Parameters Influencing the Correct Thermal Safety Evaluations of Autocatalytic Reactions

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The paper presents the results of simulations of the influence of the reaction progress of the material at the moment of the beginning of the thermal experiment (called as $\alpha_{storage}$) on the thermal behavior in mg- (as in DSC), kg- (SADT or cookoff), and ton- (TMR_{ad}) scales. Simulations were carried out using the general autocatalytic (first-order reaction with autocatalysis, Kamal-Sourour, KS), nucleation (Avrami-Erofeev, A4) and first-order (F1) reaction models. Results of simulation show that influence of $\alpha_{storage}$ is significant for materials decomposing according to autocatalytic models and negligible for those decomposing according to the first-order kinetics. For the determination of the importance of $\alpha_{storage}$ value on the course of reaction and, further, on the simulations of the thermal behavior of the materials, we propose the simple AKTS test which requires only two non-isothermal runs with identical, arbitrarily chosen heating rates. The goal of this test consists in controlled, artificial aging of the sample, reflecting the minor changes of reaction progress during sample storage. In other words, the test allows comparison of the thermal behavior of the same sample having, however, in two following experiments, slightly different $\alpha_{storage}$ values. Additionally we present the simulations of the dependence of thermal properties of the materials on the $\alpha_{storage}$ under real, climate conditions. All presented results indicate that the decomposition progress of the materials at the beginning of any thermal treatment must be considered as an important parameter, beside commonly applied kinetic triplet, during prediction of the sample properties.

1. Introduction

One cannot exclude that the materials after their formation may slowly decompose during further storage even under ambient conditions, however, the thermal history of the sample after its synthesis has not been considered yet as an important factor during the kinetic predictions and simulations of the thermal behavior of the materials. The monitoring of this aging process is often very difficult when the reaction progress changes only in the range say from 1×10^{-10} till 1×10^{-2} i.e. till the 1 %. Rate of thermal aging, resulting in sometimes hardly observable reaction progress occurring in the time laps between sample synthesis and the moment of the beginning of any thermal experiment, depends on two factors: (i) the intrinsic properties of substance such as its kinetic triplet (pre-exponential factor A, activation energy E and the form of the function f(α) dependent on the decomposition mechanism (where α represents the reaction progress)) and (ii) time and temperature of the storage. Both these factors may in different ways influence this, unknown for user, small change of the reaction progress occurring during storage, called throughout this paper as $\alpha_{storage}$. Our former results (Roduit et al., 2011) have shown that the application of the correct kinetic function f(α) is of great importance.

In presented paper we discuss the peculiarities of the often applied autocatalytic models (Varhegyi at al, 2012). We present the simulations showing how the thermal aging of the sample influences its thermal behavior depending on the f(α) model applied. The simulations were done for the materials in mg - (as e.g. during DSC experiments), kg- (as e.g. during the determination of the cookoff ignition temperature, Self

Accelerating Decomposition Temperature SADT, etc.) and ton- scales (as e.g. when determining Time to Maximum Rate TMR_{ad} for various initial temperatures).

2. Simulation of influence of $\alpha_{storage}$ on the thermal behaviour of materials

In order to illustrate in more details the influence of the $\alpha_{storage}$ on the course of the decomposition and its dependence on the form of the $f(\alpha)$ function we performed the simulations for three commonly applied functions:

- First-order reaction F1 with $f(\alpha) = 1-\alpha$.
- General autocatalytic model: first-order reaction with autocatalysis (Sourour and Kamal, 1976) (KS) equation $f(\alpha) = (1-\alpha)(Z+\alpha)$ with $Z = k_1/k_2$ and $d\alpha/dt = k_2 f(\alpha)$ which consists of two reactions: primary decomposition with k_1 in which the catalytically active product is formed being followed by the autocatalytic reaction with k_2. Note that if $Z = k_1/k_2 \sim 0$ then KS model can be simplified to commonly used Prout-Tompkins (PT) model (Prout and Tompkins, 1944).
- Nucleation controlled Avrami-Erofeev model A4 with $f(\alpha) = 4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$ which is characterized by the sigmoidal-type dependence in coordinates α-time under isothermal conditions similar to those observed in autocatalytic reactions.

