Methodology and software for Reactivity Rating

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Abstract

Reactivity of a chemical system should be known for solving various problems dealing with creation of a process, stability analysis, and hazard assessment. Specifically, the National Fire Protection Association (NFPA) requires use of the reactivity rating number (RRN) for describing such reactivity potentials as thermal stability, interaction with water, and gas generation. A far as assessment of thermal stability of a substance is concerned the new quantitative approach based on the idea of "Instantaneous Power Density" had been accepted recently by NFPA. Though it has many advantages compared to the largely qualitative previous approach there is one serious limitation of the new method, namely it doesn't take into account peculiarities of such complex cases as self-accelerating or multi-stage reactions, which can cause obtaining unsafe results.

It is proposed in this paper to generalize the concept of instantaneous power density by considering the maximal power density as the quantitative measure of the reactivity, which allows taking proper account of the kinetics complexity. Then the ReRank software is briefly discussed that had been developed for reactivity rating in general and, specifically, for calculating reactivity rating numbers.

Introduction

Necessity in reactivity rating of a chemical system arises when solving such problems as creation of a process, stability analysis, reaction hazards assessment, and so on. One important example of applying reactivity rating concerns the characterization of short-term acute hazards of materials in fire or emergency situations. Specifically, in accordance with the regulations of the National Fire Protection Association (NFPA) the reactivity rating number should be used for describing such kinds of reactivity potential as thermal stability, interaction with water and gas generation potential in either of the preceding cases [1]. The aim of this paper is to consider only one of these aspects – assessment of thermal stability of a substance.

The procedures for obtaining the hazard rating for health and flammability are based upon measured quantities, but till recently the basis for assigning reactivity ratings was largely qualitative [2]. Specifically, the guidelines suggested use of DSC detection temperatures. This quantity alone is insufficient for the accurate estimate of thermal hazards and may depend strongly on the DSC operating parameters [3]. The new quantitative approach had been proposed in [4] to reflect, as accurately as possible, the amount and rate of energy, which could be released by a given amount of material under a given set of conditions (e.g., temperature). It is based on the idea of "Instantaneous Power Density" (abbreviated IPD). The value is calculated as the zeroth-order rate of energy release per

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volume of material and may be derived from combination of the estimated initial (i.e. zeroth order) rate of decomposition of a material at a given temperature, the enthalpy released for that decomposition and the density of the material. The procedure aimed at obtaining these parameters from common laboratory measurements was developed and reasonable correlation of IPD at 250°C with reactivity rating numbers for some commonly produced organic materials was demonstrated. Recently this approach has been accepted by NFPA and was included in the thermal stability guidelines [5].

The proposed method is very attractive because of its clearness and simplicity. In fact all the necessary calculations can be implemented by hand or by using any spreadsheet. But this simplicity inheres in simple single stage reactions. Often one can encounter an obstacle dealing with complex multi-stage reactions.

Firstly, the procedure ceases to be plain one - one has to construct various reaction models, analyze interconnections between the stages, etc. Therefore necessary calculations turn out to be rather laborious and complicated.

Secondly, for self-accelerating and some multi-stage reactions maximal power density (abbreviated MPD) doesn't correspond to the initial instant, moreover IPD may be much smaller than MPD and the real hazard rating will be significantly underestimated. Though this peculiarity is not considered in the thermal stability guidelines currently in force, such cases should be analyzed carefully. In this situation the calculations become even more complex and typically they cannot be performed without some appropriate code.

All this makes desirable to have specialized software for reactivity rating in general and, specifically, for calculating the reactivity rating numbers (RRN).

The discussion of two circumstances mentioned above is the aim of this article.

Peculiarities of self accelerating and consecutive reactions

Self accelerating reactions

Consider at first the isothermal behavior of a simple self-accelerating reaction described by the well-known single-stage autocatalysis model:

$$w = \frac{d\alpha}{dt} = k(1-\alpha)(\alpha + z); \ k = k_0 \exp(-\frac{E}{RT}); \ \frac{dQ}{dt} = \overline{Q} \cdot w \qquad (1)$$

The autocatalysis constant, z, is very small – its typical value for pronounced self-acceleration ranges from 0.001 to 0.01. We will use for further analysis the mean value $z = 0.005$.

