

EVALUATING THERMAL EXPLOSION HAZARD BY USING KINETICS-BASED SIMULATION APPROACH

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ABSTRACT

Analysis of possible development of runaway at production, storage and use of a chemical product, and subsequent choice of measures that can prevent an accident or mitigate its consequences is one of the main tasks of reaction hazards assessment. A kinetic model evaluated from calorimetric data gives the reliable basis for implementing the analysis by means of numerical simulation. The purpose of this paper is to discuss some features of the approach as applied to such typical problems as determination of critical conditions of thermal explosion and the SADT for solid and liquid reactive chemicals.

Firstly the brief survey of some popular simplified theories is discussed to reveal their main limitations.

Secondly the mathematical models of thermal explosion in solid and liquid reacting systems are presented followed by a basic sketch of the numerical methods chosen for solving the problems.

Finally the practical usefulness of the kinetics-based simulation approach for analyzing influence of various factors on explosion development is illustrated with several examples.

The discussed models and methods were embodied in the ThermEx and ConvEx program packages developed by CISP. All the presented results have been obtained by means of this software

Keywords: reaction hazard; thermal explosion; numerical simulation

INTRODUCTION

Study of thermal explosion of a reactive chemical aimed at ensuring safety of its storage, transportation and use is one of the important practical aspects of reactive hazard assessment.

As a matter of fact this study comes to determination of critical conditions that separate explosive and non-explosive domains of reaction proceeding, and evaluation of induction period of an explosion if it appears. Two main approaches are used in practice for obtaining necessary data. They are based either on direct determination of the explosion characteristics by means of explosive experiments or on applying theoretical calculations. Explosive experiments (for example, US test and DEWAR storage test for determining the SADT (Recommend. on TDG, UN, 1995), and some others) are rather dangerous, expensive and time consuming (see, for instance, (Fisher and Goetz, 1993)). Besides, all such methods require significant amount of a product (from several kilograms to several dozens of kilograms) so that they cannot be applied on a laboratory stage of creation of a new product.

One of the most important advantages of theoretical methods is that they can be applied as soon as a kinetic model had been evaluated from data of the laboratory-scale kinetic experiments. In particular, they allow estimation of runaway parameters on the earliest stages of the life circle of a chemical product thus ensuring elimination or significant reduction of the necessity in explosive experiments.

The approach based on the mathematical combustion theory, in its turn, unites two branches – the family of semi-analytical methods, and more sophisticated numerical simulation methods.

The grounds of the semi-analytical simplified theories developed by Frank-Kamenetskii, Semenov and others (Frank-Kamenetskii, 1969; Merzanov and Dubovitski, 1960; Bowes, 1984) are

well known. They give convenient approximate analytical relations that don't require complicated calculations and are currently used as a rule for estimation of critical parameters.

However, application domain of these theories is essentially limited, therefore many practical problems cannot be solved without applying comprehensive models that require use of numerical calculations. Below this approach will be referred to as the simulation-based approach.

In spite of great capabilities of numerical simulation there are some serious difficulties that impede the wide use of this method. One of them is the need in more precise knowledge in reaction kinetics and substance properties. Furthermore, mathematical complexity of the approach renders it impossible to apply simulation without powerful computers and appropriate software. Therefore it is no wonder that only in the early 70's some works appeared showing the results of the computer-aided study of thermal explosion.

As far as software is concerned there are several well-known commercial codes of general designation that can be used for this purpose. Let us mention as the examples the CFX (ANSYS Inc.) and FLUENT (FLUENT Inc.) software. However, these universal codes are very expensive, difficult for use and often turn out to be not efficient enough for solving specific problems. Therefore, development of problem-oriented software (for example AKTS-TA-Software, Switzerland) is a challenging decision.

The aim of this paper is to reveal the limitations of popular simplified approaches and to present a family of comprehensive explosion models intended for reaction hazard assessment. These models have been embodied in the problem-oriented ThermEx and ConvEx program packages developed by CISP. The overview of the numerical methods used is given. Several practical examples demonstrate the usefulness of simulation-based approach for hazard assessment.

SIMPLIFIED THEORIES OF THERMAL EXPLOSION

This overview has twofold aim. Firstly, the simplified methods may be really helpful for fast preliminary estimates provided that the fundamentals of these methods and their limitations have been clearly understood. Secondly, brief survey of simplified theories provides better comprehension of the role and merits of the simulation-based approach.

Non-stationary theory

The non-stationary (Semenov's) theory (Frank-Kamenetskii, 1969) is based on the model of a process that occurs in a well-stirred vessel. It is assumed that temperature and concentration distributions are uniform. An exothermic reaction that proceeds in a vessel is represented by the simplest single-stage zero-order kinetic model so that the specific heat generation rate is expressed as:

$$\varpi_r = \rho Q^\infty k_0 e^{-E/RT} \quad (1)$$

Process thermal mode depends on the balance between heat released by a reaction and heat removal from a vessel. For simulation of the heat exchange between the vessel and environment the boundary condition of 3-rd kind (Newtonian condition) is used. The mode can be fully characterized by one governing parameter – Semonov criterion:

$$Se = \frac{W_r V}{\chi S} \frac{E}{RT_e^2} \quad (2)$$

Its critical value $Se_{cr} \approx e^{-1}$ separates explosive ($Se > Se_{cr}$) and non-explosive domains of process proceeding. The theory gives also the expression for estimation of adiabatic induction period of an explosion

$$\tau_{ad} = \frac{C_p}{Q^\infty} \frac{RT_0^2}{E} \frac{1}{k_0} \exp(E/(RT_0)) \quad (3)$$

More complex formula had also been derived for evaluating non-adiabatic induction period.