The total time of decomposition of a sample required for its full decomposition ($\alpha = 1$) is the sum of its storage time denominated as $t_{storage}$ and the time of the experimental decomposition t_{exp} necessary to complete the reaction (see Equation 1). In summary, the end of the storage time $t_{storage}$ when the sample reaches $\alpha_{storage}$ corresponds to the time of beginning of any experiment which amounts to t_{exp}. We can write:

$$t_{\alpha=1} = t_{storage} + t_{exp} = \int_0^{t_{\alpha=1}} dt = \int_{\alpha_0}^{\alpha_{storage}} \frac{d\alpha}{k(T_{storage}) \cdot f(\alpha)} + \int_{\alpha_{storage}}^{\alpha=1} \frac{d\alpha}{k(T_{exp}) \cdot f(\alpha)} \quad (1)$$

The simulations were carried out using AKTS-Thermokinetics Software (2012) and their results are depicted in Figure 1. This figure shows the influence of the $\alpha_{storage}$ value (ranging from 1×10^{-10} to 1×10^{-1}) on the thermal behavior of the sample in mg-(DSC), kg-(SADT and slow cookoff) and ton-(TMR_{ad24h}) scales. ΔT marked on curves display the influence of aging (i.e. the influence of change of $\alpha_{storage}$) on the chosen thermal properties.
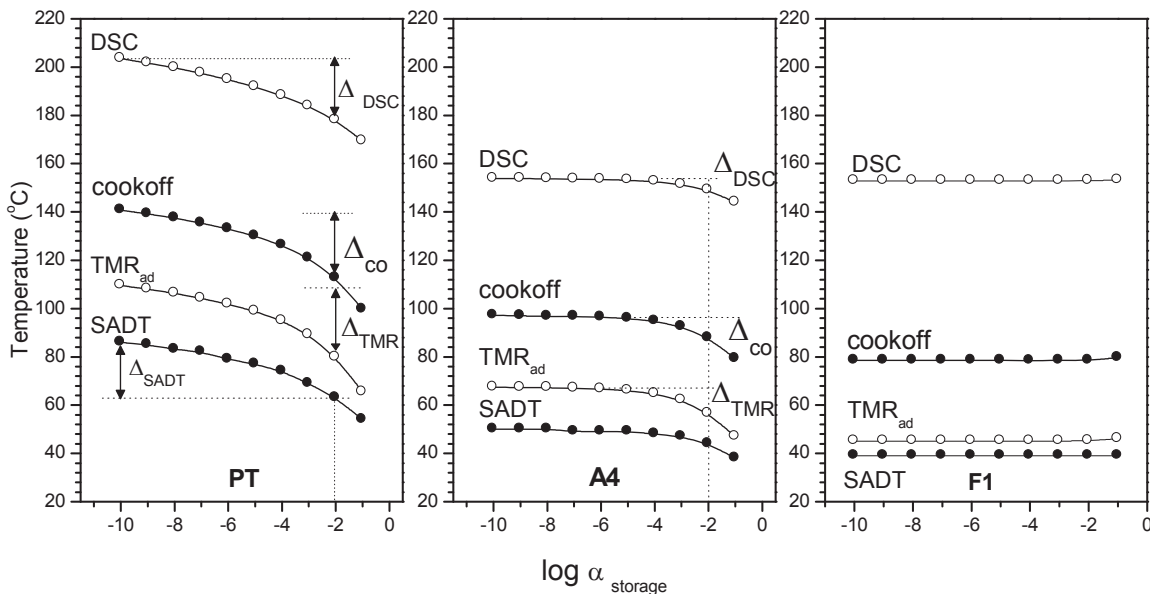

