An advanced approach to reactivity rating

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Abstract

Reactive hazards remain a significant safety challenge in the chemical industry despite continual attention devoted to this problem. The application of various criteria, which are recommended by the guidelines for assessment of reactive hazards, often causes unsafe results to be obtained. The main origins of such failures are as follows: (a) reactivity of a compound is considered as an inherent property of a compound; (b) some appropriate criteria are determined by using too simple methods that cannot reveal potential hazards properly. Four well-known hazard indicators—time to certain conversion limit, TCL; adiabatic time to maximum rate, TMR; adiabatic temperature rise; and NFPA reactivity rating number, N_r—are analyzed in the paper. It was ascertained that they could be safely used for preliminary assessment of reactive hazards provided that: (a) the selected indicator is appropriate for the specific conditions of a process; (b) the indicators have been determined by using the pertinent methods. The applicability limits for every indicator were determined and the advanced kinetics-based simulation approach, which allows reliable determination of the indicators, is proposed. The technique of applying this approach is illustrated by two practical examples.
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Keywords: Reactive hazard; Reactivity rating; Kinetics; Mathematical simulation

1. Introduction

The current situation with reactivity hazard assessment can be generally characterized as unsatisfactory. This conclusion can be confirmed by numerous recent publications (let us mention only the detailed CSB report [1]), and several roundtable discussions held recently by OSHA, EPA, CSB, AIHce, and DIERS. As it was emphasized "there is little consensus about how to deal with reactive chemical hazards . . . representatives from government, industry, labor and the academic world agreed on one point: reactive chemical incidents pose a significant safety problem that must be addressed" [2].

The multilateral problem of proper assessment of reactivity hazards involves regulatory, technical and methodological aspects. Discussion of regulatory issues is out of the scope of this paper (see, for example, [1]). We will concentrate on some technical and methodological questions.

One of the main problems related to evaluating reactivity hazard is that the attempts are often made to consider reactivity as an inherent property of a substance whereas hazards arise 'from combinations of chemicals and process specific conditions' [1]. Moreover, even assuming the acceptability of an idea of 'inherent hazardous property', the attempts to use it in practice often cause unsafe results to be obtained because of three essential facts:

- Any of the parameters applied is based, implicitly or explicitly, on some assumptions regarding the conditions under which a reaction proceeds. Insufficient attention to the parameter-related conditions is one of the typical reasons for mistakes.
- There is no way to find any single universal parameter that would allow general characterization of reactivity of a substance or reactive mixture. For instance, "NFPA instability ratings are insufficient as the sole basis for determining coverage of reactive hazards . . ." [1]. One has to choose a certain (limited) set of parameters that would shed light

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Nomenclature

E_i	activation energy of the ith stage in the Arrhenius equation (kJ/mol)
k_i	Arrhenius-type rate constant of the ith stage; $k_i = k_{0i} \exp(-E_i/RT)$
k_{0i}	pre exponent in the Arrhenius equation (s^{-1})
n_{ij}	jth reaction order of the ith stage
Q_i	heat of a reaction of the ith stage; kJ/kg in formal models and kJ/mol in concentration-based descriptive models
r_i	rate of the ith stage
R	gas constant (J/(mol K))
t	time (s)
T	temperature (K)
$[X]$	concentration of species X (mol/m^3)

Greek letter
α	degree of conversion

Indices
i	denotes number of a stage in the multi-stage model
j	denotes number of the reaction order in the equation of the ith stage

upon different cases when potential reactivity hazards come about.
- Methods that are usually applied for reactivity rating often turn out to be too simple to reveal real potential hazards of a compound.

Ideally, the general approach to such problems should involve performing a comprehensive analysis of the process hazards. However, such an analysis is usually a difficult and time-consuming procedure. Therefore, the concept of using an indicator or set of indicators of reactive hazards that would give at least some preliminary and rapid estimates remains very attractive. Fortunately, the situation is not hopeless—provided that the set of reactivity hazard indicators is chosen properly, they are determined by using adequate methods and due attention is paid to the conditions under which the use of one or another indicator is pertinent. The aim of this paper is to analyze the applicability limits of some well-known hazard indicators and to propose an advanced method for their determination that provides a higher level of reliability. The main discussion is illustrated by the abstract examples (if it is not specified separately) that are capable of conveying the ideas without superfluous details and complications. Then we finalize the paper by two real examples that demonstrate how the approach can be used in practice.
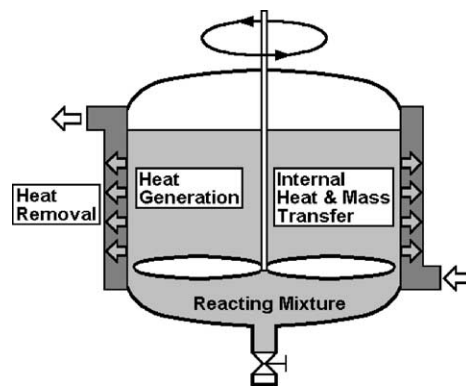

Fig. 1. Scheme of a batch reactor: governing events.

