoxide.

a) Fitting of calorimetric data by the kinetic model: I - 75 °C; II - 80 °C; III - 83 °C; IV - 88 °C.

**** - experiment; — - simulation.

b) - d) influence of various factors on the reactivity of the solution (at T=88 °C):

b) CHP/Cumene ratio (mass fractions): 1 - 0.8/0.2; 2 - 0.6/0.4; 3 - 0.9/0.1.

c) presence of the R radical; CHP/Cumene/R ratio: 4 - 0.8/0.18/0.02; 5 - 0.8/0.16/0.04.

d) presence of the OH radical; CHP/Cumene/OH ratio: 6 - 0.8/0.18/0.02; 7 - 0.8/0.16/0.04.

Then the mathematical simulation was applied to analyze reactivity of a mixture depending on

solution concentration (Fig. 3b) and presence of some radicals in the initial composition (Fig. 3c, d). The results give valuable information. Specifically,

- The solution composition that contains 80% of CHP is most hazardous, some decrease or even increase of the content of CHP significantly reduces the heat release rate.
- As expected, presence of small amounts of radicals in the initial composition accelerates the reaction. It turns out that the R radical-catalyst affects the initial rate of the reaction but its maximal rate and time to maximum rate remain almost unchanged (Fig. 3c). Quite the contrary the OH radical doesn't affect the initial rate but increase of OH concentration causes significant rise of maximal rate and reduction of time to maximum rate (Fig. 3d). Thus, from the safety point of view, the OH radical represents very dangerous contaminant.

This example illustrates well the usefulness and universality of applying simulation to the analysis of reactivity and stability of a substance.

3. Defining Critical Parameters of Thermal Explosion

Determination of critical parameters of thermal explosion is an important task, which is to be solved for choice of safe conditions of storage, transportation or application of hazardous materials. The well-known simplified theories developed by Frank-Kamenetskii and Semenov (see, for instance, [4]) give convenient analytical expressions that provide simple calculation of critical parameters. However they are valid only for the simplest kinetics and geometry. Therefore many practical problems cannot be solved without applying numerical simulation [5].

Consider the exothermic decomposition of a solid substance that was investigated by DSC. Two available data sets obtained at different heating rates 0.2 and 0.5 K/min reveal complex reaction mechanism and the model of two consecutive stages (1-2) is supposed to be relevant in this case. Kinetic parameters estimated on the basis of both data sets result in good data fitting (Fig. 4).

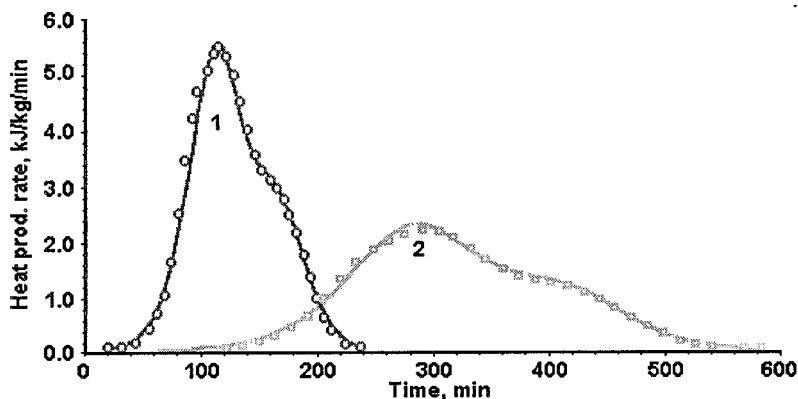


Fig. 4. Decomposition of a solid product. Fitting of DSC data by the kinetic model.

1 – Heating rate 0.5 K/min; 2 - Heating rate 0.2 K/min; ■■■□□ - experiment; ——— - simulation

Then the model was used for simulation of thermal explosion in the barrel filled with the substance. The simulation had to answer two questions:

- What is the potential thermal explosion hazard?
- How does the material of a container affect the reaction course?

