New Kinetic Approach for Evaluation of Hazard Indicators Based on Merging DSC and ARC or Large Scale Tests

Bertrand Roduit[a*], Marco Hartmann[a], Patric Folly[b], Alexandre Sarbach[b], Pierre Brodard[c], Richard Baltensperger[c]

[a] AKTS AG, TECHNOArk 1, 3960 CH-Siders, Switzerland
[b] armasuisse, Science and Technology Centre, 3602 CH-Thun, Switzerland
[c] University of Applied Sciences of Western Switzerland, Bd de Pérolles 80, 1705 CH-Fribourg
b.roduit@akts.com

The present study describes two methods of evaluation of hazard indicators such as Self Accelerating Decomposition Temperature (SADT) or Time to Maximum Rate under adiabatic conditions (TMR_{ad}) from the results of the experiments performed in mg scale by Differential Scanning Calorimetry (DSC). We discuss here: (i) the kinetic workflow in which the kinetic parameters of the investigated reaction evaluated from the DSC are used with the heat balance of the system and (ii) a novel merging approach in which DSC data are simultaneously considered with the results of other, temperature recorded experiments as e.g. Accelerating Rate Calorimetry (ARC), large scale experiments as e.g. cookoff, Dewar or SADT determination according to STANAG 4383 and UN regulations (Tests H.4 and H.1), respectively. The commonly kinetic-based approach is discussed and its results confirmed by those obtained in common project with Federal Institute for Materials Research and Testing, Berlin, Germany (BAM) in which the SADT for AIBN was investigated. The novel merging approach is illustrated by the results of the linked DSC-UN test H.1 data and DSC-ARC results applied for SADT determination and for evaluation of TMR_{ad} for any starting temperature for AIBN.

1. Introduction

The estimation of the hazard probability of "reactive or self-reactive chemicals" is a very important issue especially for the safety analysis of many technological processes or packaged materials during transport conditions. The dangerous runaway scenario is quantitatively characterized by the thermal hazard indicators such as SADT and TMR_{ad}. Due to the fact that significant amount of heat is evolved during the decomposition of self-reactive chemicals their thermal properties are frequently investigated in laboratory at mg- or g-scales under non-isothermal or isothermal conditions using Differential Scanning Calorimetry (DSC) or, more sensitive, Heat Flow Calorimetry (HFC) techniques. The elaboration of the heat flow data monitored by these both techniques allows determination of the kinetic parameters of the decomposition process which describe the rate of the heat generation in the conditions of the ideal heat exchange with the surroundings. However, the correct scale-up of the results obtained by DSC or HFC requires the application of the proper heat balance in the simulated system. In kg-scale, due to increasing sample mass, the conditions of the heat exchange with the environment significantly change what, in turn, may significantly increase the reaction rate and the spatial evolution of the sample temperature.

The hazard indicators as SADT, TMR_{ad}, cookoff are generally measured in large scale experiments in which the amount of tested materials is in the range of hundreds of grams or, in specific measurements, even 50 kg. It seems to be obvious that there is a need of elaboration and testing methods which allow for determination of the hazard indicators from mg scale experiment. The comparison of the results of large scale experiments with those obtained in mg scale and elaborated by kinetic-based approach has been the main topic of the recent project described in details by Roduit at al. (2015). Results of this project clearly indicate that simulation of the hazard indicators (in this case SADT of AIBN) can be successfully done with DSC experimental data. In the present study we briefly depict the principle of commonly used kinetic based approach and propose new kinetic workflow in which the DSC data (mg scale) are linked with the experiments carried out with other techniques: ARC and UN H.1 tests.

2. Kinetic based approach

Two main steps of kinetic-based approach are: (i) determination of kinetic parameters of the decomposition reaction which allow quantifying rate of the heat production and (ii) the heat balance which allows quantifying the rate of the heat loss in g- and kg-scales.