Figure 1: Influence of $\alpha_{storage}$ on the thermal behavior in mg- (T_{DSCmax} for heating rate of 5 K·min^{-1} from 20 °C), kg- (SADT and cookoff) and ton-scale (TMR_{ad24h}) for the autocatalytic reaction expressed by KS with $Z \sim 0$ (i.e. PT) (left), A4 (middle) and first order F1 models (right) simulated for $A = 1 \times 10^{10}$ s^{-1}, $E = 100$ kJ·mol^{-1}

For the simulations the following input parameters were applied: $A = 1 \times 10^{10}$ s^{-1}, $E = 100$ kJ·mol^{-1} (with Z ~ 0 for KS-model), heating rate of 5 K·min^{-1} from 20 °C (DSC), $\Delta H_r = -500$ J·g^{-1}, $C_p = 1.8$ J·(g·K)$^{-1}$, $\lambda = 0.3$ W·(m·K)$^{-1}$, $h = 5$ W·m^{-2}·K^{-1}, sample mass 50 kg (SADT) and 1 kg cookoff. The details of simulations of SADT, cookoff, and TMR$_{ad24h}$ are described in our papers (Roduit et al., 2008) or more recently by Dellavedova et al. (2012), respectively.

Depicted results confirm that the change of $\alpha_{storage}$ from 1×10^{-10} to 1×10^{-2} (1 % of the decomposition) leads to the drastic variation of all thermal properties in the case of autocatalytic reactions and has no influence of the thermal behavior of the samples decomposing according to the first order reaction model. For the nucleation controlled reaction A4 the influence of the $\alpha_{storage}$ values on the properties is observable, however, it is smaller than in autocatalytic reaction. The change of $\alpha_{storage}$ from 1×10^{-10} to 1×10^{-2} results in decreasing temperature of the DSC peak by 25.5; 4.8 and almost 0 K for KS (with Z~0), A4 and F1 models, respectively. By this $\alpha_{storage}$ variation, the change of SADT amounts to 23; 6 and 0 K, the change of the cookoff ignition temperature amounts to 28; 9.1 and almost 0 K and the temperature at which the sample reaches the TMR$_{ad24h}$ decreases by 29.8; 10.8 and 0 K for KS, A4 and F1 models, respectively.
In daily life, the $\alpha_{storage}$ value is unknown for the user, therefore, nobody can interpret for the investigated substance the dependences shown in Figure 1. However, the results presented in Figure 1 clearly illustrate that the controlled thermal aging of the sample, resulting in formation of the sample having larger $\alpha_{storage}$, may be used as a tool allowing determination of interesting properties of the materials.
For determination of the dependence of the thermal properties of the materials on the $\alpha_{storage}$ value we propose the simple AKTS test which requires only two non-isothermal runs with identical, arbitrarily chosen heating rates. The goal of this test consists in controlled, artificial aging of the sample, reflecting the minor changes of the reaction progress during sample storage. In other words, the test allows comparison of the thermal properties of the same sample having, however, in two following experiments, slightly different $\alpha_{storage}$ values. The scheme of the test is displayed in the Figure 2. The difference between the temperature of peak maxima (T_{max1} and T_{max2}) and final temperatures of decomposition (T_{f1} and T_{f2}) measured in the 1-st and 2-nd run indicate the influence of the $\alpha_{storage}$ value on the reaction course. The values of $\alpha_{storage}$ at room temperature for the 1-st (point A) and 2-nd run after aging (point D) have been denoted in the following test as $\alpha_{storageA}$ and $\alpha_{storageD}$, respectively.
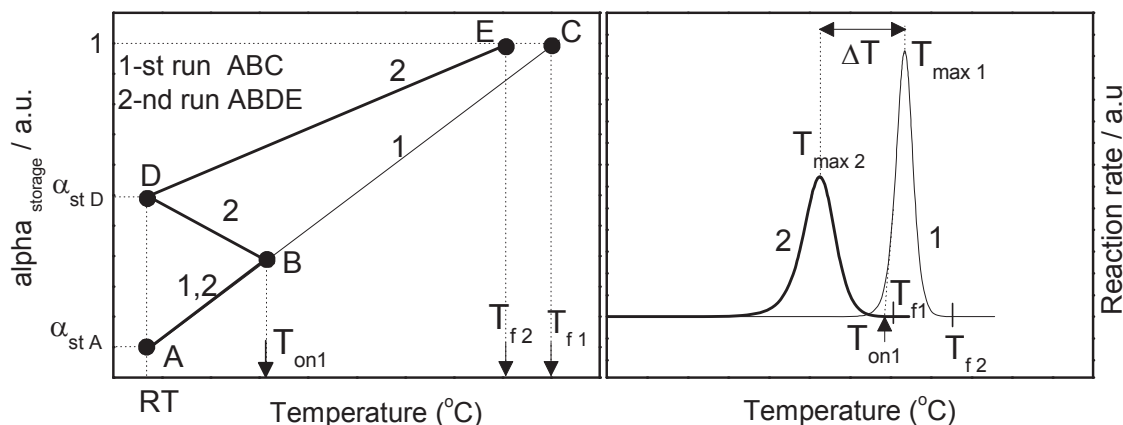