Quasi-stationary theory

Development of thermal explosion in case of an autocatalytic reaction has several particular features that were reflected in the quasi-stationary theory derived by A.G. Merzanov (Merzanov and

Dubovitski, 1960). This theory deals with the process model similar to the previous one with the exception that the reaction is described by the autocatalytic model

$$\varpi_r(T) = \rho Q^\infty k_0 (1 - \alpha)(\alpha + z) \exp(-E/RT) . \quad (4)$$

Contrary to the Semenov theory the heat release rate of an autocatalytic reaction principally depends on conversion, α . Specific features of thermal explosion development are as follows:

1. Initially the reaction is slow and accelerates with rise of conversion. At small conversions heat release slightly exceeds heat removal and substance temperature remains almost constant. Reaction starts and proceeds in the non-explosive domain until quasi-isothermal reaction rate reaches its maximum.
2. It can be shown that for pronounced autocatalysis ($z \leq 0.001$) critical conditions will be achieved when $\alpha = \alpha_m = (1 - z)/2$ so that the maximal heat release rate is expressed as

$$\varpi_{r,max} = \rho Q^\infty k_0 e^{-E/RT} (1 + z)^2 / 4 \quad (5)$$

3. Critical conditions can be evaluated from the Semenov criterion (2) after substituting the maximal reaction rate:

$$Se_{cr} \approx \frac{4}{(1 + z)^2} e^{-1} \quad (6)$$

An important feature of thermal explosion in case of an autocatalysis is that the induction period may be longer than that for non-self accelerating reaction followed by extremely sharp temperature rise. At that the temperature elevation of a reactant during the induction period is small.

Steady-state theory

The Frank-Kamenetskii theory (Frank-Kamenetskii, 1969), as opposed to Semenov's theory, considers the case, when thermal conductivity governs heat transfer within the reacting system. The temperature and concentration distributions are taken into account. The steady-state theory had been developed under the assumption that the single-stage zero-order exothermic reaction occurs. The mathematical model of a process consists of the thermal conductivity equation coupled with the kinetic equation. Originally it was supposed that the heat exchange of a system with the environment is very intensive (i.e. $Bi \rightarrow \infty$) and thermal resistance of the vessel walls is negligible, so that the walls temperature equals to the ambient temperature, $T_w = T_e$.

As in previous cases thermal mode is characterized by the single parameter, the Frank-Kamenetskii number

$$\delta = \frac{Q^\infty \rho}{\lambda} \frac{E}{RT_e^2} L^2 k_0 \exp\left(-\frac{E}{RT_e}\right) \quad (7)$$

Critical conditions correspond to the case when the thermal conductivity equation loses the steady-state solution. It happens when Frank- Kamenetskii number reaches its critical value $\delta = \delta_{cr}$, Values of δ_{cr} for such simple forms as sphere, infinite slab and cylinder have been derived.

Limitations of simplified theories

For decades these and some other simplified methods were developed in order to widen the range of their applicability by taking into account reactants consumption, different kinetic schemes and operating conditions (see, for instance (Bowes, 1984)). The role of these efforts must not be understated. Simplified theories provided better understanding of fundamentals of this complex physical-chemical phenomenon. They give the approximate analytical relations for practical use that allow obtaining safe results provided that a case under consideration matches the domain of applicability of a certain theory.

Nevertheless the main and principal limitation of simplified methods is that they cannot be applied in the majority of practical cases. Table 1 summarizes features and limitations of the discussed approaches.

Table 1

Comparative analysis of the simplified theories of thermal explosion
(CR denotes reactant consumption, BC denotes boundary conditions)

Governing factor	Unsteady-state	Quasi-stationary	Steady-state	Beyond the scope:
Kinetics	Zero-order; CR is neglected	Auto-catalysis; CR is considered	Zero-order; CR is neglected	1. Complex models 2. CR is significant
Heat exchange	Newton law; valid for Bi<0.3; constant parameters	Newton law; valid for Bi<0.3; constant parameters	BC of the 1 st kind, valid for Bi>50; constant parameters	1. 0.3<Bi<50 2. BC of any kind 3. BC with variable parameters
Timing data	Estimate of induction time	Estimate of induction time	No data	Getting detailed temporal data
Geometry	Insensitive	Insensitive	Simple forms	Arbitrary geometry
Constructive details	No	No	No	Modelling of shell, partitions, etc.
Temperature & concentrations distribution	Uniform	Uniform	Non-uniform, maximum in the center	Transient mode from explosion to ignition, flame propagation
Physical state	Well stirred gas or liquid	Well stirred gas or liquid	Solid phase	Liquid phase with convection

NUMERICAL SIMULATION OF THERMAL EXPLOSION

Numerical simulation of thermal explosion represents the general approach that allows taking into account major chemical and physical processes within an exothermic reacting system without significant simplifications. Therefore the approach can help in those cases when simplified theories are inapplicable.

In this section we will give the overview of the mathematical models of thermal explosion development in reactive solids and liquids and discuss some features of the numerical methods required for simulation. These models and methods served as the ground for the design of the problem-oriented program packages ThermEx and ConvEx developed by CISP for simulation of explosions in solids and liquids correspondingly. Then we will present some examples that illustrate the capabilities of the simulation-based approach..