2.1. Determination of the kinetic parameters

The kinetic-based approach for the determination of SADT requires the accurate determination of the kinetic parameters which are used to numerically describe the rate and progress of the investigated reaction as a function of time and/or temperature. If the decomposition follows a single kinetic model, then the reaction can be described in terms of a single pair of Arrhenius parameters and the commonly used set of functions $f(\alpha)$ reflecting the mechanism of the process, where α expresses the reaction extent, varying between 0 and 1. The reaction rate can be described by one value of the activation energy E and one value of the pre-exponential factor A with the following expression:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT(t)}\right) f(\alpha) \tag{1}$$

where t is time, T - temperature and R - the gas constant. Numerous sets of kinetic models are available in the literature, see e.g. Pérez-Maqueda at al. (2006) or Vyazovkin at al. (2011). The truncated Šesták-Berggren (SB) model (Šesták and Berggren,1971) can be used as a very first approximation either for single or multi-step reactions. In this second case, when the process proceeds via several sub-reactions, the general rate expression for the model containing l stages can be depicted as:

$$\frac{d\alpha}{dt} = \sum_{i=1}^{l} k_i (1-\alpha)^{n_i} \alpha^{m_i} \tag{2}$$

For example, the application of Eq.(2) for two sub-reactions by setting $m_1=0$ gives

$$\frac{d\alpha}{dt} = k_1 (1-\alpha)^{n_1} + k_2 (1-\alpha)^{n_2} \alpha^{m_2} \tag{3}$$

With the exponents n and m taken as integers and by setting $n_1=1, m_1=0, n_2=1, m_2=1$, the reaction rate follows an autocatalytic behaviour and can be in this simplified case expressed as:

$$\frac{d\alpha}{dt} = k_2 (1-\alpha)(Z+\alpha) \tag{4}$$

with $Z(T) = \dfrac{k_1(T)}{k_2(T)}$: the ratio of the reaction rate constants which depends on the temperature.

When the mechanism of the decomposition of a material is more complicated and not fully recognized, the isoconversional differential approach of Friedman (1963) can be advantageous in the kinetic computations. Such isoconversional techniques and evaluation methods, see e.g. Roduit at al. (2014) or AKTS software (2015), are very commonly applied in solid state kinetics for the prediction of the reaction rate and progress under any new temperature profiles. The isoconversional techniques avoid cumbersome, time- consuming and sometimes very arbitrary approaches of introducing the assumption concerning the existence of several reaction models and activation energy values necessary for the kinetic analysis of the investigated process. Because the isoconversional analysis approach does not require any knowledge of the decomposition mechanism, it avoids the risk of selecting a wrong model, which may be incorrect from a chemical point of view, which, in turn, may result in very dangerous consequences for predicting e.g. thermal ageing or hazard evaluation. In isoconversional analysis, the reaction rate for any temperature profile $T(t)$ can be determined, as reported by Roduit at al. (2008), by applying the corresponding $E(\alpha)$ and $A(\alpha)f(\alpha)$ values in Eq. (5) at different degrees of conversion α

$$\frac{d\alpha}{dt_\alpha} = A(\alpha)f(\alpha)\exp\left(-\frac{E(\alpha)}{R}\frac{1}{T_\alpha}\right) \tag{5}$$

where t_α T_α $E(\alpha)$ and $A(\alpha)$ are the time, temperature, apparent activation energy and pre-exponential factor, at the reaction extent α. The expression for $E(\alpha)$ and $A(\alpha)f(\alpha)$ can be obtained by Friedman analysis from the slope and the intercept with the vertical axis of the plot depicting the dependence $ln(d\alpha/dt_\alpha)$ vs. $1/T_\alpha$. The time necessary to reach any reaction progress α is then estimated by isoconversional kinetic predictions i.e. by the separation of the terms followed by an integration:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^\alpha \frac{d\alpha}{A(\alpha)f(\alpha)e^{-\frac{E(\alpha)}{RT_\alpha}}} \qquad (6)$$

In this study, we have applied the isoconversional" kinetic analysis for evaluation of the kinetic parameters required further for SADT determination of AIBN.

2.2. Applying the kinetic parameters and the heat balance for the determination hazard indicators

The experimental data collected in mg scale are very often used for the evaluation of the kinetic parameters, see e.g. Brown at al. (2000), Vyazovkin at al. (2014). In such experiments (as e.g. DSC) experiments, the problem of the influence of the heat balance on the reaction course is generally not considered because of the small sample sizes. In the kg scale the heat evolved during reaction cannot be instantaneously exchanged with the surroundings. The possible self-heating, leading to a temperature rise in the sample, is strongly dependent on the user-controlled parameters such as the sample mass and the physical state (liquid or solid) of the materials. In the case of self-heating, the expression for the rate of change of the sample temperature commonly applied at the mg-scale in kinetic analysis

