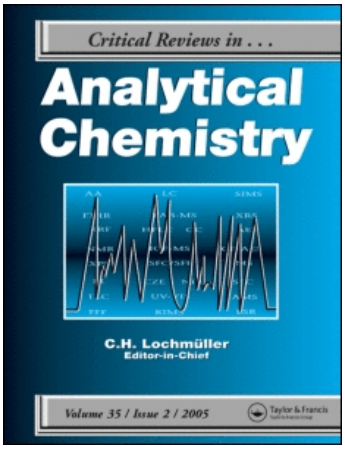

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The problems of safety and environment protection at developing new processes of chemical technology.

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The problems of safety and environment protection at developing new processes of chemical technology.

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Modern chemical processes used for the production of a wide range of chemical products are characterized with the following factors:

- a considerable complexity and multi-stage character of operation;
- a wide range and varying quality of raw materials to be utilized;
- high temperatures and pressures to be reached in chemical reactors;
- complicated and multi-range control systems used.

For these reasons modern chemical processes should be considered as rather dangerous objects. They can be the reason of an environmental pollution. Special steps should be taken to provide their high safety level and prevent pollution and other emergency situations.

Two main kinds of danger can be considered in chemical processes:

1. The so-called "internal", or potential danger. It is connected with (1) the possibility of an explosion and/or fire if a process is run out of normal parameters of its functioning; and (2) the equipment is damaged because of corrosion, mechanical wear or any external reasons.
2. A continuous negative action of the process upon environment in the form of gaseous and solid wastes and waste waters production. This action always takes place at normal conditions of a chemical process functioning.

In order to decrease the level of potential danger for a chemical process and mitigate its negative action upon environment in runaway conditions the following steps should be taken.

1) It is necessary to carry out a profound study on determining the potential danger reasons. 2) It is necessary to develop special automated systems of a process blocking up and protection. These systems can (and should) prevent effectively different runaway situations at the very beginning. 3) A special engineering work should be done on developing modern treatment and purification systems for gaseous and solid wastes, waste waters utilization and so on. Surely, the more (and the most)

effective solution to this problem could be the development of totally clean technologies without any wastes. These technologies (if they exist) can provide full transformation of raw materials to useful final products. The work in this direction is always done by chemists and chemical engineers at developing new technological processes. But this is not always possible and economically efficient. In this case the problem of wastes volume diminishing and mitigating the environmental pollution is solved in terms of developing highly efficient systems of wastes rendering and transformation.

Let us consider the possible ways of increasing the level of a chemical process safety. We will discuss the two mentioned problems: 1) the problem of internal (potential) danger of a chemical process and 2) the problem of mitigating its negative action upon environment.

Solution of the first problem is based upon a thorough investigation of raw materials, intermediate and final products properties and the main scientific (physico-chemical) grounds of a chemical process. This includes (1)-the intrinsic study of mechanism and kinetics of all the main and side reactions; (2)-detailed analysis of reactor scheme and engineering equipment; and (3)-development of a representative kinetic model of a chemical process for the chosen reactor kind. Analysis of the obtained mathematical models and computer simulation of different conditions of the process functioning will allow to determine dangerous regimes that may lead to runaway conditions. Information on the regimes and reasons that may result in an explosion or fire and emission of the reactor content with dangerous explosive and toxic products will allow to avoid effectively emergency and runaway situations.

Alongside with traditional kinetic experiments the modern calorimetric methods in combination with different analytical techniques have become widely used for this task. A calorimetric experiment gives the full and precise information on heat generation phenomena and characteristics (including the kinetic information). Analytical techniques give information of reaction mixture content in any chosen point of the calorimetric experiment. This approach has become especially effective with the development of a new generation of calorimetric instruments. These instruments are largely oriented to solving fundamental and applied tasks of chemistry and chemical technology. They are : "Setaram" C-80 and BT-2.15, and later - special reaction calorimeters "Mettler" RC-1 and its analogs.

A considerable experience has been obtained in RSC "Applied Chemistry" for applying the C-80 "Setaram" calorimeter for these purposes. A wide range of standard and original experimental vessels made of different materials allow to perform different experiments in the temperature range from ambient to ~290C at pressures from

vacuum to 150 at., in different modes (batch, flow, with gas circulation etc.), in aggressive media. The technique allows to analyze the reaction vessel content after an experiment or in every selected intermediate point. An automated mode of a kinetic calorimetric experiment running, high sensitivity of calorimetric transducers and an intelligent data treatment approach based upon the instrument theory - all these factors allow to obtain very valuable information, both profound and applied.

Available experimental data on heat generation kinetics together with reaction mixture compositions make it possible to develop a detailed kinetic model of a chemical process with including all the main and side reactions. This kinetic model (in combination with the thermo-physical data, heat emission and heat exchange data) allows to develop a detailed mathematical model of a chemical process in the chosen reactor unit. Analysis of this mathematical model allows to determine precisely the conditions of a heat explosion beginning and the corresponding critical parameters values that lead to runaway conditions and heat explosion. This knowledge will allow to avoid conditions that may result in the reactor unit destruction and output of dangerous flammable and toxic substances to the environment. A protection system can be constructed in the result. It will allow to avoid heat explosion development and make the potentially dangerous process a safe one for the personnel and environment.

A system of scientific investigations "Thermal Stability" has been developed in Russian Scientific Center "Applied Chemistry" on the base of the discussed approach. This system allows to carry out all the necessary investigations on determining safety conditions of chemical reactors and equipment functioning for the processes of dangerous chemical products production, transportation and storing.