2. How to reveal potential hazards of a compound?

As mentioned above, reactivity hazards are not an inherent property of a substance but arise from a combination of chemicals and process specific conditions. The attempts to find hazard indicators come to the choice of process conditions that would be the most revealing of the potential hazards of a chemical or a reactive mixture, i.e. one could eliminate as much as possible the influence of process specific conditions (size, geometry, etc.). To analyze such a possibility, consider at first the general case of a batch reactor (Fig. 1).

There are three governing events that define the thermal mode of a process and therefore are most important for further discussion:

- Heat generation due to a reaction (which depends on the mass of a reacting mixture and, hence, on the reactor's size). The quantity and rate of heat generation are described by the reaction kinetics.
- Capacity for heat removal (the overall heat exchange with the environment), in particular, depends on the reactor's surface.
- Internal heat and mass transfer that depend on the physical state of a mixture, its thermophysical properties, and use of agitation.

Consider now two extreme cases.

2.1. Well-stirred reactor with very intensive (unlimited) heat removal

This idealized case has three specific features:

1. Temperature and concentration distributions within the reactor are uniform.
2. Temperature of the reacting mixture is always equal to the environment temperature because there is no heat accumulation.
3. Process parameters do not depend on the geometry and size of the reactor.

This case is extremely convenient since all the observable process parameters (heat and gas generation,

variation of mixture composition, etc.) are defined solely by the reaction. The only external (independent) variable is temperature. The majority of reactivity characteristics are being determined for this very case (as a rule for isothermal conditions) often without referring to the basic assumptions. The examples are thermal stability of a substance, NFPA reactivity rating number, N_r, [3] and so forth.

The real process can be more or less close to this ideal case if it is carried out in a jacketed reactor filled with liquid, the cooling capacity is very high and intensive natural or forced convection provides efficient mixing. Therefore, strictly speaking, any reactivity indicator based on the assumption about uniform and constant temperature of a sample (hereinafter referred to as isothermal indicator) can be applied only to the above-mentioned process type.

In the case of a highly viscous liquid or, all the more, a solid compound, uniformity and constancy of the sample temperature can rarely be attained. Nevertheless, even in these cases such indicators as thermal stability and N_r are applicable with certain limitations.

Thermal stability can be assessed if the conversion, which is estimated, is small. In this case, the deviation of the sample temperature from uniformity and constancy can be neglected because of the small heat release.

When evaluating the N_r in accordance with the NFPA Guideline [3], one should be aware that only a thin layer of the substance adjacent to the surface can be considered as the isothermal zone and no concern is taken for the status of the bulk of the material. Otherwise, more comprehensive and complicated analysis of the possibility of thermal explosion is required.

2.2. Adiabatic reactor

An adiabatic process is another extreme case that allows elimination of all the specific features of a reactor (except complete thermal insulation) because all the process is governed solely by the heat of reaction. The only exception is the thermal inertia of the reactor walls, which is significant mainly for the small-size bombs of adiabatic calorimeters. Again, in this case, uniformity of temperature and concentrations is provided during the whole process time though both these state variables vary significantly. The adiabatic mode allows revealing two important properties of a compound (hereinafter referred to as adiabatic indicators)—energy content determined via maximal temperature rise, and the time to maximum rate as a function of initial temperature. The first indicator characterizes the potential severity of an accident; the second one can be correlated with the probability of explosive development in case of an accident [4].

The important advantage of the adiabatic mode is that its features do not depend on the physical state of a substance so that both adiabatic indicators can be determined correctly for both liquids and solids.

2.3. Set of indicators for reactive hazard assessment

Comparison of isothermal and adiabatic indicators shows that, in general, adiabatic ones are less dependent on specific conditions and properties and, therefore, reveal in more detail the potential reactive hazards of a compound by itself. Nevertheless, we believe that the following set of indicators is appropriate for multilateral characterization of reactivity:

1. Time to conversion limit under isothermal conditions, TCL, as a function of temperature TCL(T), which reflects thermal stability of a compound and can be used for comparison of substances.
2. The modified reactivity rating number, N_r, evaluated from maximal power density instead of instantaneous power density (see Section 3.2), which characterizes the potential short-term hazard of a chemical under fire conditions.
3. Adiabatic time to maximum rate, TMR, as a function of initial temperature TMR(T_{in}), which indicates the probability of an explosive accident.
4. Energy content or total energy release, TER, which can be used to measure the potential severity of an accident. We will show in Section 3.4 that under adiabatic conditions this quantity may also depend on initial temperature, i.e. TER = TER(T_{in}).