The simulation was made for the barrel with diameter $D = 1$ m; height $H = 1$ m; thickness of the wall was 0.02 m. (Fig. 5a). Thermal conductivity of the substance is $\lambda = 0.2$ W/m/K whereas the

container material is almost thermal insulator with $\lambda = 0.01$ W/m/K.

The results of simulation are presented in Fig. 5b-d.

Fig. 5b indicates that under given conditions the reaction in the pure substance proceeds smoothly almost without overheating and there is no explosion whereas presence of the insulation wall changes dramatically the thermal mode. Simulation can provide the detailed data upon variation of temperature distribution in time (Fig. 5c) and localization of temperature (Fig. 5d) and conversions extremes using 3-dimensional plot.

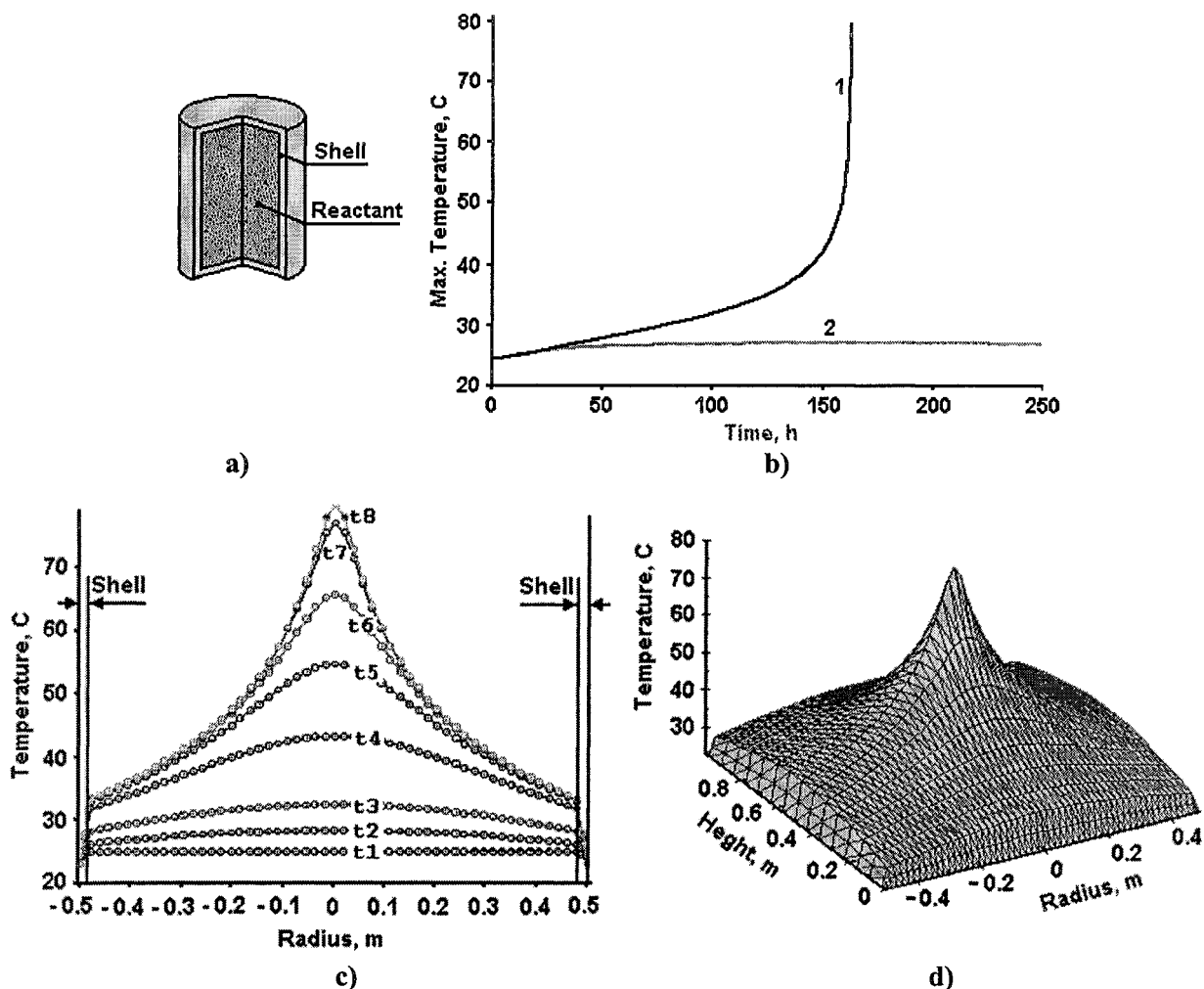


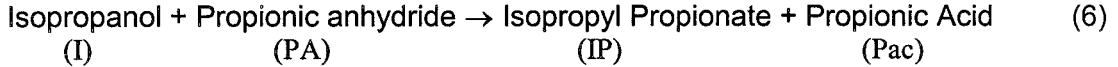
Fig. 5. Influence of insulation shell on the explosion in a barrel.

a) – Sectional view of a barrel; b) - Variation of maximal temperature in time, 1 – shelled barrel, 2 – barrel without a shell; c) - Temperature profiles in the shelled barrel ($t_1 < t_2 < t_3 \dots < t_8$); d) - 3-D presentation of temperature distribution in the shelled barrel (corresponds to t_8)

4. Simulating Runaway and Vent Sizing

Design of the Emergency Relief System for protection of an industrial reactor at runaway is another important task of reaction hazard assessment. Numerical simulation is used for this purpose much more actively than in previous cases (mention for instance such software as SAPHIRE, RELIEF, SuperChems). Kinetic model of a reaction is the key element necessary for simulation.

The recent example, which is very relevant for demonstration, is the Round-Robin test proposed by Health and Safety Executive (HSE) [6]. The equimolar esterification reaction between propionic anhydride and isopropanol was chosen for the vapor pressure system exercise:



Two experimental data sets obtained at different onset temperatures by using the Phi-Tech adiabatic calorimeter were available (see Fig. 6).

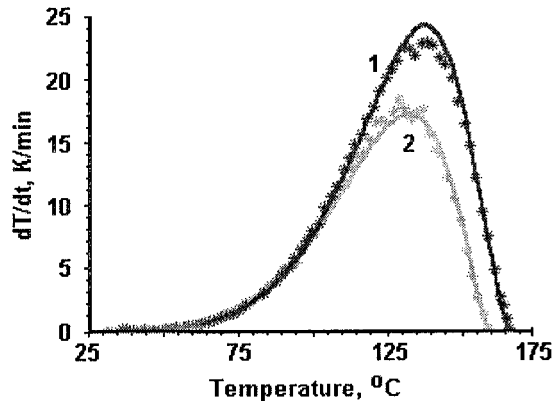
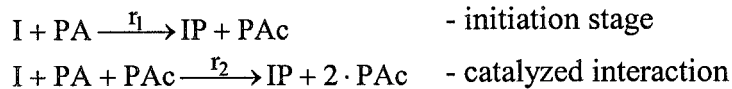


Fig. 6. Adiabatic data on esterification reaction.

1 – Onset temperature 35 °C; 2 – Onset temperature 25 °C; * – experiment; — – simulation

In this case the kinetics evaluation has one important peculiarity. The matter is that either single data set doesn't reveal any complexity of a reaction though it is known that the esterification reactions are characterized by self-acceleration. From the formal point of view every single data set can be fitted well by the N-order model. But it turns out that this model cannot fit two data sets at a time. Only the model of autocatalysis ensures good fitting of all the available data. So we meet the case when reliable discrimination of the adequate reaction model can be achieved only by using all existing data. Therefore simultaneous use of two data sets is on principle.

The reaction scheme that describes the autocatalytic effect of an acid reaction product is:



Estimated kinetic parameters of the model provide an appropriate data fitting (see Fig. 6).

Then this model was used for simulation of runaway in the reactor with relief system for the conditions of pilot-scale experiment implemented by HSE. The detailed information regarding this experiment can be found in [6]. Here we give only some basic data.

The reactor is a 312 liters vertical cylindrical tank with heat exchange (heat transfer coefficient $U = 270 \text{ W/m}^2/\text{K}$, heat exchange surface $S = 1.53 \text{ m}^2$).