The system consists of a number of commercial instruments and special experimental set-ups for studying heat generation kinetics and chemical conversion, and special original software for effective solving different tasks. This software is used for the following purposes: 1) a kinetic experiment control, 2) experimental data collecting, 3) initial treatment of experimental data, 4) kinetic analysis and developing kinetic models, 5) developing models of a process running in different chemical reactors and 6) testing different reactor schemes. On the base of the full final mathematical model of a process one can make necessary simulation and analysis procedures and determine initial conditions of a possible heat explosion. Then it is possible to calculate the kind, dimensions and characteristics of safety devices (and simulate their functioning as well).

And now let us pass to details and examples. In Fig.1 you can see the general scheme of investigations for developing a kinetic model and the ways of its further application. In Fig.2 one can see the corresponding software programs used for developing and applying the process kinetic

models and their functions. Here it is shown type of used experimental units.

In Fig.3 you can see the system used for thermal danger evaluation and the conditions of thermal safety determination. It follows from Fig.3 that a kinetic model of the process obtained in the result of an experimental study is the base for determining safe conditions of applying liquid and solid reactive substances.

In the next Fig. (N 4) you can see the structure and functions of software used for simulating heat explosion in solid systems and liquid systems with high viscosity.

The methods and algorithms of solving the most typical problems of the chemical processes thermal safety are given in Fig.5.

This approach of providing the process thermal safety is illustrated with several examples connected with chemistry and production of peroxide compounds. This class of products is widely used in chemical technology and it is considered to be rather dangerous.

The results of kinetic study and developing a kinetic model for the process of hydrogen peroxide thermal decomposition are presented in Fig.6. The mathematical model of heat generation at H2O2 thermal decomposition is presented (a technological H2O2 sample). The quality of fitting real experimental data of heat production with the corresponding kinetic model is given. This model has been used for determining safe conditions of storing and further purification and transformation of intermediate H2O2 compositions to the final concentrated product.

In the next Figure (Fig.7) you can see simulation results of H2O2 thermal decomposition for the samples with different chemical pre-history and with different content of impurities - for the selected initial conditions. This kinetic model has been used for determining the safe conditions of a rectification column functioning and evaluation of the critical parameters values to be used in a safety system. This safety system should provide safe conditions of H2O2 concentration process functioning and provide an automatic protection from emerging a possible runaway situation.

Fig.8 illustrates the results of a thermal decomposition study for di-tretbutyl-peroxide. The obtained kinetic model was added with heat transfer equations in a two-dimensional form and heat exchange conditions at the boundaries of the storage tank. This full mathematical model allowed to determine the critical values of parameters that lead to non-controllable temperature increase that may cause thermal explosion. Information on regions of the space where critical parameters values may be reached was used for developing a monitoring system that makes it possible to provide the process safety.

On Fig.9 it is shown some typical results of simulation processes at different conditions of thermo conductivity in solid and liquids
These were several examples to illustrate how we can solve the problem of providing the so-called internal safety and decrease the influence of potentially dangerous chemical processes upon environment.

And now we will discuss the problems connected with a continuous negative action of chemical processes upon environment at normal conditions of a chemical process functioning. These problems include first of all those problems connected with gaseous and solid wastes and waste waters production. There are two main ways to mitigate their action upon environment:

1. Reduction of the volume of gaseous and solid wastes and waste waters and their utilization and transformation to useful products. This way is individual for every chemical process and the solution is in performing constant improvements to the basic technological process and in developing new methods of industrial wastes utilization.
2. Development of more effective systems of catching and neutralization of gaseous wastes, waste waters treatment and purification.
3. Development of systems and technologies for dangerous solid wastes neutralization, their transformation to non-toxic and non-dangerous derivatives that can be stored and buried safely. These procedures include in their turn neutralization and purification of "secondary" gaseous wastes that will be produced at thermal treatment of solid wastes. This procedure is necessary as it allows to reduce considerably the volume of initial wastes.

There is much in common at solving these problems for different technological processes. These common approaches should be widely used at reconstruction and modification of the existing processes and at developing the new ones.

And now we will discuss some possible effective methods of gases and gaseous wastes purification. One of important problems here is the task of purifying ventilation outputs from the workshops with toxic chemical products. The peculiarity of this process is in the fact that it is necessary to purify very large volumes of air up to very high degrees of purification. And the content of toxic products after purification should not exceed the level of sanitary permissible content of these products in air (the values of mg/m3 order). Besides, hydraulic resistance of these gas purification systems should be very small in order to work with ordinary ventilation systems. This is a common problem for all the processes of

dangerous chemicals production where output ventilation is used to provide a safe level of the chemicals concentration for the personnel in the control and service zones. And safe concentrations of toxic chemicals should be provided at the output of air to atmosphere as well.

An original construction of empty spray scrubbers with a multilevel location of the injectors has been developed in RSC "Applied Chemistry" for solving this problem. The multilevel location of injectors provides the necessary density of washing and a high degree of purification. Special devices for drops catching have also been proposed. They provide a high degree of purification.

The apparatus discussed above is rather effective for purification of ventilation outputs from gaseous impurities. If you need to purify very large volumes of gases from both solid particles and gaseous impurities - you should better use the construction given in the Fig.10. Dust particles and gaseous impurities are absorbed in the liquid layer that moves in an active hydrodynamic mode that provides a high value of mass transfer coefficient.