3. Methods for determining indicators of reactive hazards
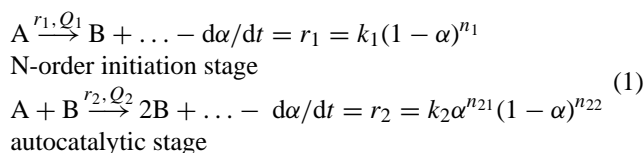
As we noted the use of simplified methods for reactivity, rating is one of the main causes of obtaining unsafe results. In this section, we will discuss the application of an advanced, more general method that can guarantee much higher reliability of estimates. This is the method of kinetics-based simulation. One can argue that the simplified methods also use some assumptions on a kinetic model. It is quite true, but the problem is that all these methods are based on the use of the simplest single stage model, typically the model of zero-order or, at best, of an N-order reaction. Therefore, they fail at the slightest complication of the reaction mechanism.

3.1. Determining thermal stability

Typically, thermal stability is associated with prolonged storage at (usually) ambient temperatures but it is equally important to be able to estimate stability under conditions of use of a substance even at high temperatures. Thermal stability is characterized by the time necessary to reach a certain level of conversion at certain constant temperature (time to conversion limit, TCL). A typical experimental basis for stability evaluation is scanning calorimetry. As a rule, experiments are carried out at elevated temperatures, and then the results have to be extrapolated. The only method to implement such an extrapolation reliably is to evaluate the reaction kinetics and then perform a simulation for the conditions of interest. For a

simple reaction (single stage, without self-acceleration), the model can be evaluated without significant difficulty, and the corresponding calculations can be implemented easily. Such a simplified procedure is the obligatory part of almost every program that is delivered together with a thermoanalytical device. However, any complication of a reaction will result in the necessity to apply sophisticated numerical methods both for model creation and for simulation. The following example illustrates vividly the case.

Consider the reaction that includes two parallel stages

$$A \xrightarrow{r_1, Q_1} B + \ldots - d\alpha/dt = r_1 = k_1(1-\alpha)^{n_1}$$
N-order initiation stage

$$A + B \xrightarrow{r_2, Q_2} 2B + \ldots - d\alpha/dt = r_2 = k_2\alpha^{n_{21}}(1-\alpha)^{n_{22}} \quad (1)$$
autocatalytic stage

where $k_{01} = 2.98 \times 10^3 \, \text{s}^{-1}$; $E_1 = 75.6 \, \text{kJ/mol}$; $k_{02} = 1.17 \times 10^{16} \, \text{s}^{-1}$; $E_2 = 151.2 \, \text{kJ/mol}$; $n_1 = n_{21} = n_{22} = 1$.

This scheme represents the model of full autocatalysis. The first (initiation) stage generates some small amount of the product-catalyst B, which triggers self-acceleration. In the case of pronounced autocatalysis, the contribution of the first stage is very small everywhere except the very beginning of a reaction. The first stage has essentially smaller activation energy than the second one.

Fig. 2 depicts the graph TCL(T) for three different conversions 1, 4 and 10%.

As it can be seen all the plots TCL(T) turn out to be the curves rather than the habitual straight lines. For the smallest conversion, the contribution of the autocatalytic stage is small in the lower part of the temperature range (40–80 °C), so that within these limits the plot log(TCL) versus $1/T$ is close to linear and its slope is more or less proportional to E_1. For intermediate and highest conversion, the impact of both stages is comparable and changes with temperature; therefore, the
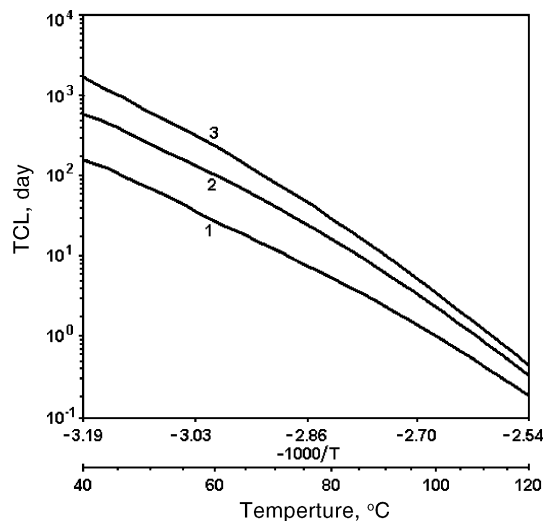
corresponding plots prove to be curved.