Figure 2: Temperature ramps (left plot) applied for determination of the influence of $\alpha_{storage}$ on the thermal properties of the sample (right plot).

The proposed test requires two experiments:
(1) Conventional thermoanalytical run (here displayed in the form of the reaction rate as a function of the temperature) performed with generally used heating rate of e.g. 5 K·min^{-1} from the room (RT) till the final temperature (T_f) when the reaction is completed. This temperature ramp is depicted by points ABC, the $\alpha_{storage}$ value at point A is denoted as $\alpha_{storageA}$ and represents the reaction progress of the sample at the moment of the beginning of the thermal investigations.
(2) Second run (ABDE) is performed with a new sample possessing, as in (1), the $\alpha_{storageA}$ at the beginning of the experiment. The run is stopped at the temperature of T_{on1} (ramp AB). This temperature is conventionally determined according to ICTAC nomenclature as the temperature at which the line drawn through the almost linear section of the ascending peak slope intersects the base line. At T_{on1} (point B), the

temperature is decreased to the RT (till point D) with the same rate as during heating. Finally, the sample with larger decomposition progress named as $\alpha_{storageD}$ is heated with previous heating rate till the full decomposition (ramp DE).

The magnitude of the change of the position of T_{DSCmax} (depicted as ΔT in the right plot, Figure 2) is a measure of the influence of $\alpha_{storage}$ on the thermal behavior of the sample. The kinetic parameters of both samples, having at the beginning of the experiments the $\alpha_{storage}$ values represented as points A and D (see Figure 2, left plot), are the same (or very similar). In this situation, the shift of the position of the DSC peak (and change of other parameters in kg- or ton scales) is due to the change of the $\alpha_{storage}$ value. This important observation indicates that, for the prediction of the thermal behavior of the materials beside the commonly used kinetic triplet, the $\alpha_{storage}$ value has to be additionally introduced. The results of the simulations of the thermal properties during proposed test are displayed in Figure 3.
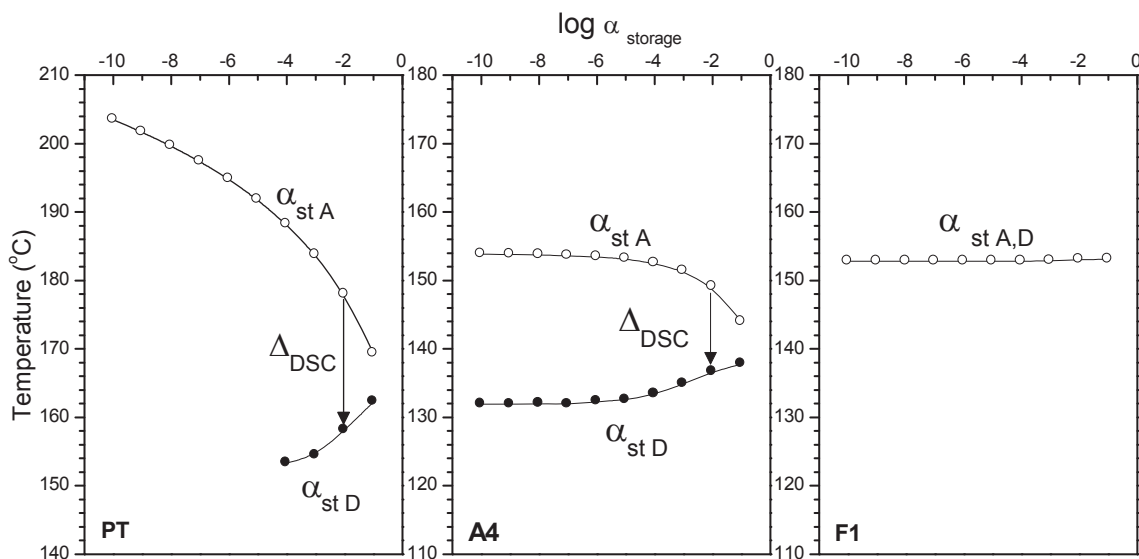

Figure 3. Change of the position of T_{DSCmax} on the simulated DSC curves during proposed test as a function of initial value of $\alpha_{storageA}$ and the form of $f(\alpha)$ function.