Mathematical models have been developed for these units of gases purification in order to carry out simulation and modeling of the industrial scale systems. Scaling coefficients and other factors are taken into account at modeling. A special experimental set-up has been made for studying the influence of scaling factors upon the processes of gases purification. One can study the intrinsic characteristics of absorption on smaller scrubber units similar to the industrial ones. Specially prepared model gas mixtures are applied in this case. This approach makes it possible to study the scaling factors influence upon mass transfer coefficients as well. It gives the necessary information for the modeling and optimal construction of better industrial scrubber units and gas purification units.

The approaches being developed in RSC "Applied Chemistry" allow to mitigate effectively the negative action of chemical processes upon environment. This makes it possible to develop new, ecologically friendly processes and technologies that have better reliability in all their components and up-to-date protection from emergency and runaway situations.

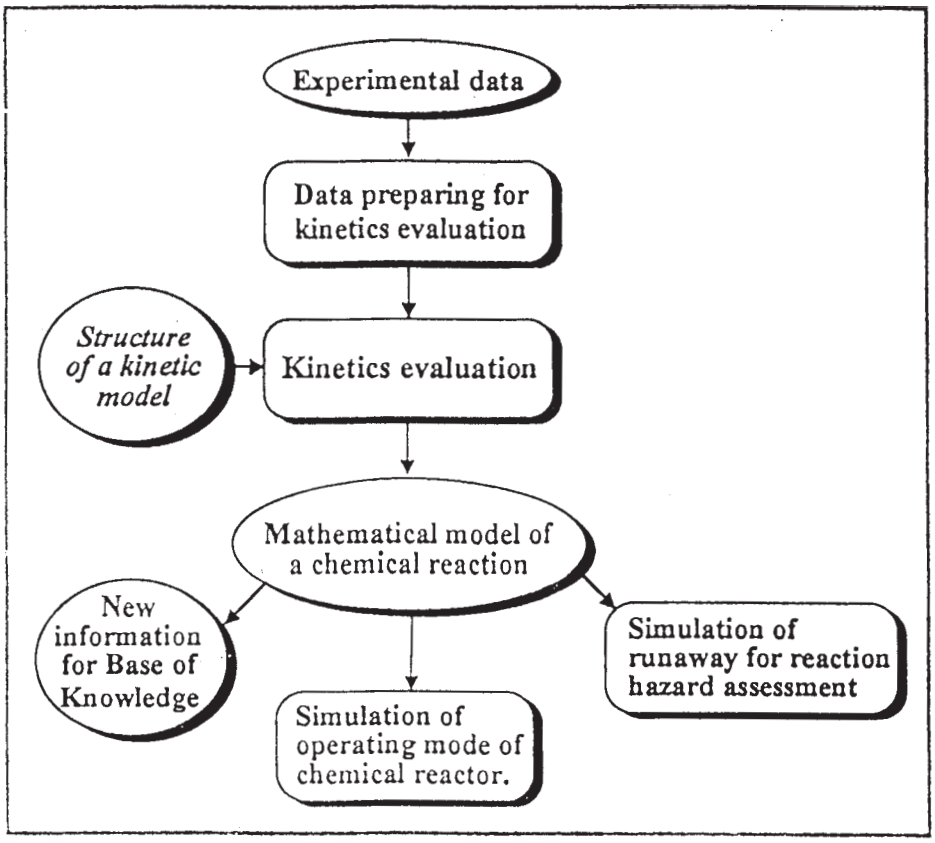


Fig.1. General scheme of the investigation for developing mathematical models and using them for simulation.

Advantages of applying the Simulation Methods for Study of Chemical Processes:

- allows the dynamics of the process proceeding in wide range of operating conditions to be investigated;
- gives the principal solution of the scaling problem and optimization of a process;
- provides fast and reliable analysis of the influence of condition's variations on process proceeding;
- ensures choice of measures for inherent safety of a process.

Software for experimental Data Processing

Software		Methods of thermal analysis				Adiabatic calorimetry			
Name	Intention	DSC; TG; DSC+TG	Isothermal calorim.	DTA	Reaction calorim. (RC-1,..)	ARC	VSP	Phi-Tec	DEWAR
TFConv	Converting free format ASCII data files	√	√	√		√	√	√	√
TDPro	Thorough data processing	√	√	√					
ADPro	Thorough data processing					√	√	√	√

Software for Kinetics Evaluation

Software		Type of kinetic reactor					
Name	Kind of kinetic models	BATCH	CSTR	PLUG FLOW	FIXED BED		Free reactor programming is required
ForK	Formal models	√		√			
DesK	Descriptive models homogeneous reactions (generalized Law of active mass)	√	√	√			
MKF	1. Homogeneous reactions based on generalized Law of active mass 2. Free models programming is required	√	√	√			√
MKH	Heterogeneous catalytic reactions including free models				√	√	

Software for Reactors Simulation

Software		Type of kinetic reactor				
Name	Intention	BATCH	CSTR	Plug Flow	Fixed Bed	Free Model
ForK	Simulation of a process to assess: • inherent safety	√ (Well stirred)				
DesK	• product stability • runaway	√ (Well stirred)	√	√		
MKF	Simulation of a process to determine	√ (Well stirred)	√	√		√
CR	optimal technological mode				√ (set of models)	
STE	Runaway simulation in solids	√ (Non-uniform distributions)				
LTE	Runaway simulation in liquids with natural convection	√ (Non-uniform distributions)				
BST	Runaway simulation and emergency relief system calculation	√ (Well stirred)				

Fig 2. Types of experimental units and corresponding software used for treatment experimental data and simulation of chemical reactors.