The vent system is mounted on the top and has the following parameters:

- total length - 4.82 m;
- diameter - 7 cm;
- maximal allowed pressure - 1.5 bar; overpressure - 5%; back pressure - 1 bar.

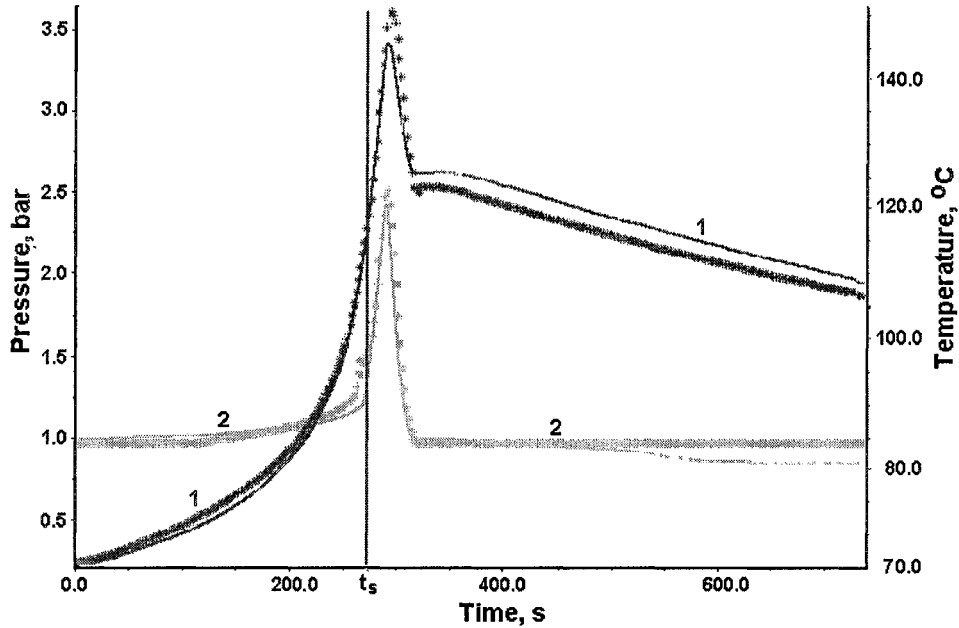


Fig. 7. HSE round robin test. Comparison of simulated data and results of pilot-scale experiment.

1 – temperature profile; 2 – pressure profile; t_s – start of venting; * – experiment; — – simulation.

Comparison of the simulated results with data of the pilot-scale experiment presented in Fig. 7 confirms correctness of the modeling.

5. Designing Inherently Safer Semi-Batch Process

The last example illustrates usefulness of applying simulation for reactor's optimization and design of inherently safer processes. The concept of inherent safety covers a wide variety of aspects. Here we will discuss only one of them – how to prevent rise of a reactor temperature above some permissible limit in the worst case of cooling failure (an accident). From this point of view design of an inherently safer process comes to defining its normal course so as to avoid superfluous accumulation of unexpended energy in a reactor. This problem can be solved by optimizing a process (the detailed statement can be found in [7]).

Consider the same esterification reaction (6) assuming that it is intended for synthesis of a product. As we could see, the batch process proceeds in the runaway mode despite the cooling of the tank. Let us try to design the inherently safe semi-batch process. The size and cooling capacity of the tank are the same as in previous example. Initially the tank is filled with isopropanol at 70 °C and then propionic anhydride is added. The optimization was aimed at searching for such feed rate profile of this reactant that could satisfy the optimization criterion

$$\min_{t \in [0, t_f]} (\text{MTR} - \text{MPT}) \quad (7)$$

where MPT – maximal permissible temperature; MTR – maximal temperature of synthesis reaction, which corresponds to the worst case scenario; $\text{MTR} = \max_{t_{cf} \in [0, t_f]} (T_{cf})$, T_{cf} is the

adiabatic temperature attained in the reactor after all the energy accumulated in the reactor by the time t is released, and if cooling failure occurs at that time and adiabatic thermal explosion develops in the reactor.