As it can be derived from (1) the reaction rate at constant temperature will achieve its maximal value, w_{max}, at $\alpha \approx 0.5$ (at $z = 0$ this approximate equality would become the exact one). Now one can easily compare the initial and maximal rate of a reaction:

$$t = 0; \ \alpha = 0; \ w_{init} = k * z = 0.005k; \ IPD = 0.005k * \overline{Q}$$
$$t = ITMR > 0; \ \alpha \cong 0.5; \ w_{max} \approx k * 0.5 * (0.5 + z) \approx 0.25k; \ MPD = 0.25k * \overline{Q} \qquad ; \ (2)$$

where ITMR stands for isothermal time to maximum rate.
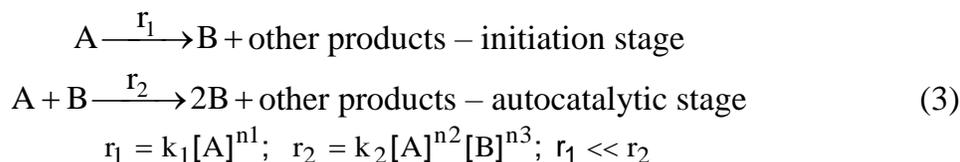
As it follows from (2) $w_{max}/w_{init} \approx 50$ so that IPD will be 50 times smaller than MPD. Let us take some typical values for kinetic parameters:

$$k_0 = 2*10^{13} \text{ s}^{-1}; E = 120 \text{ kJ/mol}; \overline{Q} = 200 \text{ J/ml}$$

At T=250°C $k \approx 21$ s^{-1}; IPD=21 W/ml; MPD=1050 W/ml. In accordance with [5] RRN(IPD<100) equals to 2 whereas, when evaluated by MPD, RRN(MPD>1000) equals to 4.

We considered the simplest case of single-stage autocatalytic reaction with the pronounced self-acceleration. Generally, self-acceleration is typical not only for autocatalysis but also for chain, topochemical and some other reactions. Mathematical models of self-accelerating reactions may be more complex so that there won't be simple analytical expressions that would be convenient for calculations. Difference between IPD and MPD may be not so significant as in our example. But it clearly demonstrates the characteristic feature of self-accelerating reactions.

The following illustration is based on one practical case. The decomposition of a nitro compound is described by the model of two parallel reactions (full autocatalysis model):

$$A \xrightarrow{r_1} B + \text{other products} - \text{initiation stage}$$

$$A + B \xrightarrow{r_2} 2B + \text{other products} - \text{autocatalytic stage} \qquad (3)$$

$$r_1 = k_1[A]^{n1}; \quad r_2 = k_2[A]^{n2}[B]^{n3}; \quad r_1 << r_2$$

In accordance with the reaction scheme the IPD will be defined solely by the first stage because $[B]|_{t=0}=0$ and $r_2=0$, i.e. $w=r_1$ (Fig.1, curve 1). The second stage starts just after production of some amount of the product-catalyst B (Fig.1, curve 2) and immediately becomes dominant so that $w \approx r_2$. Maximal power density is reached at t=ITMR=4.2 s. Calculation results in the following values: IPD=5.3 W/ml; RRN(IPD)=1; MPD=366 W/ml; RRN(MPD)=3.