3.2. Determining reactivity rating number

The N_r is used for characterization of short-term acute hazards of materials in fire or emergency situations. In accordance with the NFPA Guidelines [3], N_r should be derived from the instantaneous power density (IPD), i.e. the zero-order specific rate of energy release at standard temperature 250 °C. This method can rank reactivity properly only in case of a simple single stage reaction without self-acceleration. In practice, we usually deal with more complex reactions (multistage, autocatalytic reactions, etc.) and IPD-based estimation of the N_r may lead to getting unsafe or even completely wrong results (see [5] for more detailed analysis). Let us consider two examples of this kind.

The first example concerns the reaction consisting of two consecutive stages of the N-order type

$$A + B \xrightarrow{r_1, Q_1} C \xrightarrow{r_2, Q_2} \text{Products}, \quad (2)$$
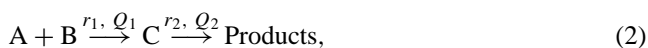
where $k_{01} = 5.91 \times 10^9 \, \text{s}^{-1}$; $E_1 = 100 \, \text{kJ/mol}$; $Q_1 = 100 \, \text{J/g}$; $k_{02} = 2.91 \times 10^{12} \, \text{s}^{-1}$; $E_2 = 120 \, \text{kJ/mol}$; $Q_2 = 600 \, \text{J/g}$; $n_1 = n_2 = 1$.

Depending on the ratio between stage rates and their heat effects, such a reaction under isothermal conditions can reveal maximal rate either from the beginning or after some delay. The true maximum reaction rate may be much higher than the initial one (Fig. 3). If then, following the NFPA recommendations, we evaluate N_r from the instantaneous power density, we will get $N_r = 2$, whereas evaluation from maximal power density, MPD, will give $N_r = 3$.

A similar situation may occur in the case of pronounced autocatalysis. Fig. 4 depicts the contribution of the initiation and autocatalytic stages into the total heat generation rate, which accompanies thermal decomposition of a nitrocompound (namely tetryl). This reaction is described by the model of full autocatalysis (Eq. (1)) with the following set

Fig. 2. Estimating TCL for a complex reaction. Conversion level: 1–1%; 2–4%; 3–10%.
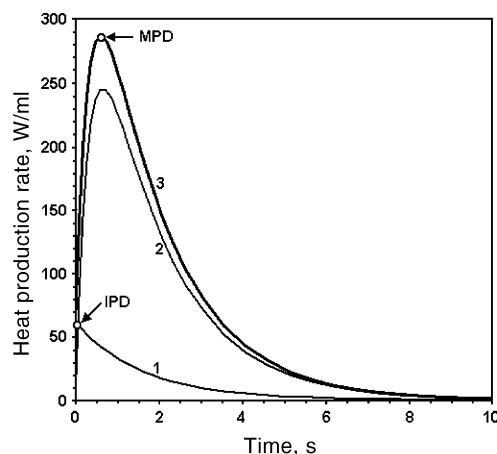

Fig. 3. Power density for complex reaction of two consecutive stages at 250 °C: (1) contribution of the first stage; (2) contribution of the second stage; (3) overall power density.
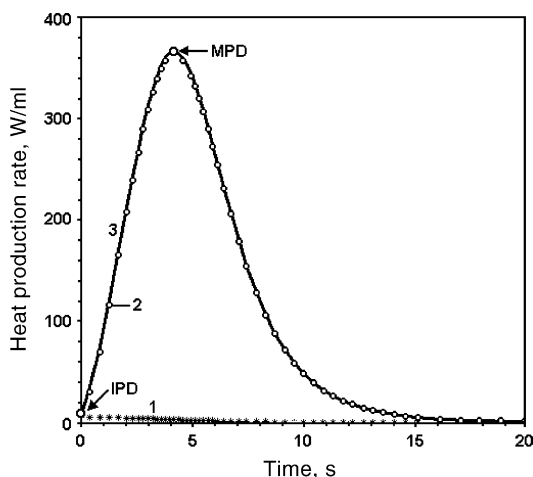
Fig. 4. Power density for autocatalytic decomposition of a nitro compound at 250 °C: (1) contribution of the first stage; (2) contribution of the second stage; (3) overall power density.
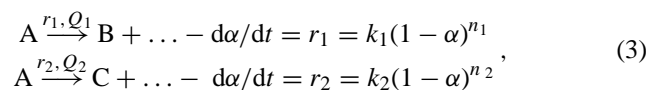
of kinetic parameters: $k_{01} = 1.13 \times 10^{11}$ s^{-1}; $E_1 = 123.45$ kJ/mol; $n_1 = 0.96$; $Q_1 = 99$ J/g; $k_{02} = 8.39 \times 10^{14}$ s^{-1}; $E_2 = 151.72$ kJ/mol; $n_{21} = 1.07$; $n_{22} = 1.14$; $Q_2 = 2820$ J/g. Apparently, the initiation stage is very weak and IPD is about 70 times lower than MPD. The difference between N_r evaluated from IPD and MPD turns out to be even more significant: 1 compared to 3!