Note that choice of MPT depends on the specific target – it may be boiling temperature of a mixture, onset temperature of secondary reactions, etc.

The feed is defined as series of 10 pulses adjoining to each other, initially all the pulses have the same duration (10 min) and amplitude (1.65 dm³/min). The sought for parameters were the amplitudes of pulses.

The simulated temperature profiles for the non-optimized process under normal and accidental conditions are shown in Fig. 8 a, b. In both cases the maximal temperature of the process exceeds MPT.

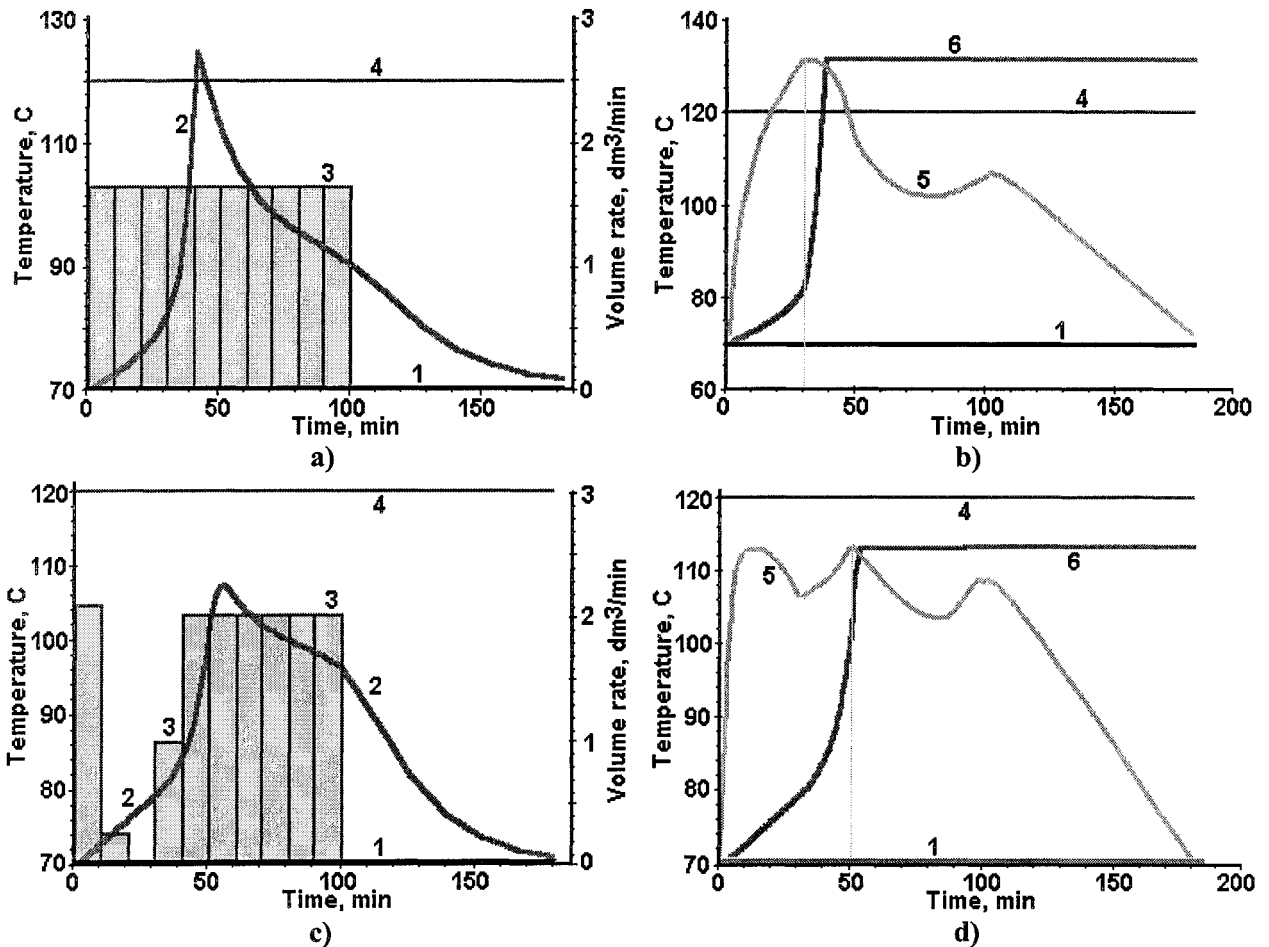


Fig. 8. Optimization of thermal mode of semi-BATCH process.