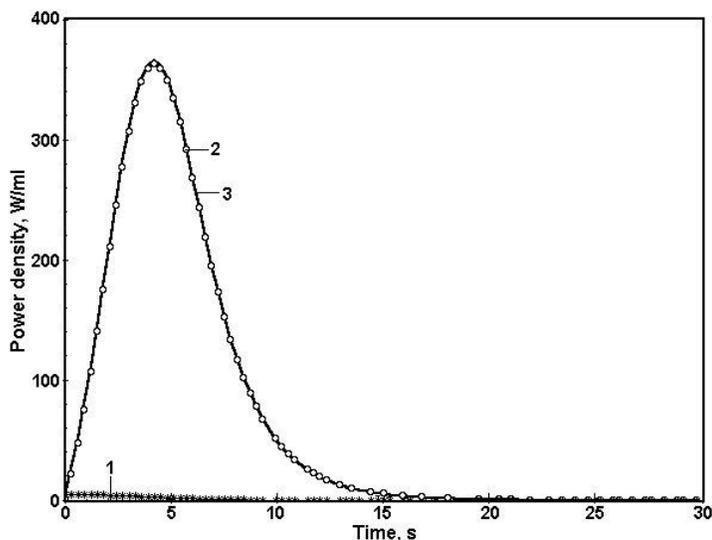
Fig. 1 Power density for autocatalytic decomposition of a nitro compound at 250°C.
1 – contribution of the first stage; 2 – contribution of the second stage; 3 – overall power density

Consecutive reactions

Another important practical case when MPD may not coincide with IPD is a reaction, which contains several consecutive stages. Consider the simplest instance of two consecutive stages

$$A + B \xrightarrow{r_1, \overline{Q}_1} C \xrightarrow{r_2, \overline{Q}_2} \text{Products}$$
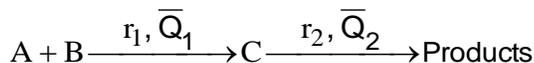
Location of MPD on the time axis (i.e. ITMR) will depend on the ratio between the stage rates and heat effects. Thus, if $r_1 \geq r_2$ and $\overline{Q}_1 \geq \overline{Q}_2$ (which means that an intermediate product C is stable enough) then MPD will be defined by the first stage and will coincide with IPD (Fig 2a).

On the contrary, if $r_1 < r_2$ (the intermediate product is unstable) MPD will be reached at t>0 so that IPD<MPD. If, in addition, the first stage is less exothermic than the second one, i.e. $\overline{Q}_1 < \overline{Q}_2$ then MPD may significantly exceed IPD (Fig. 2b). For the example presented here calculation results in the following values: IPD=68 W/ml; RRN(IPD)=2; MPD=267 W/ml; RRN(MPD)=3. Maximal power density is reached at t=ITMR=0.4 s
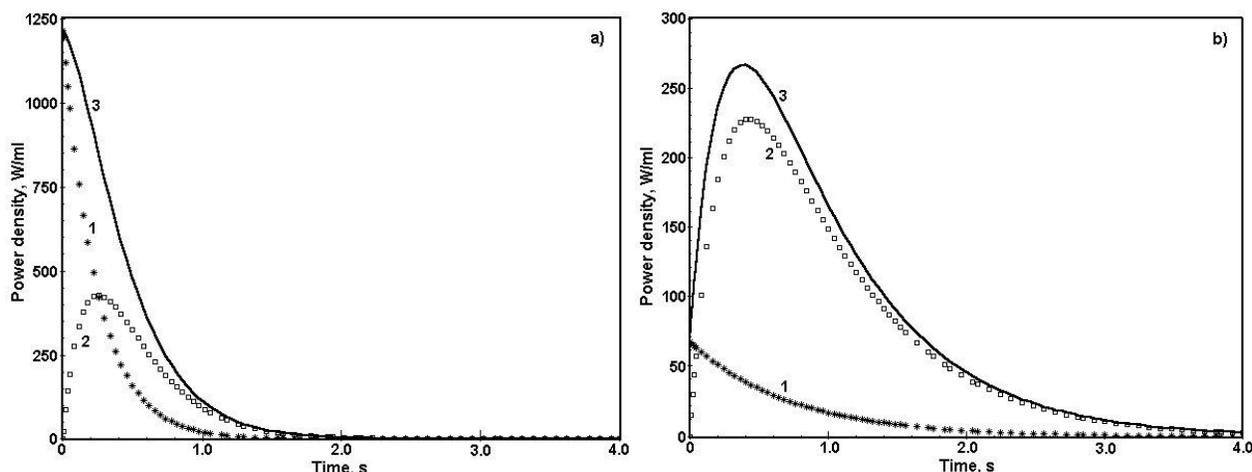