The results of the proposed test (Figure 3) show that after additional thermal aging which changes the reaction progress to $\alpha_{storageD}$ (see left plot in Figure 2) the position of $TDSC_{max}$ shifts to significantly lower temperatures for autocatalytic reactions (KS with Z~0 i.e. PT, left plot) and stays unchanged for n-th order models (F1). The samples with very small values of $\alpha_{storageA}$ laying in the range 1×10^{-10} till 1×10^{-5} are fully decomposed during the ramp BD for the autocatalytic reactions (KS, left plot). The arrows display the change of T_{DSCmax} after proposed test for the sample decomposed in 1 % (i.e. $\alpha_{storageA} = 1\times10^{-2}$) at the beginning of the thermal experiment in case of KS and A4 models, respectively. Presented simulations indicate that one can relatively easy check the influence of the aging process on the thermal behavior of the materials. This influence is especially notable for the materials with very small decomposition progress i.e. for those with very small, immeasurable $\alpha_{storage}$ values. However, even in the case of samples being already decomposed during storage till 1 %, the AKTS test will allow detecting that during prediction of their properties additionally to the kinetic parameters also the $\alpha_{storage}$ has to be introduced into simulation procedure. The arrows placed in Figure 3 illustrate that sample having at the beginning of the thermoanalytical experiment the reaction progress of 1 % ($\alpha_{storageA}$ value of 1×10^{-2}) will after test lower its T_{DSCmax} value by 19.8 or 12.4 K for KS and A4 models, respectively.

It is necessary to underline that for materials decomposing with n-th order kinetics, even moderate changes (below 10 %) of the reaction progress during storage do not influence their thermal behavior. The data presented in Figures 1 and 3 show that such materials do not change their thermal properties in mg, kg and ton scales in a noticeable way even when reaching the $\alpha_{storage}$ values of 1×10^{-2}. This observation partly explains the lack of considerations of the role of $\alpha_{storage}$ in simulations of the thermal properties of the materials. The large majority of the published results were based on the assumptions that the reaction is of the n-th order (as e.g. first-order F1) and in mathematical treatment of experimental data these model functions were mainly applied even if a reaction presents an autocatalytic behavior. The results of our