As we can see, in both these cases, the use of IPD for determining N_r results in serious underrating of the reactive hazard. The use of MPD as the basis for evaluating N_r gives much more conservative results though it requires application of more detailed kinetics coupled with mathematical simulation.

3.3. Determining adiabatic time to maximum rate

Usually, adiabatic time to maximum rate is determined as the induction period of adiabatic explosion using the analytical formula derived by O. Todes (see, for instance, [6]) for the single stage zero-order reaction model. The estimate of activation energy necessary for calculation is evaluated from some experimental data (adiabatic or scanning calorimetry). For complex reactions—multi stage, autocatalytic, etc., there is no other way to determine TMR rather than evaluating the complete kinetic model followed by simulation.

Let us consider the reaction that has two parallel stages.

$$\begin{aligned} A \xrightarrow{r_1, Q_1} B + \ldots - d\alpha/dt = r_1 = k_1(1-\alpha)^{n_1} \\ A \xrightarrow{r_2, Q_2} C + \ldots - d\alpha/dt = r_2 = k_2(1-\alpha)^{n_2} \end{aligned}, \quad (3)$$

where $k_{01} = 2.21 \times 10^4$ s^{-1}; $E_1 = 70$ kJ/mol; $n_1 = 1$; $Q_1 = 100$ J/g; $k_{02} = 1.19 \times 10^{11}$ s^{-1}; $E_2 = 130$ kJ/mol; $Q_2 = 300$ J/g; $n_2 = 1$.

As in the previous example, $E_1 < E_2$. This causes a significant change of contribution of each stage into the total heat generation at different temperatures. As a result, TMR turns
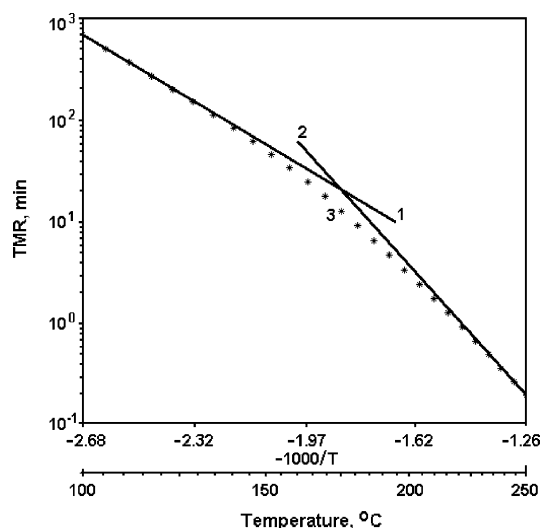

Fig. 5. Determining TMR for complex reaction: (1) TMR for single stage A → B; (2) TMR for single stage A → C; (3) TMR for complete model.

out to be a complex function of temperature (Fig. 5). One can see that only at low and very high temperatures can TMR be estimated on the basis of a single stage A → B or A → C, respectively.

3.4. Determining total energy release

It is usually assumed that the energy content of a reacting system estimated for adiabatic conditions does not depend on the initial temperature and can be evaluated from the adiabatic temperature rise $\Delta T = T_{max} - T_{in}$, where T_{max} denotes maximal attained temperature. This is correct for a single-stage reaction whereas for complex multi-stage reactions the total amount of energy released under adiabatic conditions may depend on initial temperature. The latter case involves mainly parallel stages in which the contribution of each stage into the total heat generation depends on the temperature profile of the reaction, which in turn depends on the initial temperature. Let us consider the same example (Eq. (3)) of two parallel stages with different activation energies.

Fig. 6 depicts the variation of contribution of the first and second stages into the total energy release depending on the initial temperature of the adiabatic mode. At the lowest temperature, almost all the energy release is defined by the first stage with small activation energy. On the contrary, at the highest temperature, the contribution of the first stage is very small. This example demonstrates vividly that any estimate based on a single adiabatic experiment would be erroneous. For instance, if energy content had been evaluated from the experiment with low initial temperature then the potential danger of a reaction at higher temperatures would be significantly understated and vice versa. Therefore, we believe that the term total energy release, TER, is more pertinent for this useful hazard indicator that should be determined as a function of initial temperature.
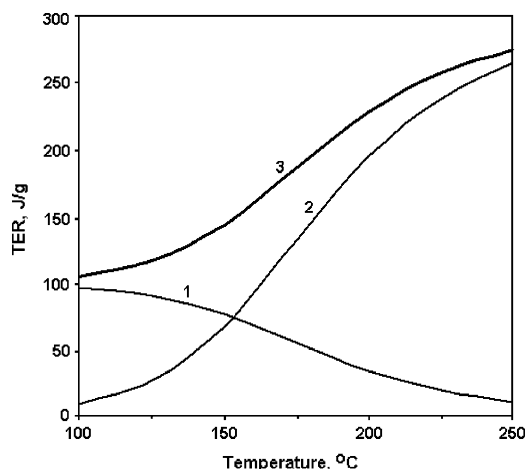
Fig. 6. Determining TER for complex reaction: (1) contribution of the first stage; (2) contribution of the second stage; (3) total energy release.