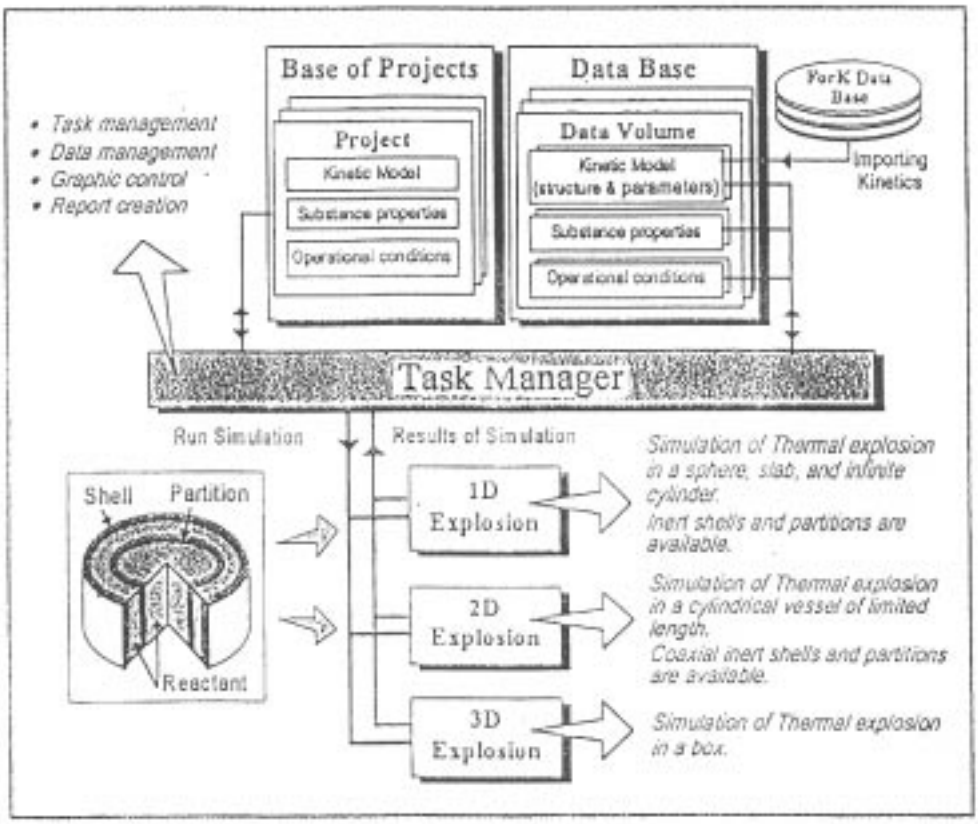


Fig.3. Program's structure and functions of software used for thermal danger evaluation and the conditions of thermal safety determination.

Main features of the program:

- Application of complex multi stage kinetic models
- Application of up-to-date numerical methods for problem solution
- Simulation of a reacting system having inert shells and partitions
- Availability of boundary conditions of the I, II and III kinds with variable parameters
- Possibility to set different conditions on every side of a vessel
- Simulation of influence of fire on a vessel by using boundary conditions of the II kind.
- Flexible graphics for viewing and analyzing results of simulation