a, b – temperature profiles of non-optimized process; a) – normal conditions; b) – accident;
c, d – temperature profiles of inherently safe process; c) – normal conditions; d) – accident;

1 – jacket temperature; 2 – temperature in the reactor; 3 – feed rate profile; 4 – MPT; 5 - T_{c6} ; 6 - MTSR.

The results of optimization presented in Fig. 8 c, d demonstrate inherent safety of the process. Even in the worst case (cooling failure occurs on the 50th minute of the process) MTSR is approximately 8 degrees lower than MPT.

No doubt the expediency matters should be taken into account when designing a process, i.e. a safer process should have reasonable yield, acceptable duration, etc. Therefore the optimization method should allow taking into account not only safety criteria but also some constraints on control and state variables. In the presented example such constraints were imposed on concentrations of

reactants and process time (the corresponding upper permissible levels shouldn't be exceeded).

General Scheme of the Simulation - Based Approach

In spite of the difference between the examples we considered, the same approach has been used for solving problems (see Fig. 9).

In the first stage necessary series of calorimetric experiments was carried out.

In the second stage the mathematical model of a reaction was created.

Finally the created model was incorporated into the model of a process and the practical target was achieved by using mathematical (numerical) simulation.

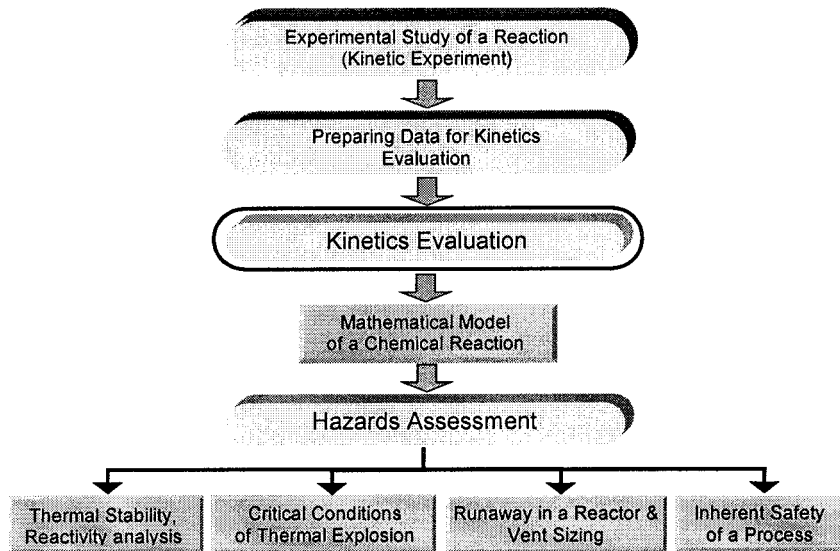


Fig. 9. General scheme of simulation-based approach.

Is this approach simple? No. We have to establish a fact that this method is complicated enough.

In practice the presented procedure turns out to be iterative rather than the plain one. Specifically we have to go back to experiment from the kinetics evaluation step to get more data necessary for validation of the created model or for discrimination of more relevant model from the set of competing ones. In the same way, the necessity may appear to perform some additional experiments and create more comprehensive kinetic model when a specific final problem is being solved.

Let us mention some other peculiarities that complicate application of the approach.

1. This is a knowledge-consuming way that requires applying methods from various fields - mathematics, numerical methods, chemical kinetics, thermal physics, etc.
2. Correctness of the results obtained on some step of investigation significantly affects the reliability and correctness of results of all the subsequent steps, therefore every step should be provided with appropriate elaborate methods. Specifically, methodology of experimental study and processing of raw data should be reviewed attentively to ensure obtaining real quantitative data suitable for kinetics creation.
3. As every step of the scheme is complex enough, involves many branches of knowledge and cannot be completely formalized, high demands have to be made to the professional skill of a

researcher.