Thermal explosion in solid and liquid chemicals: mathematical models

Kinetic models

Kinetic model of a reaction that describes heat generation plays the crucial role in the complete explosion model. Typically kinetics is evaluated from data of specialized kinetic experiments. Kinetic models evaluated from calorimetric data are especially pertinent for modelling of thermal explosion. The kinetics adequacy has strong impact on the correctness and reliability of simulation results. Therefore experimental study of a reaction and kinetics evaluation that precede explosion modelling should be implemented very accurately by applying the appropriate methods (see, for example, (Kossov and Koludarova, 1995, Kossov et al., 1998).

For a reaction proceeding in a solid compound it is hardly possible to construct any appropriate concentration kinetics. Therefore usually the formal models based on conversions as state variables are used in these cases. For the complex multi-stage reaction that may include several independent, parallel and consecutive stages the formal model is presented by the system of ordinary differential equations

$$\frac{\partial \alpha_i}{\partial t} = \sum_{(k)} r_{k,i}; r_{k,i} = k_{k,i}(T) \cdot f_{k,i}(\alpha_i); k_{k,i} = k_{0k,i} \exp\left(-\frac{E_{k,i}}{RT}\right); \quad (8)$$

where i is the number of an independent reaction in the complete kinetic model;
 k is the number of a stage in the i -th independent reaction;

$f_{k,i}$ is the kinetic function describing dependency of k-th stage rate on conversion in the i-th reaction.

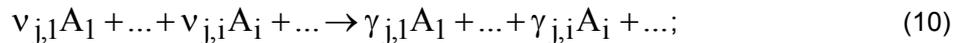
The relationship that bounds stage rates with the heat generation rate completes the model:

$$\varpi_r = \sum_{(i)} \sum_{(k)} Q_{k,i}^{\infty} r_{k,i} \quad (9)$$

Various types of kinetic functions are foreseen to represent N-order, autocatalytic, topochemical reactions and so forth (see (Kossoy and Hofelich, 2003) for more details about formal models).

If a reaction proceeds in the multi-component liquid mixture more detailed concentration-based kinetic models (see (Kossoy and Hofelich, 2003)) should be used for giving proper weight to variation of mixture composition and its properties along the reaction course. Moreover, only these models allow for liquid-vapor equilibrium calculations.

Models of this kind are more habitual for a chemist. The validity of the generalized law of mass action (GLMA) is assumed, i.e. the rate of a stage is proportional to the product of concentrations with arbitrary orders. Apparently the particular case of the exact law of mass action is foreseen when the orders coincide with the stoichiometric coefficients. For the multi stage reaction which is defined by the stoichiometric scheme



the rate of the j-th stage and rate of mass fraction variation of the species A_i will be presented by the equations:

$$r_j = k_j \prod_{(i)} [A_i]^{n_{i,j}} \quad \text{and} \quad \frac{\partial C_{A_i}}{\partial t} = \frac{\mu_i}{\rho_{av}} \sum_{(j)} (\gamma_{j,i} - v_{j,i}) r_j \quad (11)$$

with the corresponding relationship for the heat generation rate:

$$\varpi_r = \sum_{(j)} Q_j^{\infty} r_j \quad (12)$$

where j is the stage number in the complete kinetic model;
 i is the species number;
 $[A_i]$ denotes concentration of the species A_i .

Thermal explosion in solids

We will give here only a basic sketch of the problem statement referring to (Misharev et al, 1996) for more detailed discussion.

Model of heat transfer

Let us consider complex multistage exothermic chemical reaction in a solid material. It is assumed that the process is not accompanied by pore-formation or phase transition. In this case heat transfer in a solid is described by the thermal conductivity equation with nonlinear energy source (heat generation due to a reaction):

$$(\rho C_p) \frac{\partial T}{\partial t} = \text{div}(\lambda(\text{grad}(T))) + \varpi_r \quad (13)$$

As we mentioned the formal kinetic models (8)-(9) are more pertinent for simulation of an explosion in a solid, therefore equation (9) is used here for the energy source term.

Geometry and physical properties

The ThermEx program package supports modelling of explosion development in two classes of solid objects that have simple and complex geometry respectively. Any object can include several active and inert zones that may differ from each other by physical properties and kinetics (for active zones). The possibility to add inert zones allows examining the influence of various construction elements (shells, partitions, etc.) on process development.

Simple solid objects (Misharev et al, 1996) include sphere, infinite cylinder and slab (one-dimensional problem), barrel (axisymmetric two-dimensional problem), single rectangular box and stack of identical boxes (three-dimensional problem). Any of these objects may have a shell and partitions of inert material.

Complex objects can be constructed individually from rectangular infinite blocks (two-dimensional problem) and coaxial finite-dimensional cylinders (axisymmetric two-dimensional problem).

Initial and boundary conditions

The unique initial temperature can be defined for every zone. It is assumed that at initial instant temperature distribution within every zone and conversion distribution within every active zone are uniform, and all the conversions are equal to zero.

The boundary conditions of the 1st kind (temperature), of the 2nd kind (heat flux), and of the 3rd kind (Newton law of heat exchange) can be specified on the outer surfaces. When an object to be simulated has several different outer surfaces (for instance barrel, box, etc.) boundary conditions for every surface can be assigned separately. The parameters of boundary conditions can depend on time.

In order to provide the conjugation between different zones the appropriate conjugation conditions (equality of the temperatures and heat fluxes) are set on the zone interfaces.

When the stack of boxes is simulated, non-ideal contact between boxes can be taken into account by defining thermal resistance.

Thermal explosion in liquids

Physical processes that occur in a reacting liquid mixture are much more sophisticated. The peculiarity of thermal explosion in a reacting liquid is that thermal and concentrational convections can have strong impact on process proceeding. More detailed concentration-based kinetic models (10)-(12) should be used for giving proper weight to variation of mixture composition and its properties along the reaction course. Moreover, only these models allow for liquid-vapor equilibrium calculations.