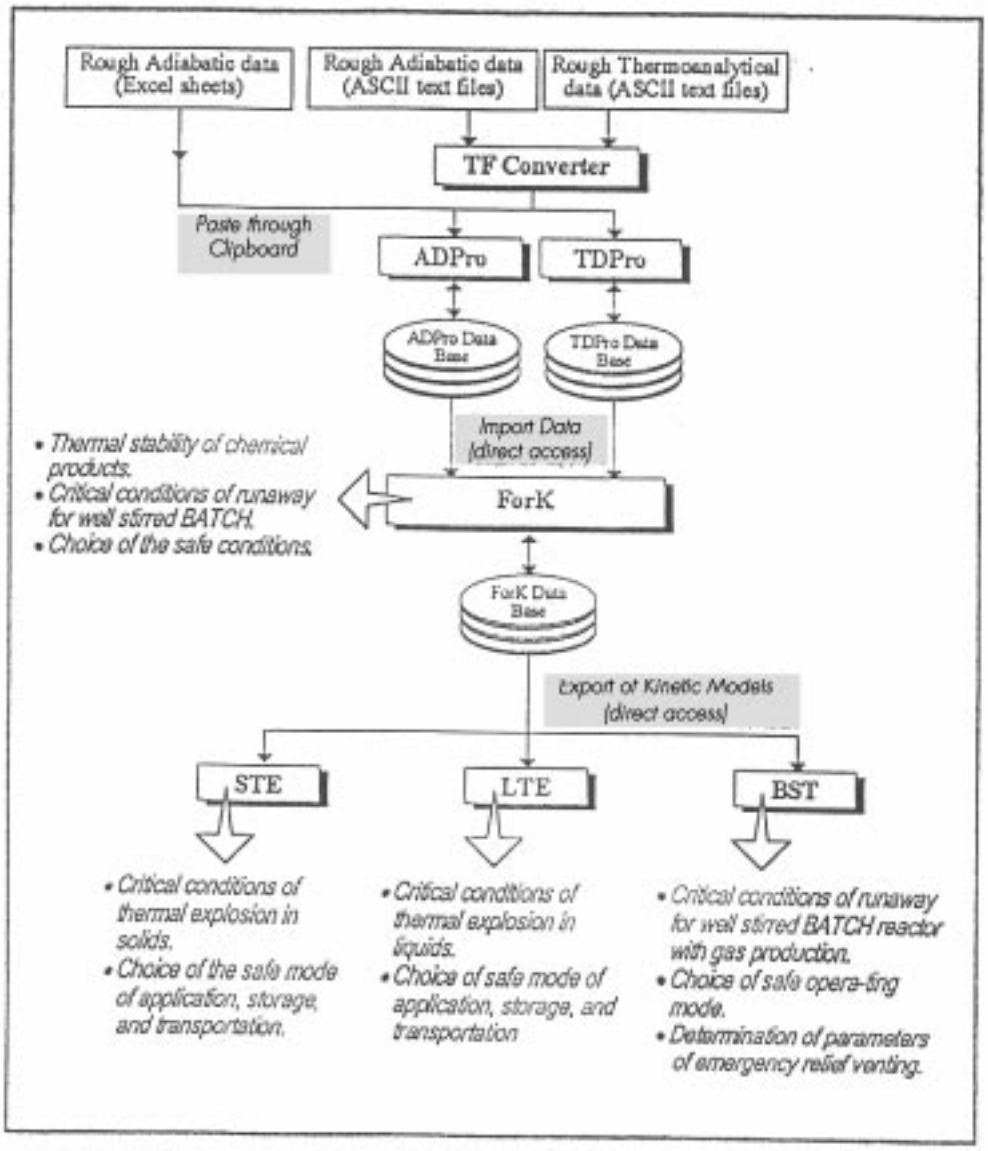


Fig.4. Structure of the system for thermal hazard assessment.

Final aim of a study	Type of reaction	Problems to be solved	Experiment used	Software for:		
				data preparing	kinetics evaluation	simulation
Thermal stability of a product	Thermal decomposition	Long term storage	DSC, DTA, TG	TDPro,	ForK	ForK
Chemical reaction hazard analysis	Exothermic reactions in reactant or chemical product	Identifying potentially hazardous reactants. Thermal Explosion of a product under storage conditions	Calorimetry	TDPro	ForK DesK	ForK STE, LTE
	Desired and secondary reactions	Safe operating conditions for BATCH; consequences of process deviations	Calorimetry, adiabatic calorimetry	TDPro, ADPro	ForK, DesK	STE, LTE
		Inherent safety of Semi-BATCH or CSTR in transient mode	Calorimetry, reaction and adiabatic calorimetry,	TDPro, ADPro MKF	MKF DesK	MKF DesK
Choice of emergency relief venting	Desired and secondary reactions	Runaway in BATCH with gas or/and vapour generation	Calorimetry, adiabatic calorimetry	TDPro, ADPro	ForK, DesK	BST

Fig.5. Some typical problems of thermal safety and its solving with using package software .

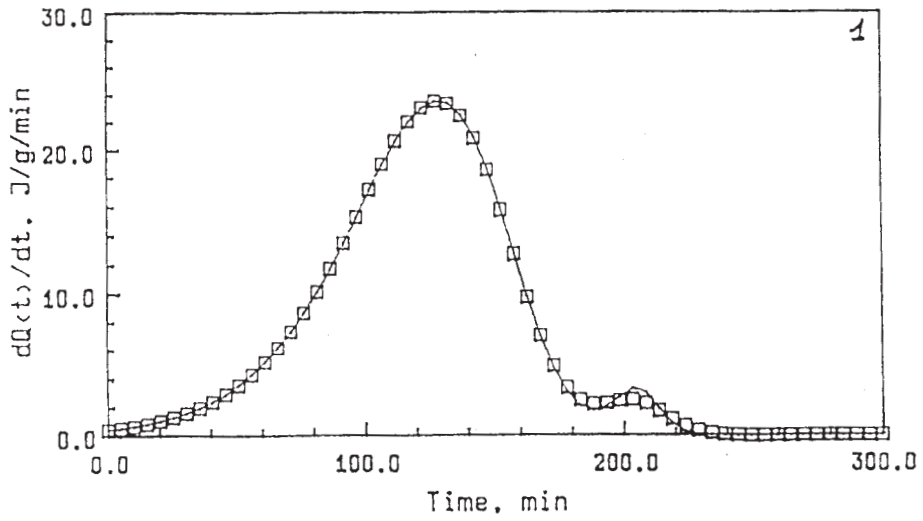


Fig.6. , Kinetic study of hydrogen peroxide (H_2O_2) thermal decomposition. Kinetic analysis and simulation: experimental and calculated heat production rate curves; sample 1. A formal-kinetic model of full autocatalysis.

1 - "Anthraquinone H_2O_2" intermediate non-purified sample U18, 68.4%, from the 1-st evaporator; 50 cycles of distillation.