$$\frac{dT}{dt} = \beta \qquad (7)$$

with $T = T_0 + \beta t$ and $T \cong T_e$ and, respectively, $\beta \neq 0$ and $\beta = 0$ for the nonisothermal and isothermal conditions, has to be replaced by a more complicated dependence which includes the heat balance in the system required for larger sample masses which in case of AIBN in solid state in a drum can be written as:

$$\frac{dT}{dt} = \frac{\lambda}{\rho Cp}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{-\Delta H_r}{Cp}\frac{d\alpha}{dt} \qquad (8)$$

where C_p, ρ, λ, $-\Delta H_r$, $d\alpha/dt$ mean, respectively: specific heat capacity (1.55 Jg^{-1}K^{-1}, see Roduit at al. (2015)), density (650 kg^{-1}m^{-3}), thermal conductivity (0.124 Wm^{-1}K^{-1}, best fit value based on 50 kg AIBN), specific heat of reaction (ca. -1428 Jg^{-1} by DSC at 78°C based on 14 mg AIBN) and reaction rate. The overall heat transfer coefficient U expressing the heat transfer from or to the surroundings has been taken as 5 Wm^{-2}K^{-1} (typical for SADT, see Malow at al. (2010)).

3. Determination of SADT based on merging DSC with ARC or H1 tests data

The differential isoconversional analysis can be applied to obtain a precise kinetic description of the reaction measured by DSC. It can be assumed that in small conversion ranges $\Delta\alpha$ the apparent activation energy $E(\alpha)$ and the term $A(\alpha)f(\alpha)$ do not change significantly so that their ratio can be considered as approximately constant and we can write:

$$\ln(A(\alpha)\cdot f(\alpha)) \cong C\cdot E(\alpha) \qquad (9)$$

where C denotes a constant of proportionality. Similar approach is widely used when applying the integral isoconversional method for the determination of the activation energy $E(\alpha)$ by integration over a small segment of $\Delta\alpha$ as reported by Vyazovkin (2001). Because the criterion of SADT of AIBN with an overheat of 6°C ($\Delta T6$) is fulfilled already at the beginning of the decomposition when the reaction progress α is small, Equation (9) may be also applicable for the SADT evaluation due to considering of relatively very narrow conversion range. Integration in small α segments yields $E(\alpha)$ values that are practically identical with those obtained by the differential isoconversional analysis which rewritten in logarithmic form gives

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) = \ln(A(\alpha)f(\alpha)) - \frac{E(\alpha)}{R}\frac{1}{T(t_\alpha)} \qquad (10)$$

By considering Eq.(9) one can write

$$\ln\left(\frac{d\alpha}{dt_\alpha}\right) \cong E(\alpha)(C - \frac{1}{RT(t_\alpha)}) \qquad (11)$$

After final recombination of Eq.(11), one obtains the following expression allowing evaluation of the activation energy $E(\alpha)$

$$E(\alpha) \cong \frac{\ln\left(\dfrac{d\alpha}{dt_\alpha}\right)}{C - \dfrac{1}{RT(t_\alpha)}} \tag{12}$$