Pressure rise in a void volume of a vessel, which results from vaporization of volatile components and evolution of non-condensable gas products, may be just as dangerous as the explosion by itself because pressure can exceed permissible level and cause vessel rupture long before the occurrence of thermal explosion. Therefore, this aspect must also be taken into account when simulation.

Model of heat and mass transfer in a liquid

Heat and mass transfer in a reacting liquid is governed by heat conductivity and natural convection. Jones and Shtessel ((Jones, 1974), (Shtessel, 1977)) pioneered the study of Influence of temperature stratification due to natural convection on development of thermal explosion in liquids and gases.

Usually, the classical Boussinesq approximation is applied for describing convective heat and mass transfer in a liquid. However when it concerns thermal explosion there are two factors that result in quite a significant change of density and other properties of a reacting mixture. They are: rapid elevation of the average temperature in a vessel and variation of mixture composition in time. Moreover it is necessary to take into account pressure rise of of the gas-vapor phase. Therefore the advanced model of weakly compressible flow (Lapin, Strelets, 1989) has been chosen. At the moment we restricted ourselves to consideration of laminar convection, for simulation of turbulent convection in a reacting liquid is a standalone complex problem, which requires separate analysis.

The governing equations for processes in a liquid are as follows:

continuity equation:

$$\operatorname{div} \vec{V} = 0; \quad (14)$$

momentum equation:

$$\frac{\partial \vec{V}}{\partial t} + (\vec{V} \cdot \nabla) \vec{V} = -\frac{1}{\rho_{av}} (\operatorname{grad}(p') - 2\operatorname{Div}(\mu \dot{S})) - (\beta_t (T - T_{av}) + \sum_{(i)} \beta_{ci} (C_{A_i} - C_{av_i})) \vec{g}; \quad (15)$$

where i denotes the species number;

energy equation:

$$(\rho_{av} C_p) \left(\frac{\partial T}{\partial t} + (\vec{V} \cdot \nabla) T \right) = \operatorname{div}(\lambda(\operatorname{grad}(T))) + \varpi_r \quad (16)$$

were the source term ϖ_r for concentration kinetic models is expressed by (12), and transport equation for the i-th species:

$$\rho_{av} \left(\frac{\partial C_{Ai}}{\partial t} + (\vec{V} \cdot \nabla) C_{Ai} \right) = -\text{div}(\vec{J}_i) + \mu_i \sum_{(j)} (\gamma_{j,i} - \nu_{j,i}) r_j, \quad (17)$$

The model presented here is derived for the concentration-based models (10)-(12). Sometimes it is impossible to create such a model because of lack of data about the reaction. Formal kinetic models (8)-(9) can be used in these cases. The model of a process in the reacting liquid is similar to the model (14)-(17) with some simplifications:

- the liquid is considered as pseudo-component one;
- concentrational convection is omitted;
- only fully filled vessels are subject to simulation.

Model of heat and mass transfer in gas-vapor phase

The void volume of a vessel is filled with insoluble gases and vapors of the liquid components. The gas-vapor mixture is considered to be quasi one-component chemically inert medium. The partial vapor pressure is estimated as the saturated vapor pressure that corresponds to the temperature of the liquid–gas interface averaged by radius for every time instant. The partial pressure of the insoluble gases is calculated at the averaged gas temperature and obeys the Mendelejev - Clapeyron equation. Density of the gas-vapor mixture is estimated as

$$\rho = \sum_{(i)} P_{vi} m_{vi} \frac{1}{RV_g} \int \frac{dV}{V_g} + \sum_{(k)} \frac{P_{gk} m_{gk}}{RT_{av}}, \quad (18)$$

where k is the number of a component of the gas-vapor mixture.

The system of equations describing the heat and mass transfer in the gas–vapor mixture includes equation (14), equation (15) without the concentrational convection term, equation (16) where the energy source term is replaced with the pressure work term $\beta_t (\partial P / \partial t) / T$ (here P is the total pressure), and state equation (18).

Model of heat transfer in a shell

Heat transfer in the vessel shell is described by the heat conductivity equation (13) without the energy source term.

Geometry and physical properties

The ConvEx program package allows simulation of processes in partly or fully filled shelled vertical finite-dimensions cylinder in axisymmetric two-dimensional approach and in shelled fully filled horizontal infinite cylinder and sphere.

The physical properties of liquid and gas-vapor mixtures depend on temperature and composition. The specialized Mixture software developed by CISP is used for calculation of saturated vapor pressure, properties of multi-component liquid and gas-vapor mixtures (Kosoy A., Benin A., 2003). The possibility is foreseen for a user to define the set of simplified properties manually when simulation of fully filled vessels.

Initial and boundary conditions

Initial distribution of temperature within the vessel and distribution of species concentrations in the liquid are assumed to be uniform. Initial values of the total pressure and mass fractions of the insoluble gaseous components are specified. The liquid and gas are immovable at the initial instant.

The symmetry conditions for temperature, concentrations and velocity components are assigned on the symmetry axis. All the features for defining boundary conditions on the outer surfaces of the vessel walls are the same as where described in the section “Thermal explosion in solids”. The standard continuity boundary conditions for temperatures and heat fluxes are assigned on the inner wall surfaces. Both the velocity components are set to zero on the walls.