4. The ReRank software

The kinetics-based simulation is a promising approach that gives the general way for reliable estimation of reactive hazards. However, it is somewhat complex since it requires the application of numerical methods. In addition, appropriate sophisticated methods must be used for evaluating complex models of reaction kinetics from experimental data. In practice, this approach can be widely applied provided that the specialized problem-oriented software is available. The thermal safety software (TSS) developed by ChemInform St. Petersburg (CISP) Ltd. that provides solution of all these problems can be mentioned as one example of the required tool. The general information about the TSS can be found in [7,8]. Here we will give the overview of one component of TSS, which is intended directly for determination of the reactivity hazard indicators. This is the ReRank 2.0 program. Its predecessor, ReRank 1.0, was designed solely for determination of N_r (more details about this software can be found in [5]).

In accordance with the ideas discussed above, the program for rating reactivity and determining reactivity hazard indicators provides:

- a flexible and simple way for defining a multi-stage kinetic model;
- simulation of reaction behavior under defined conditions;
- determining instantaneous or maximal power density and assigning the N_r to a compound;
- determining TCL(T) within the user-defined temperature range as the indicator of thermal stability of a compound;
- determining adiabatic TMR(T_{in}) and TER(T_{in}) within the user-defined temperature range;
- storing the evaluated indicator accompanied by the appropriate additional information into the corresponding TCL, TMR or N_r database.
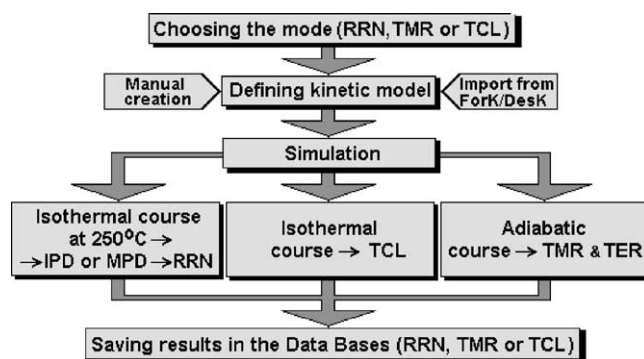

Fig. 7. Flowchart of the ReRank 2.0 software.

Determining an indicator is a straightforward procedure (see the ReRank flowchart in Fig. 7), which provides for definition of all necessary data for calculation, simulation and determination of an indicator, and storing results in the database.

Consider briefly the main steps.

Choosing necessary mode. The selected mode defines the type of indicator which is to be estimated—TCL, TMR or N_r.

Defining a kinetic model. ReRank supports several methods of defining the 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 TSS programs ForK and DesK intended for creation of kinetic models. Therefore, a model can be imported from their databases.

ReRank allows handling of two different kinds of 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 no enough information for constructing a detailed reaction mechanism with stoichiometry. Formal models can represent complex multi-stage reactions that may include several independent, parallel and consecutive stages.

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

In both cases, no programming is required for synthesis of the desired model within ReRank.

Simulating the reaction behavior. The simplest model of the well-stirred batch reactor is used in ReRank for rating reactivity. While estimating TCL or N_r, the model assumes
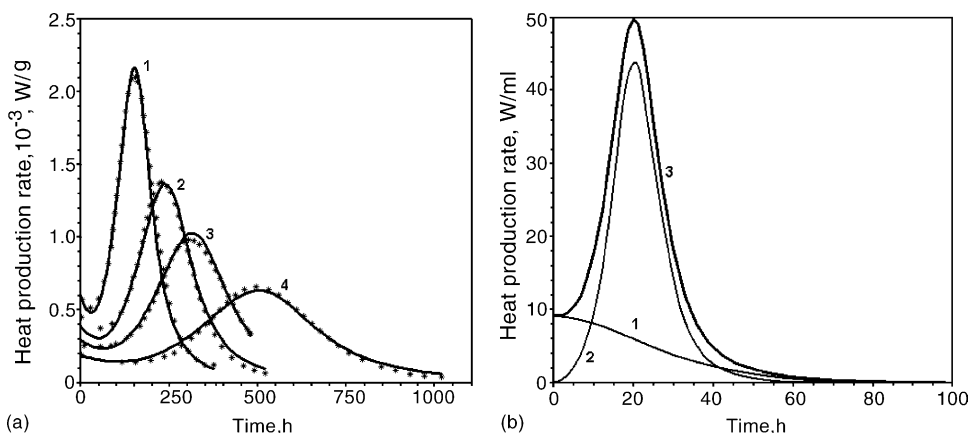
Fig. 8. Determining hazardous properties of 80% solution of CHP in cumene. (a) Thermal decomposition of CHP: (***) experiment; (——) simulation; 1–88 °C; 2–83 °C; 3–80 °C; 4–75 °C. (b) Reaction profile at 250 °C: (1) contribution of the initiation stage; (2) contribution of the autocatalytic stage; (3) total heat production rate.