Fig. 2 Power density for complex reaction of two consecutive stages at 250^0C.
1 – contribution of the first stage; 2 – contribution of the second stage; 3 – overall power density

a) $r_1 = 4\,\text{s}^{-1}$; $r_2 = 3.7\;\text{s}^{-1}$; $\overline{Q}_1 = \overline{Q}_2 = 300\,\text{J/ml}$;

b) $r_1 = 1.4\,\text{s}^{-1}$; $r_2 = 3.7\;\text{s}^{-1}$; $\overline{Q}_1 = 50\,\text{J/ml}$; $\overline{Q}_2 = 300\,\text{J/ml}$.

One can object that the attempts to take account of maximal power density of a reaction result in appearance of two parameters – ITMR and RRN instead of single one – RRN. It is truth and in principle it would be necessary to design some new integral parameter for rating the hazard that would give proper weigh of both temporal and energy factors. But in practice isothermal time to maximum rate proves to be very small at high temperatures that are typical for fire conditions. Therefore potential hazard can be characterized as before by the single reactivity rating parameter evaluated from MPD.

We considered only two typical examples when power density reaches its maximal value after some induction period has elapsed. The same situation can be often met when more complex multi-stage reactions proceed. The generic feature of all these cases is that

there is no simple universal method for analyzing the case, rating of the system reactivity or determining reactivity rating number. The solution of this problem is in applying the specialized software. This subject is being discussed in the next section.

ReRank – software for rating reactivity

Overview – aim of the software, its structure and functionality

In accordance with the ideas considered above a code for rating reactivity and determination of reactivity rating numbers must provide:

‒ Flexible and simple way for defining a muli-stage kinetic model;

‒ Simulating a reaction behavior under predefined conditions;

‒ Determining instantaneous or maximal power density and assigning the RRN to a compound;

‒ Storing RRN accompanied with the appropriate additional information into the RRN database.

The ReRank software developed by ChemInform St-Petersburg Ltd. (CISP) as a component of the Thermal Safety Software (TSS) series [6] satisfies all these requirements.

Determining RRN is a plain procedure (see the ReRank flowchart in Fig. 3) which provides defining all necessary data for calculation, performing simulation and determination of RRN, and storing results in the RRN data base.

Consider briefly the main steps.

Entering the Compound Descriptor. The descriptor contains information necessary for identifying a compound, namely official name, empirical chemical formula, trade mark, values of RRN and ITMR (they are added automatically after calculation), etc. The reason of including ITMR into the descriptor is that it allows easy recognition of whether a reaction is characterized by self-acceleration or not.
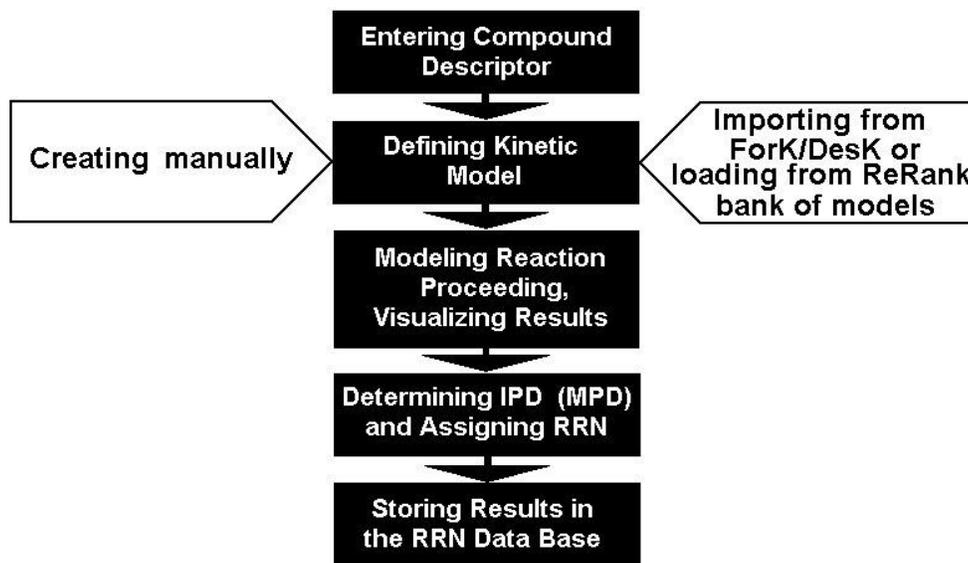
Fig. 3. Flowchart of the ReRank software

Defining a kinetic model. As it follows from the flowchart there are several methods of defining a kinetic model.