It is assumed that the liquid – gas interface is flat and immovable. Tangential stresses on both sides of the interface are equal to each other. Normal velocity on the interface is equal to zero. The

difference between heat fluxes on both sides of the interface equals to the heat consumption due to evaporation:

$$-\lambda_l \frac{\partial T}{\partial y} \Big|_l = -\lambda_g \frac{\partial T}{\partial y} \Big|_g + j_v L_v \quad (19)$$
$$j_v = \frac{1}{S_{in}} \frac{dM_v}{d\tau}, \quad M_v = \sum_{(i)} \frac{m_i p_{si}}{R} \int_{V_g} \frac{dV}{T}$$

Features of numerical methods

Thermal explosion has several particular features that hamper calculations, namely:

- Combination of the slow increase of a reactant temperature during the induction period with the following sharp temperature rise when the explosion develops;
- Presence of zones with considerable spatial gradients of temperature, concentrations, etc.

Therefore special attention has been paid to selection of the most relevant methods and algorithms.

Numerical simulation of explosions in solids and liquids is performed by using the finite differences method.

The uniform grid is used as a rule for simulation of processes in solids. Nevertheless the adaptive grid can be chosen in case of one-dimensional problem, which allows proper simulation of flame propagation along the solid reactant.

When simulating processes in liquids and gases the spatial derivatives are approximated on the staggered grid. The method uses the non-uniform grid that condenses near the walls and gas-liquid interface.

The terms of diffusive type are approximated by central differences of the second order, whereas upwind differences of the second order approximate the convective terms.

The algorithm uses splitting along physical processes and coordinates (the alternating direction implicit method, ADI).

At first only the chemical process is considered when solving the energy and mass transport equations within the liquid zone. The nonlinear chemical terms are linearized by the Taylor series expansion. The resulting system of ordinary differential equations for temperature and concentrations is solved simultaneously.

Then the physical processes (heat and mass transfer) are considered. The momentum, continuity, energy and mass transfer equations are solved sequentially. Iterations are used for calculation of vapor mass flux from the gas-liquid interface when integrating the energy equation.

Solution of the whole conjugate problem (that is, simulation of processes in different zones in case of solids, and shell, liquid and gas mixture in the void volume of a vessel in case of liquids) is performed by applying the shock-capturing method. The implicit time approximation is applied for the energy and mass transfer equations. The implicit projection method (R. Peyret, T.D. Taylor, 1990) is used for solving the momentum and continuity equations. The time step varies automatically during simulation.

EXAMPLES OF APPLYING NUMERICAL SIMULATION

Synergistic effect of concurrent reactions

Consider at first one specific case that cannot be predicted by any of simplified theories. This is the thermal synergistic effect of two independent exothermic reactions $A \xrightarrow{r_1} B$; $C \xrightarrow{r_2} D$ that occur in a solid mixture. Both reactions are of the first-order:

$$\frac{\partial \alpha_1}{\partial t} = r_1 = (1 - \alpha_1) k_{01} \exp\left(-\frac{E_1}{RT}\right); \quad \frac{\partial \alpha_2}{\partial t} = r_2 = (1 - \alpha_2) k_{02} \exp\left(-\frac{E_2}{RT}\right);$$

$$\varpi_r = Q_1^\infty r_1 + Q_2^\infty r_2.$$

A spherical tank with the diameter equal to 40 cm had been simulated.

The first reaction has big heat effect but rather small activation energy ($Q_1^\infty = 700$ J/g; $E_1 = 70$ kJ/mol), which results in weak temperature dependency of the reaction rate. If only this reaction proceeds then there is no explosion though the maximal overheating is about 17°C (Fig. 1a, curve 1).

On the contrary the second reaction has much smaller heat effect but bigger activation energy ($Q_2^\infty = 300$ J/g; $E_2 = 110$ kJ/mol). This reaction alone causes only very small overheating and doesn't induce thermal explosion (Fig. 1a, curve 2). The reason is that the obligatory condition of thermal explosion – high temperature dependency of the reaction rate is satisfied but the reaction energy is insufficient for explosion development at the given initial temperature.

However when both the reactions proceed simultaneously the pronounced thermal explosion occurs (Fig. 1a, curve 3). Moreover, the temperature distribution across the vessel (Fig. 1b) suggests that the system is well above the criticality. This case represents the thermal synergism – the first reaction provides preliminary elevation of the substance temperature to the extent where the energy potential of the second reaction becomes sufficient for triggering thermal explosion.

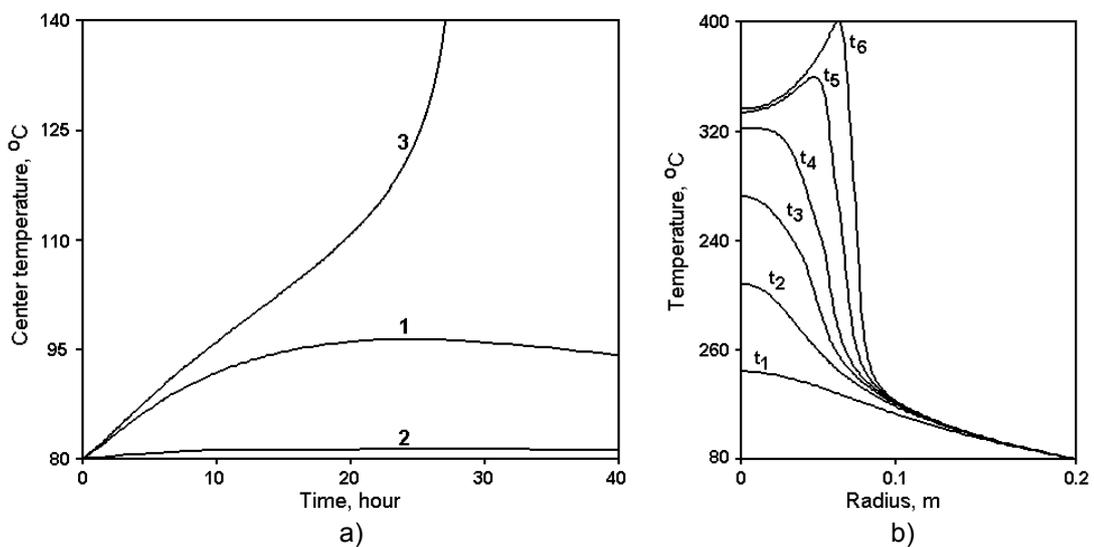


Fig. 1. Synergistic effect of the concurrent reactions.