isothermal mode. The adiabatic thermal mode is set for calculating TMR and TER.

A multi-stage kinetic model of a reaction is represented by the system of ordinary differential equations (ODE), which is integrated numerically by using a specialized up-to-date algorithm.

Storing the results. Microsoft Access-compatible databases support all the necessary types of data management—selecting one of the existing databases or importing a database, searching, filtering, sorting, editing a record, creating a report, etc.

5. Examples of applying the approach

The following two real examples illustrate how the proposed approach can be applied in practice.

Let us consider at first thermal decomposition of cumene hydro-peroxide (CHP). This product is widely used in chemical industry and is known as thermally unstable and hazardous. Several severe explosive accidents that happened involved CHP. Therefore, the indicators that can characterize reactive properties of this product under storage conditions, i.e. N_r and TCL, are of primary interest. The kinetic model necessary for their determination had been evaluated from the set of isothermal experiments with 80% solution of CHP in cumene carried out by using the thermal activity monitor (TMA). Experimental data that revealed strong autocatalytic decomposition (Fig. 8a) were fitted properly by the formal model of full autocatalysis (Eq. (1)) with the following values of the kinetic parameters: $k_{01} = 1.32 \times 10^8\,\text{s}^{-1}$; $E_1 = 98.46\,\text{kJ/mol}$; $n_1 = 0.56$; $Q_1 = 596\,\text{J/g}$; $k_{02} = 1.15 \times 10^{10}\,\text{s}^{-1}$; $E_2 = 99.63\,\text{kJ/mol}$; $n_{21} = 3.02$; $n_{22} = 2.57$; $Q_2 = 2010\,\text{J/g}$.

Then the reaction course at 250 °C had been simulated in order to determine the N_r. Fig. 8b depicts that IPD is about 5.5 times less than MPD so that the N_r evaluated from IPD equals to 1 whereas MPD-based value of the N_r equals to

2. Apparently, the use of IPD results in underrating of the reactive hazard.
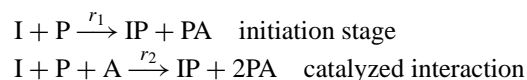
Stability of the solution had been estimated by determining TCL for conversion limit equal to 5%. Values of TCL at 20, 30 and 40 °C are 624, 170 and 50 days, respectively. One can see that elevation of the storage temperature strongly diminishes the product stability and temperature control is required for long-term storage of the product.

The second example illustrates how the adiabatic indicators TMR and TER can be applied for preliminary assessment of reactive hazard of a process. We used for this purpose the equimolar esterification reaction between propionic anhydride and isopropanol proposed by health and safety executive (HSE) for the Round-Robin test on chemical reactor relief system models [9]:

Isopropanol + Propionic anhydride →
(I)   (P)

Isopropyl Propionate + Propionic Acid
(IP)   (PA)
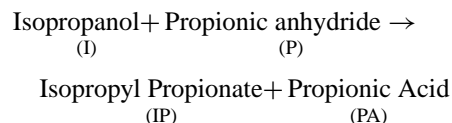
Two experimental data sets obtained at different onset temperatures by using the Phi-Tech adiabatic calorimeter were available (see Fig. 9a).