1. It can be created manually if a model is taken from some external sources.

2. A model can be loaded from the ReRank bank of models provided that it had been stored there during some previous session.

3. As ReRank is a component of the TSS series it is compatible with the databases of the TSS codes ForK and DesK intended for creation of kinetic modes. Therefore a model can be imported from these databases.

ReRank allows handling of two different kinds of kinetic models. Taking into consideration importance of this subject we will discuss it in more detail in the next section.

Simulating the reaction behavior. The simplest model of the well-stirred batch reactor is used in ReRank for rating reactivity. Specifically, the model assumes that all the energy generated by a reaction is removed so that there is no heat accumulation in the reacting mixture and its temperature remains constant.

A multi-stage kinetic model of a reaction is represented by the system of ordinary differential equations (ODE) which is characterized by two important features:

– Essential non linearity because of exponential dependency of rate constant on temperature;

– Possible stiffness due to big difference between rates of stages that can become apparent at high temperatures.

Therefore the specialized up-to-date algorithm is applied in ReRank for numerical integration, which is capable of managing such type of ODE.

Storing the results. The Microsoft Access - compatible RRN database supports all the necessary types of data management – searching, filtering, sorting, editing, creating a report, etc.

The ReRank default settings provide the functioning mode that meets the NFPA requirements, namely:

– Reaction course is simulated at 250°C with the following determination of IPD;

– RRN is assigned on the basis of IPD.

Nevertheless the possibility is foreseen to change the settings so as to evaluate RRN from MPD or assess reactivity of a system at different temperatures. This makes ReRank more flexible and widens the range of its applicability.

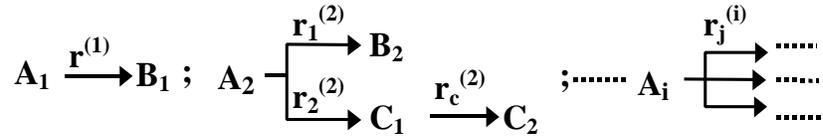**Available types of kinetic models**

ReRank provides use of two types of reaction kinetics - formal models and descriptive models.

Formal kinetic models

Formal models are based on the assumption that conversion degrees are the state variables of a reacting system. Such models are used when there is not enough information

for constructing more or less detailed reaction mechanism. This situation is typical for study of thermal decomposition of solid or high viscous liquid compounds, when some overall experimental data are only available (heat or/and gas production, mass loss and some others).

Formal models can represent complex multi-stage reactions that may include several independent, parallel and consecutive stages.

$$A_1 \xrightarrow{r^{(1)}} B_1 \; ; \quad A_2 \begin{array}{c} \xrightarrow{r_1^{(2)}} B_2 \\ \xrightarrow{r_2^{(2)}} C_1 \end{array} \xrightarrow{r_c^{(2)}} C_2 \quad ; \cdots\cdots A_i \begin{array}{c} \xrightarrow{r_j^{(i)}} \cdots\cdots \\ \rightarrow \cdots\cdots \\ \rightarrow \cdots\cdots \end{array}$$

A formal model is presented by the system of ordinary differential equations

$$\frac{d\alpha_i}{dt} = \sum_{(j)} r_j^{(i)}; \; r_j^{(i)} = k_j^{(i)}(T) \cdot f_j(\alpha_i) \; ; \; i = 1,\ldots,N; \; j = 1,\ldots,M \qquad (4)$$

$$k_j^{(i)}(T) = k_{0j}^{(i)} \exp(-\frac{E_j^{(i)}}{RT})$$

where   N   is the number of independent reactions in the complete kinetic model;

   M   is the number of stages in the i-th independent reaction;

   α_i is the conversion of the reactant of i-th independent reaction,

   $r_j^{(i)}$ is the rate of j-th stage;

   f_j is the kinetic function describing dependency of reaction (or stage) rate on conversion.