a) – variation of center temperature in time;

1-only first reaction occurs; 2- only second reaction occurs; 3 – both reactions proceed simultaneously;

b) temperature distribution: $t_1 < t_2 < t_3 < t_4 < t_5 < t_6$.

Determining SADT for a stack of boxes

In accordance with the definition the SADT should be determined for a commercial package subject to transport (Recommend. on TDG, UN, 1995). However it is usual practice to transport packaged goods in stacks rather than to carry every single package separately. Apparently the SADT for a stack will differ from those for a single package. The question is whether this difference is significant. Numerical simulation allows obtaining the detailed answer.

Let us compare the shelled box of 20x20x20 cm size containing 7.5 kg of reactive solid product and the stack of 27 (3x3x3) boxes. The product decomposes along the single-stage first order reaction

$$\frac{\partial \alpha}{\partial t} = r = (1 - \alpha)k_0 \exp\left(-\frac{E}{RT}\right); \quad \varpi_r = Q^\infty r.$$

with $E = 110$ kJ/mol, $k_0 = 1.96 \cdot 10^{11}$ 1/s, $Q^\infty = 500$ J/g.

The container wall thickness is 2 mm. We will consider two cases – metallic container ($\lambda = 16$ W/m/K) and container made of polymer ($\lambda = 0.2$ W/m/K). In both these cases thermal conductivity of a product was the same: $\lambda = 0.15$ W/m/K.

It should be mentioned that this three-dimensional problem was solved without utilizing any symmetry conditions.

Table 2

SADT and critical temperature for a box and for a stack of boxes.

Container	Single box		Stack of boxes	
	SADT, °C	Critical temperature, °C	SADT, °C	Critical temperature, °C
Metallic	57	61	48	54
Polymer	55	57	39	42

The simulated results (Table 2) allow the following conclusions:

1. Every time the SADTs turn out to be lower than the critical temperatures.
2. The SADT for the single box is much higher than those for the stack and even exceeds its critical temperature so that the use of this SADT for the stack will be absolutely unsafe. Thus, for boxes with polymer containers, the induction period of the sack explosion at ambient temperature equal to 55 °C is 4.5 days, i.e. smaller than the permissible 7 days (see (Recommend. on TDG, UN, 1995)).

The remarkable detail of the results obtained is that significant difference between the SADTs and critical temperatures for the stacked-up boxes with metallic and polymer containers is observed whereas single boxes with different container materials behave similarly. Analysis of the temperature fields in the stacks (Fig.2) gives the detailed explanation.

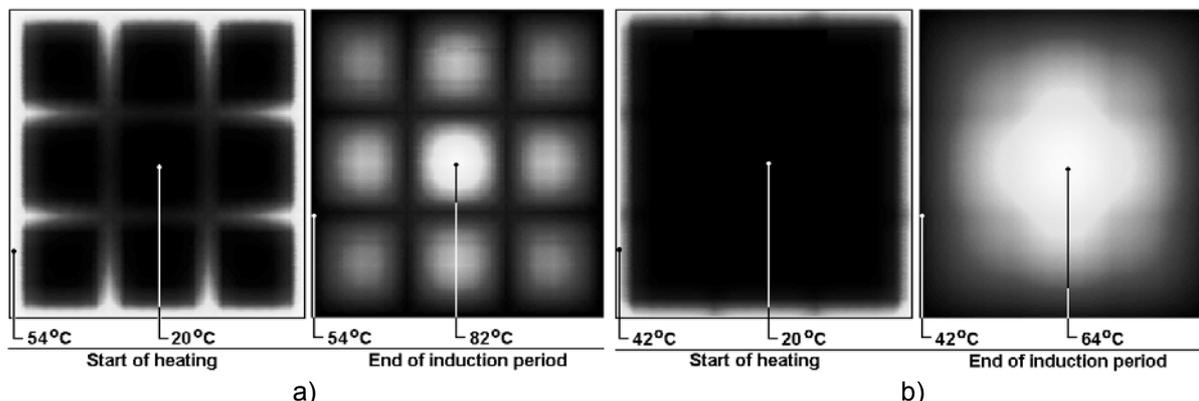


Fig.2 Temperature distribution in the stack cross-section .

a) stack of boxes with metallic containers; b) stack of boxes with polymer containers

If containers are of metal the walls, though thin enough, turn out to be very efficient heat conducting elements. At the heating stage they facilitate external heat to penetrate into a stack (Fig. 2a, left drawing) thus accelerating the heating. On the contrary, when reaction heat release becomes significant metallic walls help to withdraw heat from a stack outwards (Fig. 2a, right drawing), which leads to elevation of the SADT and critical temperature.

The polymer has about the same thermal conductivity as the reactant therefore the stack behaves almost as a monolithic box of the reactant of the same size as the stack so that both the SADT and critical temperature are much lower than for the single small box (Fig. 2b).