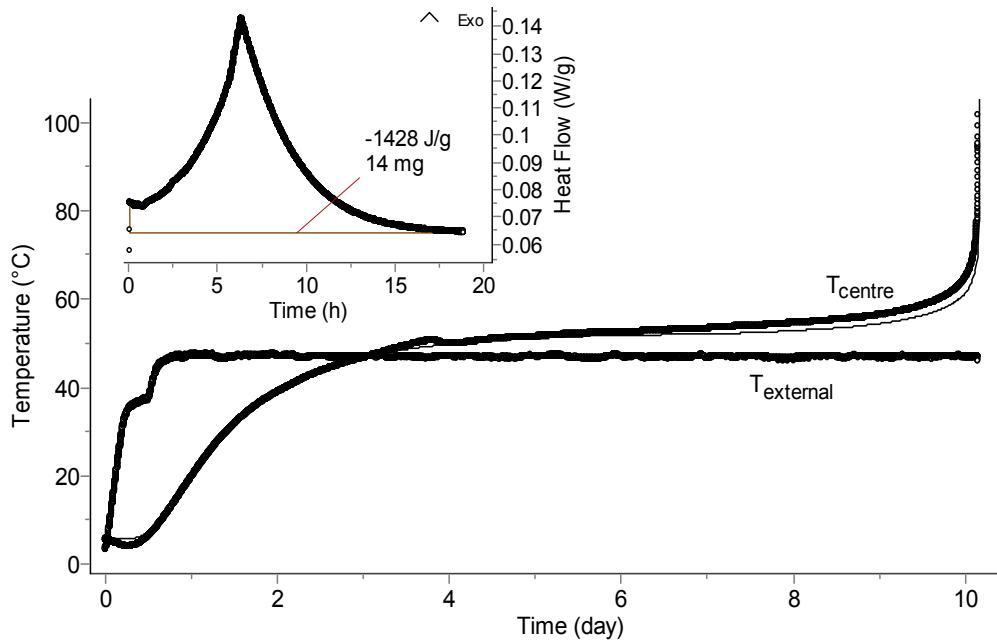*Figure 1: Experimental (symbols) vs. simulated (lines): temperature in the centre of 50 kg AIBN in a drum (filling height H = 46 cm and D = 46 cm) with corresponding thermal runaway event. DSC traces at 78°C of 14 mg of AIBN are presented in the inset.*
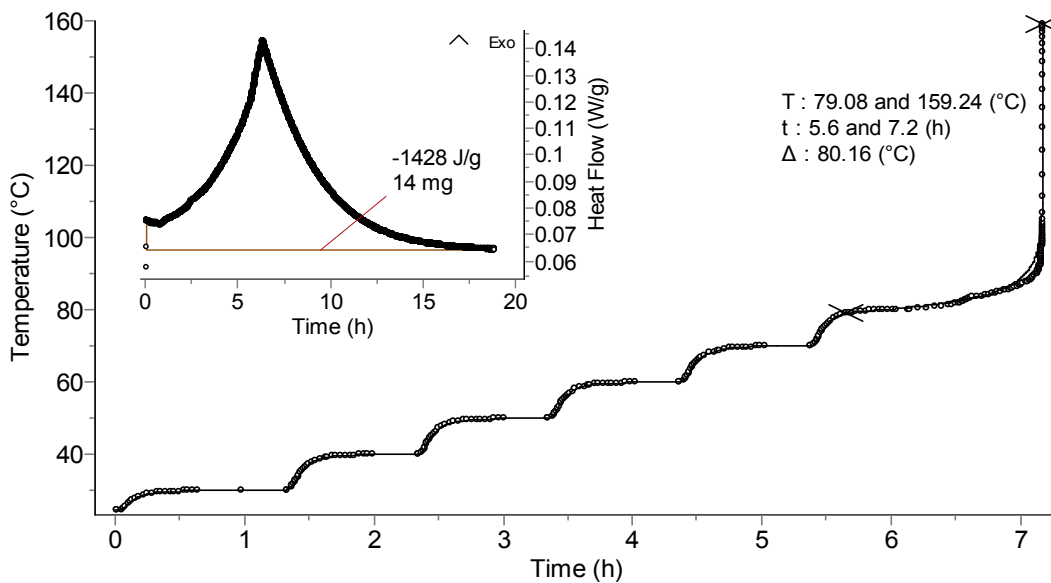

Figure 2: Experimental (symbols) vs. simulated (lines) DSC and ARC signals evaluated according merging approach. The experimental data depict the behavior of AIBN in isothermal (DSC) and HWS (ARC) modes.

The numerical estimation of the parameter C can be done by comparing the reaction progress α of the DSC signal (e.g. measured at 78°C for AIBN, Figure 1, inset) and the time of the runaway event in a large scale test (e.g. H1-test with 50 kg in a drum) with their simulated courses using the adequate expression for the heat balance (Eq. 8). In the simulation we applied the real temperature course of the ambient temperature. During the approximation of the C value, its increase or decrease results in shifting the runaway event (large scale test) towards longer or shorter times, respectively. Once the optimal value for C is determined, the activation energy $E(\alpha)$ and the term $A(\alpha)$ f(α) can be calculated as a function of the reaction progress α using Eqs. (9) and (12). The time to runaway in H.1 test can be then obtained by numerical integration using equations depending on the physical state of the material (solid state in case of AIBN).