Esterification reactions are characterized by self-acceleration, therefore the two-stage concentration-based descriptive model that describes the autocatalytic effect of an acid reaction product had been chosen for kinetics evaluation:

$$I + P \xrightarrow{r_1} IP + PA \quad \text{initiation stage}$$
$$I + P + A \xrightarrow{r_2} IP + 2PA \quad \text{catalyzed interaction}$$

$$r_1 = k_1[I]^{n_{11}}[P]^{n_{12}}; \quad r_2 = k_2[I]^{n_{21}}[P]^{n_{22}}[PA]^{n_{23}};$$

$$\frac{d[I]}{dt} = \frac{d[P]}{dt} = -r_1 - r_2; \quad \frac{d[IP]}{dt} = \frac{d[PA]}{dt} = r_1 + r_2;$$

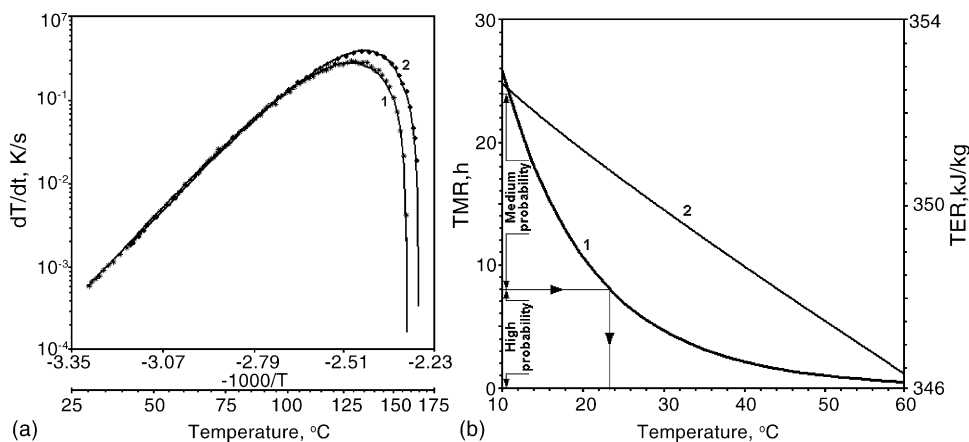$$k_i = k_{0i}e^{-E_i/RT}; \frac{dQ}{dt} = Q_1 r_1 + Q_2 r_2 \tag{4}$$

Fig. 9. Predicting reactive hazard of the esterification reaction. (a) Adiabatic data fitting: (1) onset temperature 25.2 °C; (2) onset temperature 35 °C; (●●●), (∗∗∗) experiment; (—) simulation. (b) Dependency of TMR (1) and TER (2) on temperature.

The kinetic parameters that provide satisfactory fitting of experimental data (Fig. 9a) are as follows: $k_{01} = 8.72 \times 10^5$ $(\text{mol/m}^3)^{a1} \text{s}^{-1}$; $E_1 = 66.63$ kJ/mol; $n_{11} = 0.35$; $n_{12} = 0.44$; $Q_1 = 117.6$ kJ/mol; $k_{02} = 1.99 \times 10^6$ $(\text{mol/m}^3)^{a2} \text{s}^{-1}$; $E_2 = 69.31$ kJ/mol; $n_{21} = 0.97$; $n_{22} = 0.77$; $n_{23} = 1.23$; $Q_2 = 46.22$ kJ/mol, where $a1 = 1 - n_{11} - n_{12}$; $a2 = 1 - n_{21} - n_{22} - n_{23}$.

More detailed discussion of this benchmark and some features of the kinetic model created can be found in [8].

Fig. 9b depicts the results of calculation of TMR and TER. Though TER depends on the reactant temperature, variation of this indicator is small so that for the subsequent analysis we used the mean value TER = 350 J/g.

As we mentioned, TMR characterizes the probability of an explosive accident and TER is correlated with the potential severity of an accident. According to the criteria for the assessment of probability and severity suggested in [4], the probability is considered to be high if TMR < 8 h and medium if 8 h < TMR < 24 h. Severity can be considered as medium if 120 J/g < TER < 480 J/g. For the example discussed, the severity of an accident is always medium whereas the medium probability is provided if the process temperature is less than 24 °C. Such a low temperature is unacceptable from practical point of view (provided that under normal conditions it is possible to keep the temperature constant) because the process duration exceeds six days. Higher temperatures that would ensure feasibility of a process are inadmissible due to too high risk of explosion development. As we can see even this preliminary analysis leads to very practical result that this process is absolutely unsafe if it is carried out in the batch mode, therefore semi-batch or continuous mode must be considered as an alternative.

6. Conclusions

The set of hazard indicators that includes TCL(T), TMR(T_{in}) and TER(T_{in}), and MPD-based N_r can be success-fully used for getting preliminary estimates of reactive hazards of a substance or mixture provided that two conditions are satisfied:

- the applicability limits of each indicator are taken into account;
- the indicators have been determined by using the appropriate methods.

Reliable determination of the indicators can be implemented by using the advanced kinetics-based simulation method and the corresponding ReRank program proposed in this paper.

By no means can the use of any hazard indicator(s) eliminate the comprehensive analysis of process hazards. Nevertheless, application of the proposed set of indicators can be considered as a reasonable initial step for reactive hazard assessment.

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