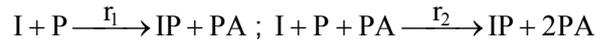
Thermal explosion of a barrel with a liquid reacting mixture

This example demonstrates the results of simulation of thermal explosion of a barrel partly filled with a reactive liquid. The concentration-based kinetic models are more pertinent to this case. They are capable of describing change of liquid composition and, in that way, allow taking into account dependency of physical properties on composition and modeling of concentrational convection along with thermal one.

The equimolar esterification reaction between isopropyl alcohol and propionic anhydride , proposed by HSE as the Round Robin test (Hare, 1999) was used for simulation:



The two-stage autocatalytic concentration model



was created on the basis of two data sets resulted from the adiabatic calorimeter experiments.

The barrel of 1 m in diameter and height filled with equi-molar mixture of isopropyl alcohol and propionic anhydride (filling ratio 0.8) at 20°C was exposed to external heating (ambient temperature is 70°C, heat transfer coefficient equals to 10 W/m²/K). These conditions are supercritical so that the pronounced thermal explosion occurs. In order to reveal whether the convection has an essential impact upon runaway simulation has been performed by using two mathematical models:

- the complete model of a distributed parameter system, and
- the simplified model of a well-stirred tank (lumped parameter system).

Simulation provided valuable data regarding the details of explosion development (Fig. 3). Firstly, there is the significant difference in induction periods predicted by the complete (~170 min) and simplified (~230 min) models (Fig. 3a). Apparently the explosion develops slower in the well-stirred tank and the induction period is about 1.3 times longer. Therefore the use of simplified estimate is unsafe.

Secondly, simulation revealed some features of temperature distribution within the barrel (Fig. 3b). Thus, the radial distribution is almost uniform except for the narrow boundary layer at the walls. At the same time there is significant thermal stratification along the symmetry axis so that the hot spot forms on the top of the liquid.

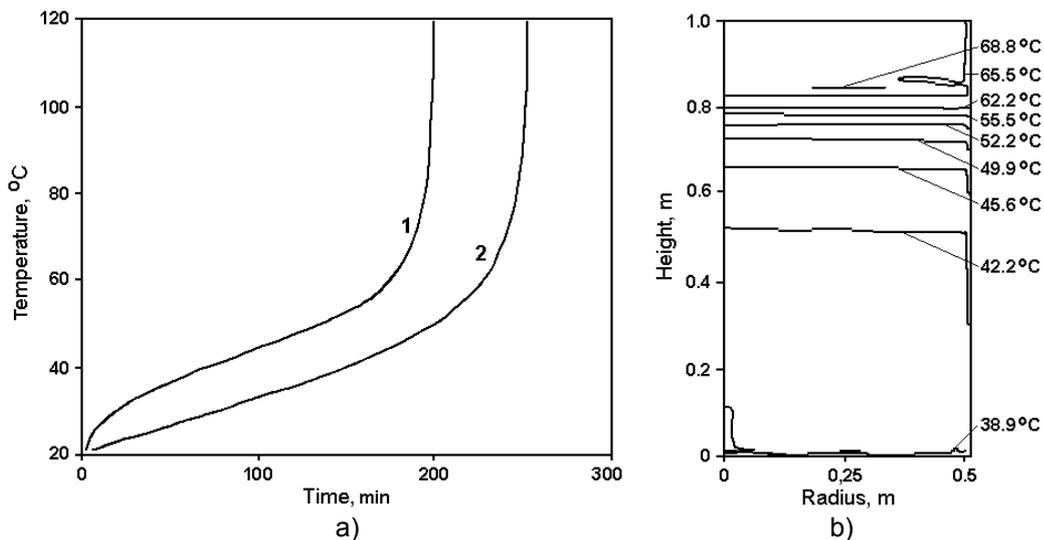


Fig.3 Thermal explosion of a barrel with the reactive liquid mixture.
 a) Variation of the maximal temperature in time; 1 – distributed parameter system,
 2 – lumped parameter system;
 b) temperature distribution in the barrel at the end of induction period (isolines).

The stratification observed explains why the well-stirred approximation gives unsafe prediction. The temperature of the upper layer of the liquid grows much faster than the bulk mean temperature and the explosion starts on the hot spot essentially earlier.

Analysis of an accident

The last example we present here concerns thermal decomposition of the 85% hydrogen peroxide. Large amount of oxygen is produced by the reaction. This time the aim of simulation was to examine the behavior of a tank engulfed in fire by solving the conjugate problem of thermal convection in a reacting liquid and in a gas/vapor phase.

The decomposition reaction was studied by using the heat flux calorimeter C-80 “Setaram” which resulted in creation of the overall single stage concentrational model $H_2O_2 \rightarrow H_2O + 0.5O_2$.