The experiment which may be used for a simultaneous consideration (merging) with DSC data can be any experiment in which the temperature of the material is monitored: ARC, Dewar, H.4, H.1, cookoff and other large scale tests. The results of merging DSC with ARC data is presented in Figure 2. In both cases the experimental heat flow signal is perfectly simulated and other tests data are well fitted by simulated traces. The best fit was obtained for the value of $C = 2.79\text{E-}4$ and $2.7\text{E-}4$ mol J^{-1} by merging DSC with the H1-test (50 kg of AIBN in a drum) and the ARC data, respectively. Excluding the value of C which was dependent on the type of merging (with the H.1 or ARC tests) all other parameters used for the packaging and physical properties of AIBN are the same during the simulations presented in Figures 1 and 2. Our simulations based on kinetic parameters evaluated from DSC signals merged with the H1 test (Fig. 1) and the ARC data (Fig.2) give SADT values of 46.6 and 49.83°C, respectively. The final SADT value of AIBN which according to the UN Recommendations is the critical ambient temperature (°C) rounded to the next higher multiple of 5°C, amount therefore to 50°C for a package of 50 kg of AIBN.
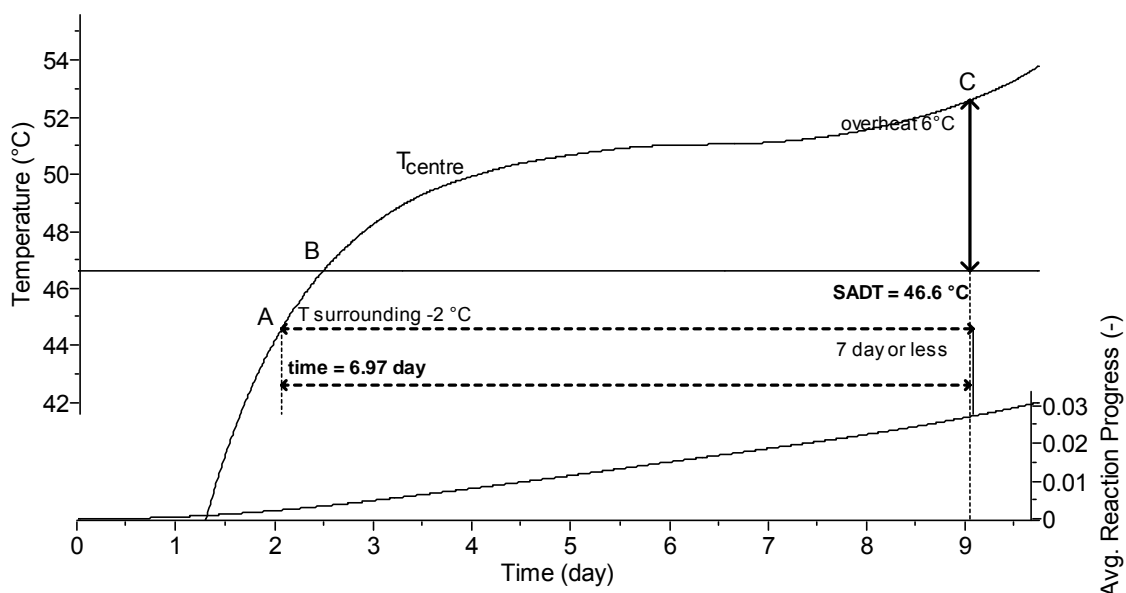

Figure 3: Simulation of the SADT for 50 kg of AIBN in a drum with filling height H = 46 cm and D = 46 cm. Our simulated SADT value according to the definition of the SADT (Test H.1) amounts to 46.6°C. Point (A) indicates the time when the packaging centre temperature reaches 2°C below the surrounding temperature (ca. 2.1 days). At point (B) (ca. 2.5 days) the sample reaches the surrounding temperature. The overheat of 6°C occurs after about 9.1 days (point C). At this time the average reaction progress of AIBN decomposition in the 50 kg package amounts to ca. 0.03 (3%) (bottom, right axis).

The SADT values of AIBN obtained in these simulations are in line with the SADT values already reported in other studies: Roduit at al. (2014, 2015), Malow at al. (2010) or Whitmore and Wilberforce (1993). Computed SADT values are additionally in very good agreement with the results of three large scale H.1-tests performed by BAM with reported SADT of 47°C, 48°C and > 49°C for 50, 20 and 5 kg, respectively (in this last experiment BAM performed two tests at 47 and 49°C, however the SADT criterion was not fulfilled at these temperatures).

The proposed new procedure, based on computing kinetic parameters from at least one large- and one small-scale test enables a considerable decrease of the amount of large scale-tests necessary for SADT determination. Since in our proposal the results evaluated from DSC data are combined with results gained in

additional tests, this new approach for SADT determination is potentially more accurate than those based on small-scale experiments and much less expensive and time consuming than those based on large-scale tests only. For merging mg- with kg-scale experiments, one can also use the experimental data collected with calorimeters such as C80 or TAM which are more sensitive than conventional DSC devices.