Kinetic model: (full autocatalysis) :

$$dQ/d\tau = K_1 \bullet (1-\alpha)^{N1} + K_2 \bullet \alpha^{N2} \bullet (1-\alpha)^{N3}$$
$$K_1 = Q_1^{\infty} \bullet K_{01} \bullet \exp\{-E_{a1}/RT\};$$
$$K_2 = Q_2^{\infty} \bullet K_{02} \bullet \exp\{-E_{a2}/RT\};$$

Kinetic constants:

E_{a1} = 18.17 kcal/mol	E_{a2} = 18.17 kcal/mol
ln K_{01} = 20.707 1/min	lnK_{02} = 7.582 1/min
N_1 = 1.0	N_2 = 0.9095
Q_1^{∞} = 1920 J/g	N_3 = 1.0
	Q_2^{∞} = 1920 J/g

Software: MK program package developed in RSC "Applied Chemistry"

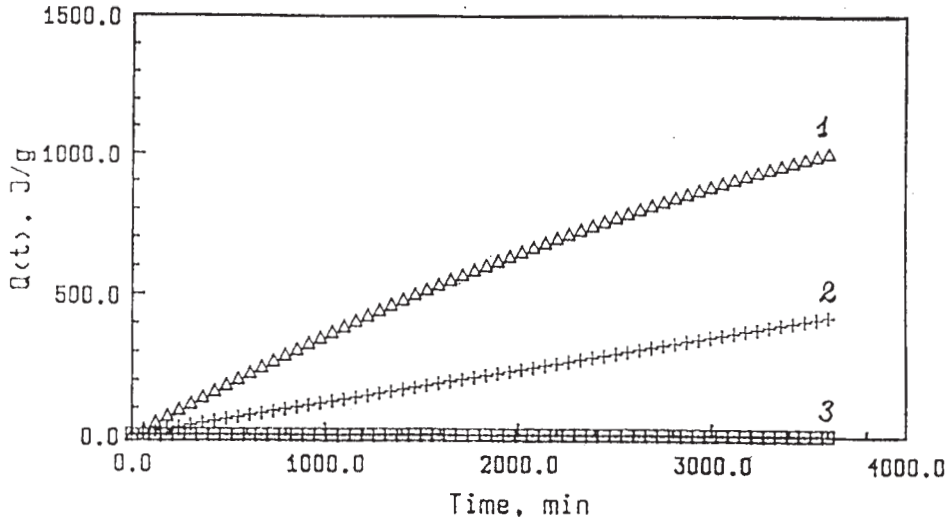


Fig.7. Modeling of thermal stability of the studied H_2O_2 samples (**1,2,3**) with applying the thermal decomposition kinetic models discussed above. Calculated heat production curves (in J/g). The conditions simulated are: Ti = 40°C; τ = 3600 min (60 hours).

Simulation results:

Sample **1** - 1003.9 J/g (52.28% decomposition) ;
Sample **2** - 423.0 J/g (18.23% decomposition) ;
Sample **3** - 3.09 J/g (0.13% decomposition)

Full decomposition **simulation:** (100%) at 40°C:

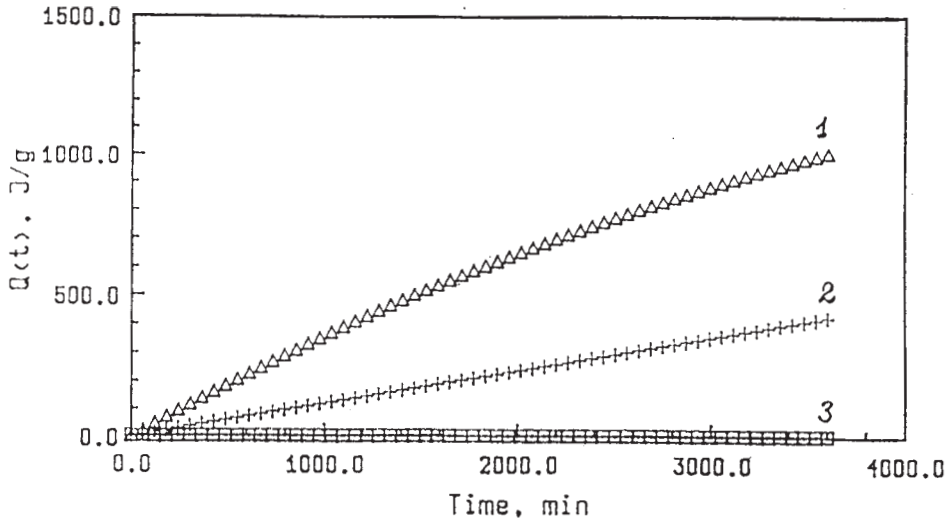
Sample **1** - 38 days (54900 min)
Sample **2** - 51 day (73220 min) ;
Sample **3** - 7.66% in 5 months.

1,2 - "Anthraquinone" H_2O_2; 3 - "Electrochemical" H_2O_2.

1 - intermediate non-purified sample U18, 68.4%, from the 1-st evaporator; 50 cycles of distillation.

2 - final purified product K-7; 74.5%, 100 cycles of distillation, no inhibitor.

3 - a model sample of highest quality electrochemical H2O2 diluted to 74.5%, without decomposition inhibitors (a target to be reached).