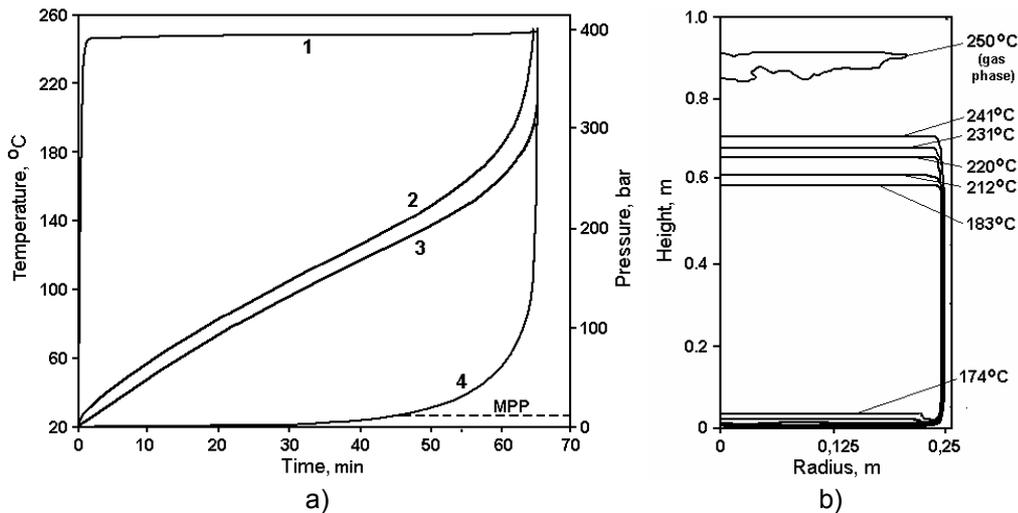


Fig.4 Thermal explosion of the barrel with hydrogen peroxide.

a) Variation of mean temperatures and pressure in time

1 – Volumetric temperature of gas/vapor mixture; 2 temperature of gas-liquid interface;
3 – Volumetric liquid temperature; 4 – Gas/vapor pressure; MPP-maximal permissible pressure.

b) temperature distribution in the barrel on the 65th minute of the process (isolines)

The explosion of the partly filled barrel (diameter 0.5 m; height 1 m; filling ratio 0.7, metal wall thickness 0.01 m) have been simulated for fire conditions (wall temperature 250°C). The results presented in Fig. 4a show that:

- Mean volumetric gas temperature jumps rapidly and becomes close to the wall temperature. The mean volumetric liquid temperature rises much slower and the explosion induction period turns out to be about 63 min.
- Pressure in the barrel reaches the permissible level on the 46th minute of the process, that is, about 20 minutes before development of the explosion. Evidently some preventive measures should be taken to protect the barrel from overpressurization.

Fig. 4b depicts temperature distribution within the barrel on the 65th minute of the process. As in the previous case the radial distribution is almost uniform whereas noticeable thermal stratification along the symmetry axis results in formation of the hot spot on the top of the liquid. Therefore maximal liquid temperature practically coincides with the temperature of the gas - liquid interface (Fig 4a, curve 2).

CONCLUSIONS

The kinetics-based simulation is a very efficient method for solving such complex challenge as assessment of thermal explosion hazards. Being free of essential simplifications this method can be applied to a wide variety of practical problems. In particular it ensures:

- proper determination of critical conditions for a reacting system with complex reaction kinetics (auto catalytic, multi stage reactions, etc.);
- reliable determination of the SADT, especially for solid chemicals;
- detailed elucidation of influence of the package walls or some other constructive details on the explosion development;
- comprehensive analysis of the behavior of a system under accidental conditions (fire, cooling failure and so forth).

Moreover, in many cases the kinetics-based simulation is the only method that is capable to give necessary answers.

NOMENCLATURE.

t- time, s
 τ_{ad} - adiabatic induction period, s
 T- temperature, K
 γ - the normal to the interface, m
 L- characteristic dimension, m
 S - heat-exchange surface, m²
 S_{in} - interface surface, m²
 χ - heat-transfer coefficient, J/(m²·K)
 V – volume, m³
 V_g –void volume of a vessel, m³
 ρ - density, kg/m³
 μ_i - molecular mass, kg/mol
 C_p - substance specific heat, J/(kg·K)
 λ - heat conductivity, W/(m·K)
 μ - dynamic viscosity, Pa·s
 β_t - coefficient of thermal expansion, K⁻¹
 β_c - coefficient that expresses dependence of density on concentration
 L_v - mixture evaporation heat, J/kg
 r - rate of a stage, s⁻¹ α - degree of conversion;
 0< α <1
 Z - auto catalytic constant
 n - reaction order
 $f(\alpha)$ - kinetic function
 ν, γ - stoichiometric coefficients
 C_{A_i} - mass fraction of the species A_i
 k_0 - pre-exponential factor, s⁻¹

E- activation energy, J/mol
 R – universal gas constant, 8.3192 J/(mol·K)
 Q^∞ - specific heat of a stage, J/kg
 ϖ_r - specific heat generation rate, W/m³
 \vec{V} - velocity, m/s
 p' - modified pressure, Pa
 P - pressure, Pa
 \dot{S} - deformation rates tensor, s⁻¹
 \vec{J}_i - diffusion flux, kg/(m²·s)
 j_v - averaged mass vapor flux, kg/(m²·s)
 M - total vapor mass , kg
 \vec{g} - gravitational acceleration, 9.8 m/s²

$$Se = \frac{V\varpi_r}{\chi S} \frac{E}{RT_e^2} - \text{Semenov criterion}$$

$$\delta = \frac{Q^\infty \rho}{\lambda} \frac{E}{RT_e^2} L^2 k_0 \exp\left(-\frac{E}{RT_e}\right) - \text{Frank-Kamenetskii parameter}$$

$$Bi = \frac{\chi L}{\lambda} - \text{Biot criterion}$$

Subscripts:

o – initial value

e – ambient

w – vessel wall

cr – critical value

i, j, k - summation indexes

max – maximal value

av - value averaged by the volume

v – vapor

g – insoluble gas

m - reacting mixture

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ACKNOWLEDGEMENTS.

Authors would like to acknowledge, and Oleg Antonov and Helen Yakubovskay for their efforts when developing the software solvers and Eugene Shvalev for his valuable contribution in the software interface creation.

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