The equation system (4) should be supplemented with the equation that bounds conversions with the heat production response:

$$\frac{dQ_i}{dt} = \sum_{(j)} \overline{Q}_j^{(i)} r_j^{(i)} \; . \qquad (5)$$

ReRank allows application of the following kinetic functions:

– $(1-\alpha)^n$ - N-order reaction;

– $(1-\alpha)^{n_1} \cdot (\alpha^{n_2} + z)$ - model of generalized auto-catalysis;

– $\alpha^{n_1} \cdot (1-\alpha)^{n_2}$ - auto-catalytic stage (when a model includes several parallel stages);

– $(1-\alpha) \cdot (-\ln(1-\alpha))^n$ - Avrami-Erofeev's model (topo-chemical reaction);

– $(1-\alpha)^{n_2} \cdot (-\ln(1-\alpha))^{n_3}$ - generalized topo-chemical model;

– $(1-\alpha)^{2/3} \cdot (1-(1-\alpha^{1/3}))^{-1}$ - Jander model (diffusion-limited gas-solid interaction)

Let us cite some examples of formal models.

1. Simple single-stage reaction **A→B**:

$$\frac{d\alpha}{dt} = k_0 e^{-\frac{E}{RT}} f(\alpha); \quad f(\alpha) = \begin{cases} (1-\alpha)^n & \text{- N - order reaction} \\ (1-\alpha)^{n1}(\alpha^{n2} + z) & \text{- auto - catalytic reaction} \end{cases}$$

2. Reaction which includes two consecutive stages: **A→B→C**:

$$\frac{d\alpha}{dt} = k_{01} e^{-\frac{E_1}{RT}} (1-\alpha)^{n1}; \quad \frac{d\gamma}{dt} = k_{02} e^{-\frac{E_2}{RT}} (\alpha - \gamma)^{n2},$$

where α and γ are conversions of the reactant A and product C correspondingly.

3. Two parallel reactions:

4. **A→B+…** - initiation stage

5. **A+B→2B+…** - auto-catalytic stage

that represent very useful model of full auto-catalysis:

$$\frac{d\alpha}{dt} = r_1(\alpha) + r_2(\alpha); \quad \begin{array}{l} r_1(\alpha) = k_1(T)(1-\alpha)^{n1} \\ r_2(\alpha) = k_2(T)\alpha^{n2}(1-\alpha)^{n3} \end{array}$$

The formal models are very flexible and convenient for use but they have one serious limitation that originates from their nature, namely, formal models cannot take into account changes of composition of reacting mixture due to non-kinetic reasons (change of the initial composition of a mixture, feed of a reactant, etc.), therefore the created formal kinetics is valid only for the same reaction mixture composition as was investigated.

No programming is required for synthesis of the desirable model within ReRank. One should just design the model structure, then assign the type of the kinetic function for every stage, and finally define the values of kinetic parameters.

Descriptive kinetic models

Descriptive models are formulated in terms of concentrations and, therefore, can describe the reaction's mechanism in more detail. 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 (LMA) is foreseen when the orders coincide with the stoichiometric coefficients.

For the multi stage reaction which is defined by the stoichiometric scheme

$$\nu_{j1}A_{j1} + \ldots + \nu_{ji}A_{ji} + \ldots \rightarrow \beta_{j1}B_{j1} + \beta_{j2}B_{j2} + \ldots \quad ; i = 1, , N; j = 1, \ldots, M \qquad (6)$$
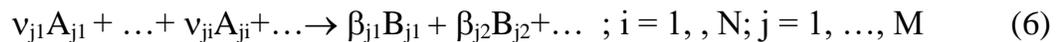
the rate of the j-th stage will be presented by the equation

$$r_j = k_j \prod_{(i)} [A_{ji}]^{\nu_{ji}} \text{ for LMA and } r_j = k_j \prod_{(i)} [A_{ji}]^{n_{ji}} \text{ for GLMA; } j = 1, \ldots, M. \quad (7)$$

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

$$\frac{dQ}{dt} = \sum_{(j)} \overline{Q}_j r_j \qquad (8)$$

Use of a descriptive model requires knowledge of some basic properties (density, molecular weight) of reactants and products.