simulations clearly indicate that for n-th order models, the $\alpha_{storage}$ has no influence on the reaction course and further thermal properties of the materials. However, for reactions presenting strong autocatalytic behavior, this additional parameter is of great importance during predictions based on the application of the kinetics. Its neglecting may lead to the dangerous overestimation of the safety parameters. The decomposition progress during storage in the range of only 1% may lead in the autocatalytic reaction to enormous lowering of SADT temperature (in our simulation by 23 K) or changing the safety diagram by lowering by 30 K the temperature at which the TMR_{ad} amounts to 24 h.

3. Simulation of the materials aging at real climate conditions

The results of simulation of the influence of the $\alpha_{storage}$ value on the predicted course of the reactions under non-isothermal conditions shown in Figures 1 and 3 indicate that even small changes of the reaction extent may significantly influence the thermal behavior of the materials decomposing autocatalytically. On the other hand, this relationship is much less significant for other reaction models or, in the case of n-th order models as in often used first-order kinetics, even negligible. In order to illustrate these dependences under real climate conditions, which are important from the practical point of view, we present the simulated data for the meteorological temperature profile of Riyadh, Saudi Arabia. The simulations of the reaction progress of the material decomposing according to KS and F1 models (with the same simulation parameters as those applied in Figure 1) and stored respectively about 10 years (PT) and 100 days (F1) in Saudi Arabia are presented in Figure 4.
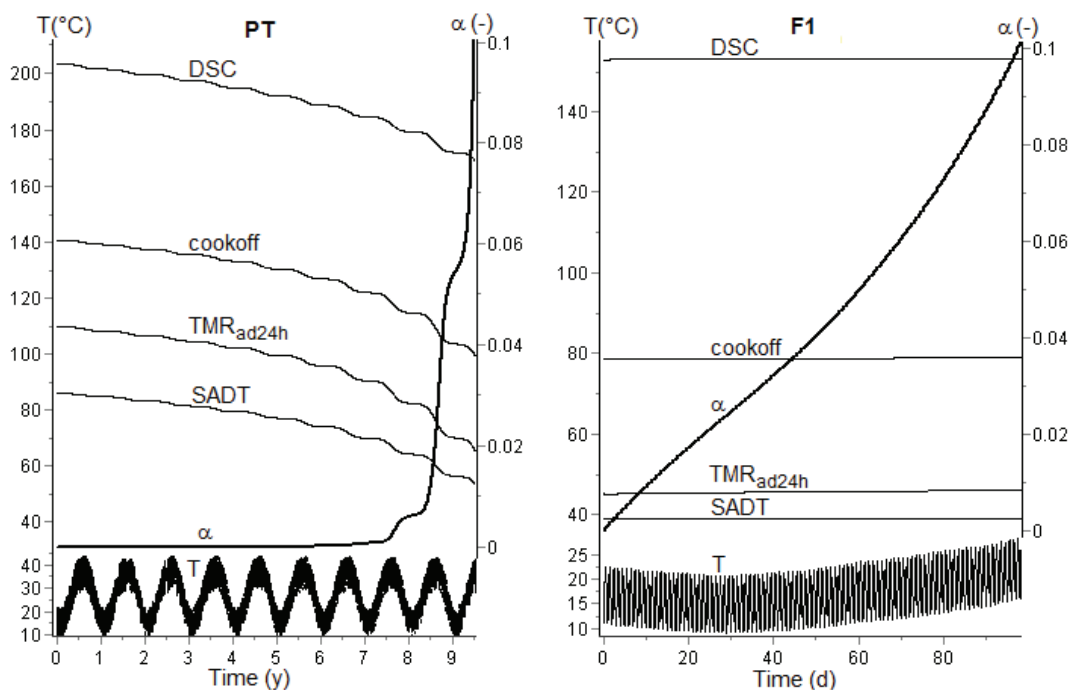

Figure 4: Simulation of the thermal behavior of the material decomposing according to autocatalytic (left) and first order kinetic models (right) during storage in Saudi Arabia. The plots show daily temperature fluctuations (T) in Riyadh, Saudi Arabia, reaction progress α, DSC_{max}, SADT, cookoff ignition temperatures and TMR_{ad24h} as a function of the storage time.