4. Conclusion

Presented results show that novel merging kinetic approach in which single DSC traces are linked with the single data obtained by another technique (ARC, or H.1 UN Test) allow the successful simulation of thermal hazard indicators such as SADT. The newly proposed merging approach, based on utilisation of the results from different experimental techniques, omits the limitations of particular experimental methods: (i) those of DSC in which the heat loss rate from the system is not measured and this important parameter is obtained by numerical heat balance only, and (ii) those of ARC or large scale tests which do not allow the precise evaluation of the second important parameter: the kinetics of the heat formation in the system. Since the limitations of these techniques are generally exclusive it seems to be advantageous to use their combination. In merging approach one can apply the results of single DSC experiment only and ARC data or the results of one large scale experiment such H.1. The advantage of merging approach lays in the fact that the results of the large-test in which required temperature rise is reached much below 7 days are also suitable for determining hazard indicators. The application of a newly proposed kinetic workflow may increase accuracy of simulations of SADT based on results collected in mg-scale and decrease the amount of ARC tests or expensive and time consuming experiments in kg-scale.

References

AKTS-Thermokinetics and AKTS-Thermal Safety Software, 2015, AKTS AG, TECHNOArk 1, Switzerland, www.akts.com

Brown M., Maciejewski M., Vyazovkin S., Nomen R., Sempere J., Burnham A., Opfermann J., Strey R., Anderson H.L., Kemmler A., Keuleers R., Janssens J., Dessseyn H.O., Li Chao-Rui, Tang Tong B., Roduit B., Malek J., Mitsuhashi T., 2000, Computational aspects of kinetic analysis. Part A: The ICTAC kinetics project – data, methods and results, Thermochim. Acta 355,125-143.

Friedman H.L,1963, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, J. Polym. Sci. Pol. Lett., C6, 183-195.

Malow M., Michael-Schulz H., Wehrstedt K.D., 2010, Evaluative comparison of two methods for SADT determination (UN H.1 and H.4), J. Loss Prevent. Proc., 23, 740-744.

Pérez-Maqueda L.A ,Criado , J.M., Sànchez-Jiménez P.E.,2006, Combined Kinetic Analysis of Solid-State Reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism, J. Phys. Chem., A110 ,12456-12462.

Roduit B., Hartmann M., Folly P., Sarbach A., Brodard P., Baltensperger R., 2015, Thermal decomposition of AIBN, Part B: Simulation of SADT value based on DSC results and large scale tests according to conventional and new kinetic merging approach, Thermochim. Acta, in print, doi:10.1016/j.tca.2015.06.014,

Roduit B., Hartmann M., Folly P., Sarbach A., Brodard P., Baltensperger R., 2014, Determination of thermal hazard from DSC measurements. Investigation of Self Accelerating Decomposition Temperature (SADT) of AIBN, J. Therm. Anal. Calorim., 117, 1017-1026.

Roduit B., Folly P., Berger B., Mathieu J., Sarbach A., Andres H, Ramin M., Vogelsanger B., 2008, Evaluating SADT by advanced kinetics-based simulation approach, J. Therm. Anal. Calorim., 93, 153-161.

Šesták J., Berggren G., 1971, Study of the kinetics of the mechanism of solid-state reactions at increasing temperatures, Thermochim. Acta, 3, 1-12.

Vyazovkin S., Modification of the integral isoconversional method to account for variation in the activation energy, 2001, J. Comput. Chem., 22, 178-183.

Vyazovkin S., Burnham A.K., Criado J.M., Pérez-Maqueda L.A., Popescu C., Sbirrazzuoli N., 2011, ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data, Thermochim. Acta, 520, 1-19.

Vyazovkin S., Chrissafis K., Di Lorenzo M.L., Koga N., Pijolat M., Roduit B., Sbirrazzuoli N., Suñol J.J., 2014, ICTAC Kinetic Committee recommendations for collecting experimental thermal analysis data for kinetic computations, Thermochim. Acta, 590, 1-23.

Whitmore M.W., Wilberforce J.K., 1993, Use of the accelerating rate calorimeter and the thermal activity monitor to estimate stability temperatures, J. Loss Prevent. Proc., 6, 95-101.