As in case of formal models no programming is needed for synthesis of a descriptive model. One should define the stoichiometric scheme of a reaction, then the program automatically generates the corresponding system of differential equations. The last step in the model construction is assigning the values of kinetic parameters.

The useful feature of descriptive models is that they can take into account variation of the initial composition of a mixture. Therefore they allow analysis of various important practical problems. An example of such analysis is represented in Fig. 4. The effect of initial composition of the cumene hydro peroxide (CHP) solution in cumene on the reactivity potential of the decomposition reaction had been analyzed by simulating the reaction at 150 ^{o}C.
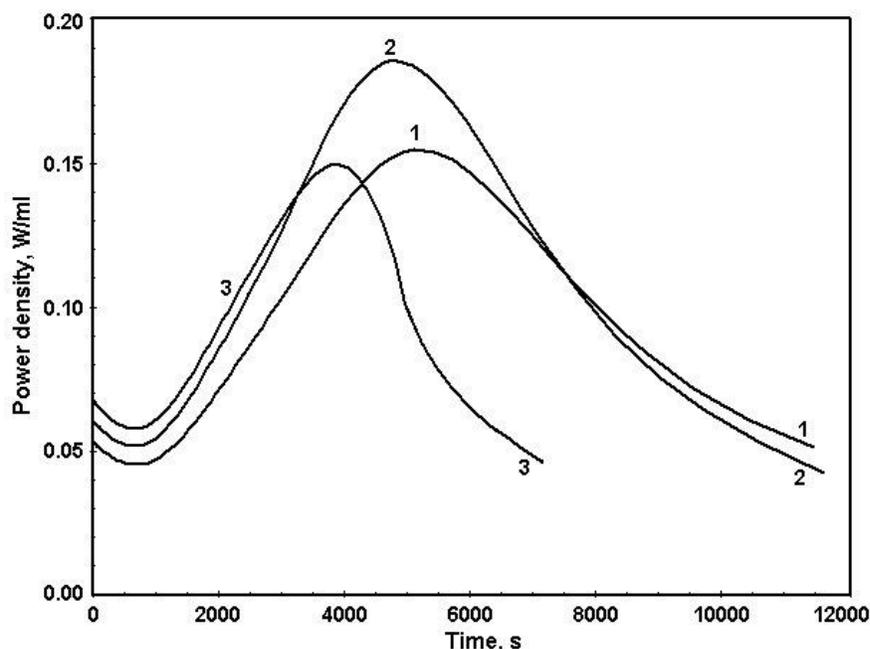

Fig. 4. Effect of initial composition on the decomposition of the CHP solution in cumene
1 – 70% of CHP; 2 – 80% of CHP; 3 – 90% of CHP

Conclusions

The concept of instantaneous power density as the quantitative measure of the reactivity of a chemical product has been generalized by considering the maximal power density as the indicator that allows taking proper account of such kinetic complications as self-acceleration or multi stage reaction mechanisms. One can easily perform the corresponding calculations by using the ReRank software that had been developed by ChemInform St. Petersburg Ltd. This code is especially useful and effective when it is applied in combination with the ForK or DesK software as sources of kinetic models.

Nomenclature

w – reaction rate;

r – rate of a stage

α, γ - degree of conversion;

z – autocatalytic constant

[A] – concentration of a species A

$\overline{Q}$ - heat effect of a reaction/stage;

k – rate constant of a reaction/stage

k_0 – pre-exponential factor;

E – activation energy;

n – reaction order;

ν - stoichiometric coefficients

t – time;

T – temperature;

R – universal gas constant

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