Therefore the methodology is intended mostly for the experts.

At the same time the approach has numerous merits that ensure its practical effectiveness. Some of them are listed below:

- possibility to apply more adequate complex mathematical models of processes;
- possibility to simulate and analyze various scenarios of process proceeding;
- possibility to model thermal explosions and runaways without essential simplifications;
- principal solution of the scale-up problem.

What measures should be undertaken in order to simplify introduction of simulation-based methods into research practice? Apparently this can be resolved by creating the problem-oriented tools that are convenient for researchers and include relevant methods and corresponding software. This has been one of the main aims of our activity during last years.

Today a problem-oriented system of this kind exists and corresponding commercially available software has been designed. Fig. 10 depicts the structure of the Thermal Safety Software (TSS) series, internal links between separate applications, and some standard tasks that can be solved.

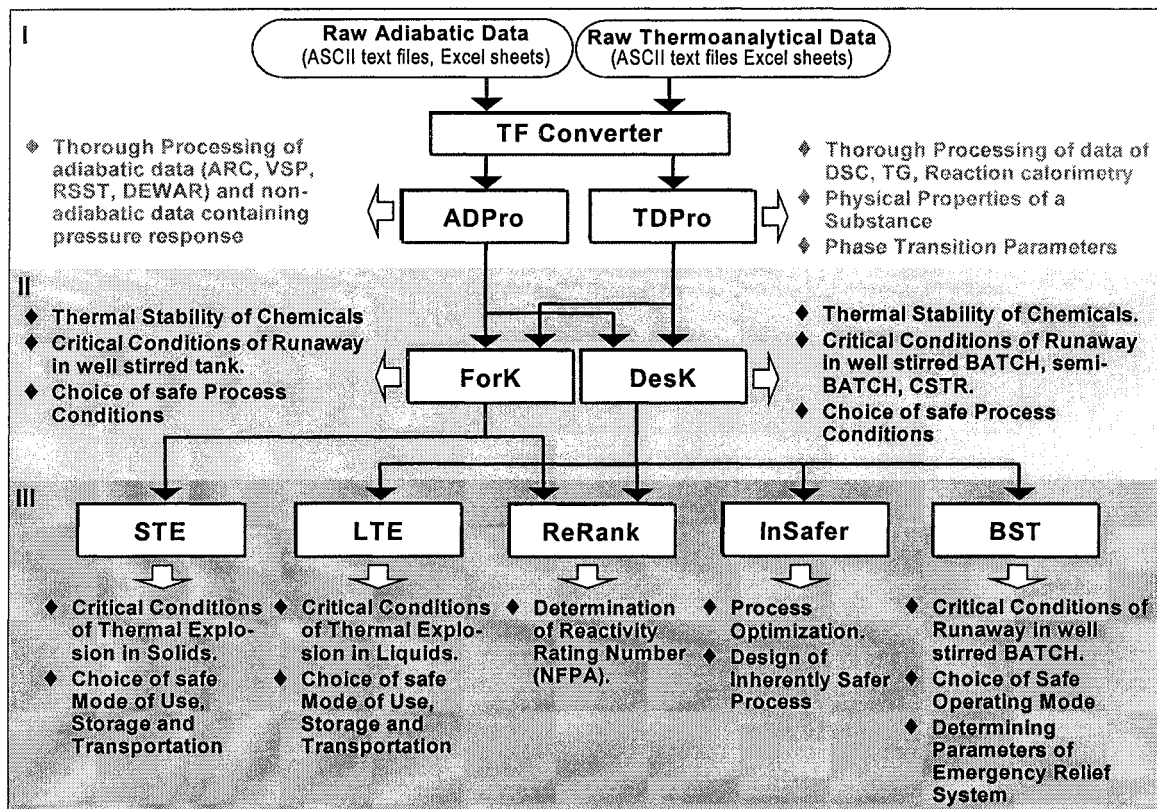


Fig. 10. Structure of the software set for reaction hazard assessment.