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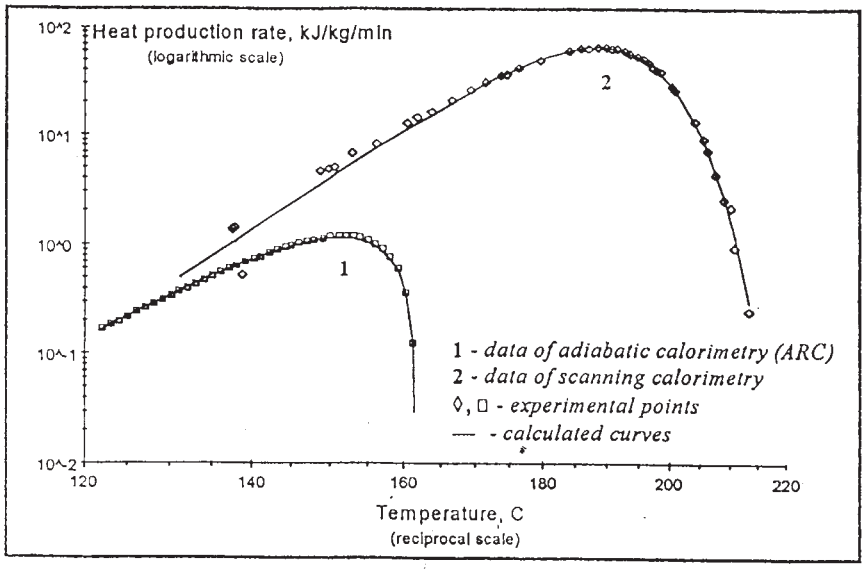
Validation of kinetic analysis method:
simultaneous treatment of data of scanning calorimetry and adiabatic data

Kinetic Model: $d\alpha/dt = K_0 e^{-E/RT}(1-\alpha)^n$, $dQ/dt = Q^\infty d\alpha/dt$



Thermal explosion of a barrel
temperature distribution along the cross section A-A B-B

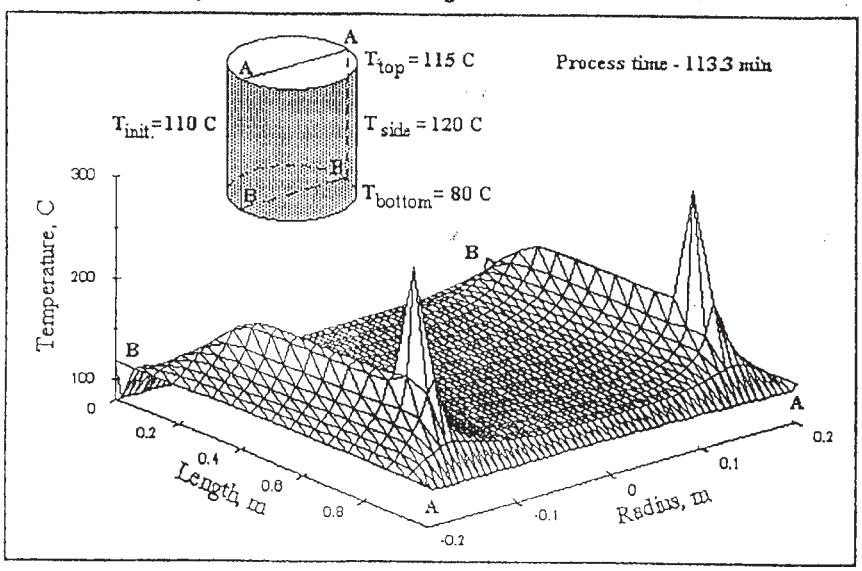
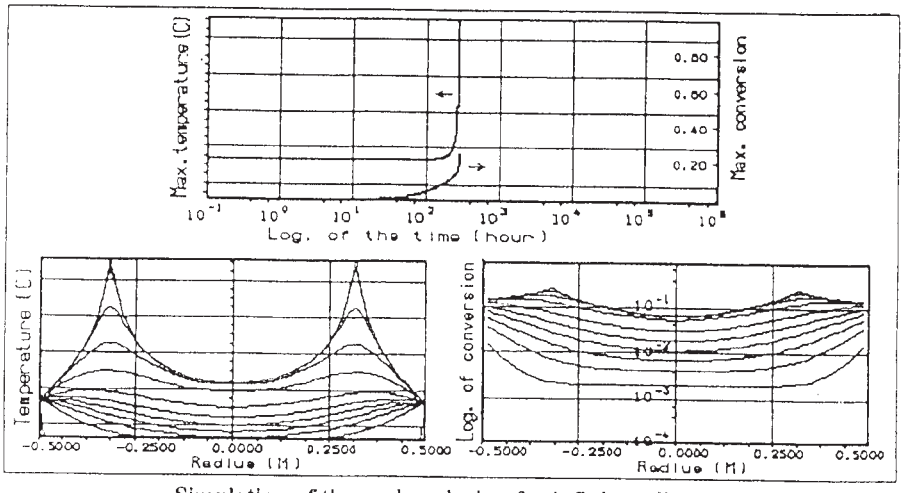
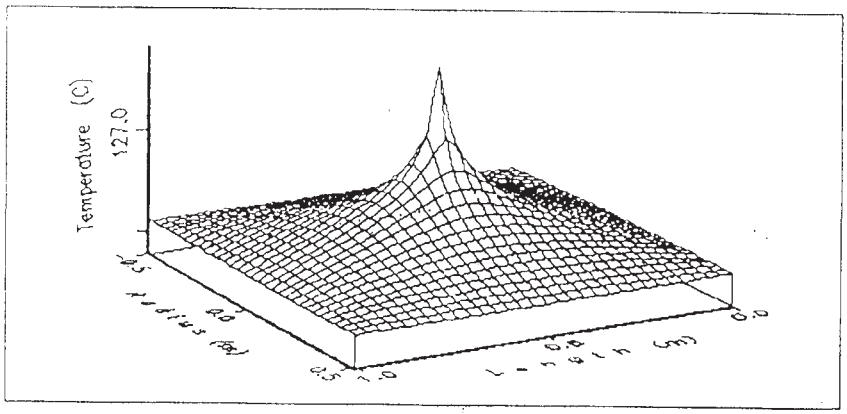


Fig.8. Thermal decomposition of di-tret-butylperoxide and simulation its heat explosion.