During storage, the material is aged, note the increasing reaction progress in time, after ca. 9.5 y (PT) and 97.5 d (F1) the α amounts to ca. 0.1 (decomposition degree of 10 %). This continuous change of the reaction progress influences the material properties which we show in Figure 4 presenting the results of the simulation of:
(i) The temperature of the peak maximum of the DSC signal (T_{DSCmax}) under non-isothermal conditions (from 20 °C, heating rate of 5 K·min^{-1}) (mg-scale),
(ii) The Self Accelerating Decomposition Temperature (SADT) applied during the transport or storage of dangerous chemicals (kg-scale),
(iii) The ignition temperature of slow cookoff (applied in defence) (kg-scale),

(iv) The initial temperature resulting in a Time to Maximum Rate under adiabatic conditions of 24 h - TMR_{ad24h} (ton-scale).

Simulation of the thermal behavior of the sample decomposing autocatalytically, possessing very small reaction progress ($\alpha_{storage}$ value = 1×10^{-10}) at the moment of the beginning of its thermal aging under real climate conditions, clearly depicts the significant variation of the parameters characteristic for the material in all, mg-, kg-, and ton- scales. For KS (or PT with Z~0) model after ca. 9.5 y of storage in the climate of Saudi Arabia the reaction progress α amounts to c.a. 10 % and T_{DSCmax}, SADT, cookoff ignition temperature and TMR_{ad24h} decrease by 34.1 K, 32 K, 41 K and 44.1 K, respectively (see Figure 4, left). However, the storage at the same conditions of the samples decomposed according to the first order kinetics has no influence on their thermal behavior: despite the same reaction progress α (even if it amounts to 10 %, see Figure 4, right) all thermal properties stay unchanged.

The results of both simulations, namely in constant heating rate mode and under real climate temperatures, confirm our conclusions that the state of the substance (characterized by $\alpha_{storage}$ value) at the moment of the beginning of thermal experiment or its exposure to daily-life temperatures has to be seriously considered. It must be taken as an important parameter, beside commonly applied kinetic triplet, during prediction of the sample properties.

4. Conclusion

Results of our simulations indicate that the initial decomposition of the materials at the moment of the beginning of any thermal treatment (called as $\alpha_{storage}$) may have a significant impact on the thermal behavior in mg-, kg- and ton-scales. This influence depends significantly on (i) the reaction model describing the kinetic of thermal decomposition process and on (ii) the progress of the sample decomposition (i.e. the $\alpha_{storage}$ value) at the beginning of the experiment. The largest impact is observed for "fresh" substances with low $\alpha_{storage}$ values and for autocatalytic reactions, for samples decomposed according n-th order kinetics this influence is negligible.

Determination of the importance of $\alpha_{storage}$ value on the course of reaction and, further, on the simulations of the thermal behavior of the materials, can be easily checked by the simple AKTS test which requires only two non-isothermal runs with identical, arbitrarily chosen heating rates. The goal of this test consists in controlled, artificial aging of the sample, reflecting the minor changes of reaction progress during sample storage.

For reactions presenting strong autocatalytic behavior, the knowledge of $\alpha_{storage}$ value is of great importance during kinetic predictions. Its neglecting may lead to the dangerous overestimation of the safety parameters. The decomposition progress during storage in the range of only 1 % may lead in the autocatalytic reaction to enormous lowering of SADT (in our simulation by 23 K) or severe changes of the safety diagram by lowering by 30 K the initial temperature at which the TMR_{ad} amounts to 24 h.

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