I – applications for initial processing of experimental data; II – applications for models creation; III - applications for simulation of runaways.

We won't discuss features and functionality of TSS in detail. Such discussion as well as consideration of some methodological aspects can be found in [8, 9]. Here we will give only overview of TSS.

All the applications of TSS form tree groups.

The group I contains the programs for initial processing of adiabatic (ADPro) and thermoanalytical (TDPro) data. Both programs are based on up-to-date methodology including some original methods. They provide performing all the necessary procedures for proper preparing data for kinetics evaluation.

The groupII includes two programs intended for creation of kinetic models. They are almost identical in terms of mathematical methods and interface but differ from each other by classes of supported kinetic models. ForK allows creation of complex formal models that are based on conversions as state variables. DesK provides use of more conventional concentration models. In both cases a model structure of any complexity is synthesized easily without any programming. The kinetics evaluation is performed by using up-to-date methods of nonlinear optimization. Although the main purpose of ForK and DesK is to create reaction models they can be used successfully for solving many kinds of final problems by simulation.

The group III units three applications intended for solving final practical tasks.

Solid and Liquid thermal Explosion programs (STE and LTE correspondingly) provide numerical simulation of thermal explosion development and allow determination of critical conditions that delimit regions of explosive and non-explosive proceeding of a reaction. These data are necessary for analysis and choice of safe conditions of application, storage and transportation of a chemical product.

STE is intended for simulation of an exothermic reaction that proceeds in a solid or viscous liquid product when internal heat transfer is effected by thermal conductivity.

LTE simulates a reaction in a fluid reacting mixture and takes into account heat transfer occurring due to thermal conductivity and natural convection.

ReRank is the software for determination of the Reactivity Rating Number in accordance with the NFPA requirements (see, for instance, [10]).

InSafer provides design of inherently safer processes and can be used as well for their optimization.

BST is the software for simulation of runaway in well-stirred batch reactor equipped with the emergency relief system and provides choice of protective measures for industrial reactors.

We conclude this section with the list of major features of the software:

- Comprehensive problem-oriented methodology as the background;
- Incorporation of mathematical methods with knowledge and intuition of a researcher into unified strategy;
- The most relevant up-to-date mathematical methods for solving problems;
- Possibility to process simultaneously results of different multi-response experiments;
- Full interconnections and co-ordination between separate programs;
- Unified elements of User's interface, flexible graphics
- Commercial availability
- Professional quality manuals; computer based training system.

All the examples presented in this paper were prepared by using the TSS series.

Conclusions

1. Creation of kinetic model ensures extraction of exhaustive information from experimental data.
2. The approach based on systematic use of mathematical simulation allows solution of various problems dealing with reactivity analysis and hazard assessment; in many cases it is the only way to get answers. However, by no means this methodology pretends to the complete replacement of the traditional, simpler one. Quite the contrary they mutually complement each other and simulation will be most helpful when the potential danger of a reaction or process has been revealed by using simplified empirical methods.
3. The problem-oriented software set developed by ChemInform can be successfully applied for study of reaction hazards.

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Nomenclature

t – time;	α, γ – degree of conversion;
t_f – finite process duration;	r – rate of a stage;
t_{cf} – cooling failure time;	k – Arrhenius equation for rate constant; $k = k_0 \exp(-E/RT)$
T – temperature	k_0, E – pre exponent and activation energy in the Arrhenius equation;
MTSR – maximal temperature of synthesis reaction;	Q^∞ – heat of a reaction stage;
T_{cf} – adiabatic temperature of synthesis reaction;	n – reaction order;
$T_{cf} = T(t_{cf}) + \frac{Q_{acc}(t_{cf})}{c\phi V(t_{cf})}, t_{cf} \in [0, t_f]$	R – gas constant;
$Q_{acc}(t_{cf})$ – accumulated unexpended energy;	ϕ – heat inertia of an adiabatic calorimeter;
λ – thermal conductivity coefficient;	$\phi = 1 + (cbmb)/(csms)$
c – specific heat;	m – mass;
	V – volume of a reacting mixture;

Indices

b – bomb of an adiabatic calorimeter;
s - sample

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