CONDUCTIVE THERMAL EXPLOSION

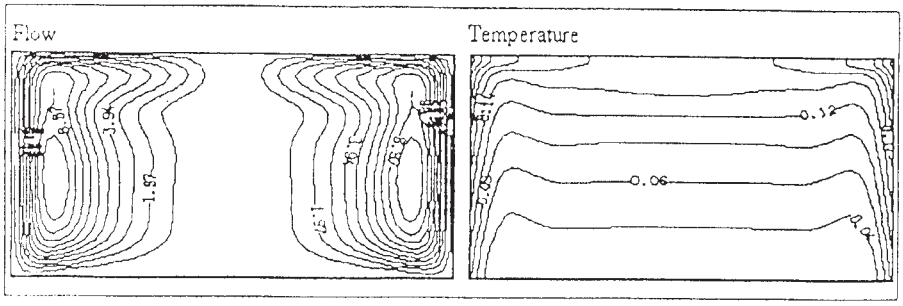


Simulation of thermal explosion for infinite cylinder.



Explosion simulation for limited cylinder; temperature distribution across cylinder.

NATURAL CONVECTION



Simulation of the behavior of a liquid reacting system in a barrel.

Fig.9. Some results of simulation of heat explosion at different conditions.

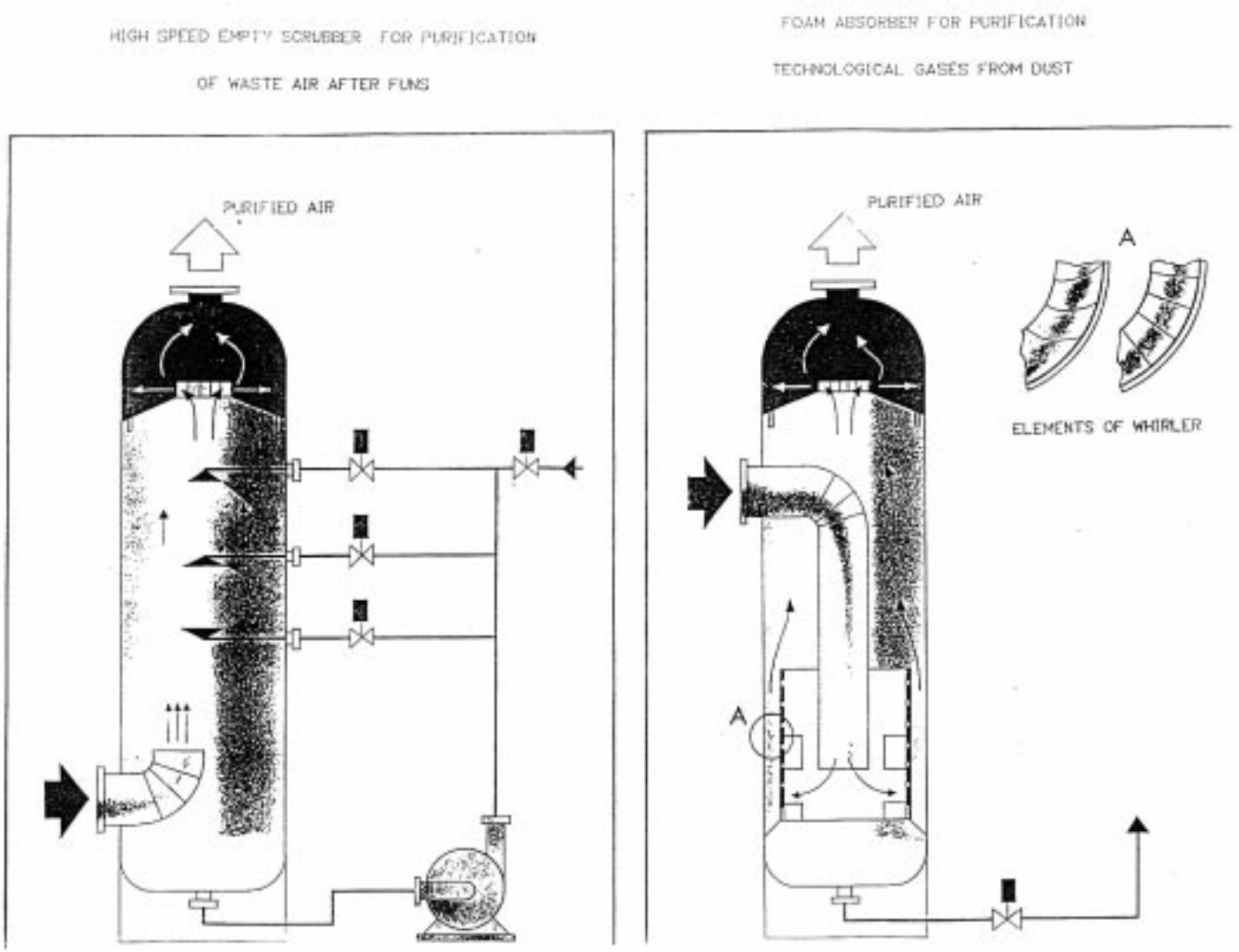


Fig.10. High effective absorbers used for purification of air from dust and gaseous impurities.