

# Consideration of Autocatalytic Behavior in Determination of Self Accelerating Decomposition Temperature

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## Abstract

When determining Self Accelerating Decomposition Temperatures (SADT) for shipment purposes, the kinetics of the decomposition reaction of the materials must be known. The simplified models assuming the first order decomposition kinetics are generally applied, however this traditional approach fails in correct SADT determination for autocatalytic and multistage overlapped reactions. For these cases a more universal, yet easily implemented, advanced method will be presented in which the detailed kinetic mechanism does not need to be known to correctly predict SADT. Using a series of DSC tests, AKTS-Thermokinetics software can extract kinetic parameters by the differential isoconversional approach. These kinetic parameters can then be applied for the prediction of the chemicals behavior in the kilogram scale. The results of the determination of the decomposition kinetics of azodicarbonamide is presented and applied to evaluate SADT for a 50 kg package. Results obtained by presented method will be compared to those determined by other methods.

## Introduction

The Self Accelerating Decomposition Temperature (SADT) of packaged materials is an important parameter that characterizes the thermal hazard possibility under transport conditions of self-reaction chemicals. Based on the value of the SADT, temperature control during shipment may be required in order to ensure safe transport.

The SADT, as defined by the United States SADT test [1], is the lowest ambient temperature at which the center of the material within the package heats to a temperature 6°C greater than the environmental temperature after a lapse of a seven days period or less. This period is measured from the time when the temperature in the center of the packaging reaches 2°C below the ambient temperature. The SADT is a measure of the combined effects of the ambient temperature, decomposition kinetics, package size, and the heat transfer properties of the substance and its packaging. When evaluating the SADT, the most important issue, however, is knowledge of the decomposition kinetics. Very often the simplified first order decomposition kinetic model is applied. When a decomposition reaction is multistage or autocatalytic, this simplified approach fails to correctly predict the SADT. Advanced Kinetics and Technology Solutions (AKTS) has developed Thermokinetics Software - Thermal Safety Version which allows the complex kinetics such as those exhibited by autocatalytic reactions to be effectively applied in calculations using a modest amount of calorimetric data. Applying AKTS-Thermokinetics software it is possible to extract kinetic parameters from heat flow data through a differential isoconversional approach. Using these kinetic parameters, the SADT of a chemical package can be easily calculated [2].

In order to demonstrate this approach, the SADT of a 50 kg package of azodicarbonamide will be simulated. The decomposition of azodicarbonamide is known to be an autocatalytic reaction and is ideal for illustrating the powerful approach used by AKTS Thermokinetics software.

## Obtaining Data Required for Kinetic Analysis

Six differential scanning calorimetry (DSC) experiments were run on a sample of azodicarbonamide. Four runs were performed at pre-programmed ramp rates of 0.25, 0.5, 1, and 2°C/min while the other two runs were performed isothermally at temperatures chosen based on results from the ramp tests (165 and 170°C).

From the DSC data the reaction progress,  $\alpha$ , at any level of conversion can be calculated as

$$\alpha = \frac{Q}{\Delta H_{rxn}} \quad (1)$$

where  $Q$  = accumulated heat at certain reaction progress,  $\alpha$  (J/g)  
 $\Delta H_{rxn}$  = total heat of reaction (J/g)

Similarly, the reaction rate,  $d\alpha/dt$ , can be calculated at any conversion as follows:

$$\frac{d\alpha}{dt} = \frac{\dot{Q}}{\Delta H_{rxn}} \quad (2)$$

where  $\dot{Q}$  = heat flow at considered reaction progress,  $\alpha$  (W/g)

### Extraction of Kinetic Parameters

Two main methods of the kinetic analysis of the experimental data are generally applied:

- (i) Model-fitting
- (ii) Isoconversional

Model-fitting methods are based on the assumption that specific reaction model (list of models see e.g. in [3]) describes the conversion dependence of the reaction rate therefore its determination is the prerequisite of the correct kinetic analysis. If the model is chosen incorrectly then the kinetic description of the process may be fully meaningless.

In isoconversional methods the value of the activation energy  $E$  and, in some extent, the pre-exponential factor  $A$  can be determined without assuming any specific reaction model. The I-st ICTAC Kinetic Project, dealing with the computational aspects of kinetic analysis [4], showed that application of both methods can result in correct determination of the kinetic parameters only when the experimental data obtained by few heating rates (non-isothermal temperature program) or temperatures (isothermal experiments) are considered. The recent ICTAC Kinetics Committee Recommendations indicate that the isoconversional methods should be applied as a second stage (after collection of the good quality data) of the kinetic analysis. Especially for the kinetic predictions, when only the dependence of  $E$  and  $A$  on the reaction progress has to be known, the evaluation of the form of the reaction model is not necessary [3].

The differential isoconversional method applied in AKTS Thermokinetics software is based on the Arrhenius equation provided in Equation 3.

$$k(T) = A \cdot \exp\left(-\frac{E}{R \cdot T(t)}\right) \quad (3)$$

where  $A$  = pre-exponential factor (1/s)  
 $E$  = activation energy (kJ/mol)  
 $T$  = temperature (K)  
 $t$  = time (s)

The differential isoconversional method assumes that the reaction rate at constant reaction progress is only a function of temperature and that the temperature dependence is contained only in the Arrhenius expression. The following equation results:

$$\frac{d\alpha}{dt} = A(\alpha) \cdot \exp\left(-\frac{E(\alpha)}{R \cdot T(t)}\right) \cdot f(\alpha) \quad (4)$$

where  $\alpha$  = reaction progress  
 $f(\alpha)$  = kinetic model function

To simplify Equation 4, one can define an apparent pre-exponential factor  $A'$  as the product of the model function and the pre-exponential factor. Equation 5 results:

$$\frac{d\alpha}{dt} = A'(\alpha) \cdot \exp\left(-\frac{E(\alpha)}{R \cdot T(t)}\right) \quad (5)$$

Taking the natural logarithm gives

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A'(\alpha)) - \frac{E(\alpha)}{R \cdot T(t)} \quad (6)$$

The logarithm of the reaction rate when plotted against inverse temperature,  $1/T$ , exhibits a linear relationship ( $y = mx + b$ ) with slope  $m = -E/R$  and intercept  $b = \ln(A')$ .

Application of this technique to the six DSC runs obtained for azodicarbonamide results in the following dependence of the apparent pre-exponential factor and the activation energy on the reaction progress  $\alpha$ :

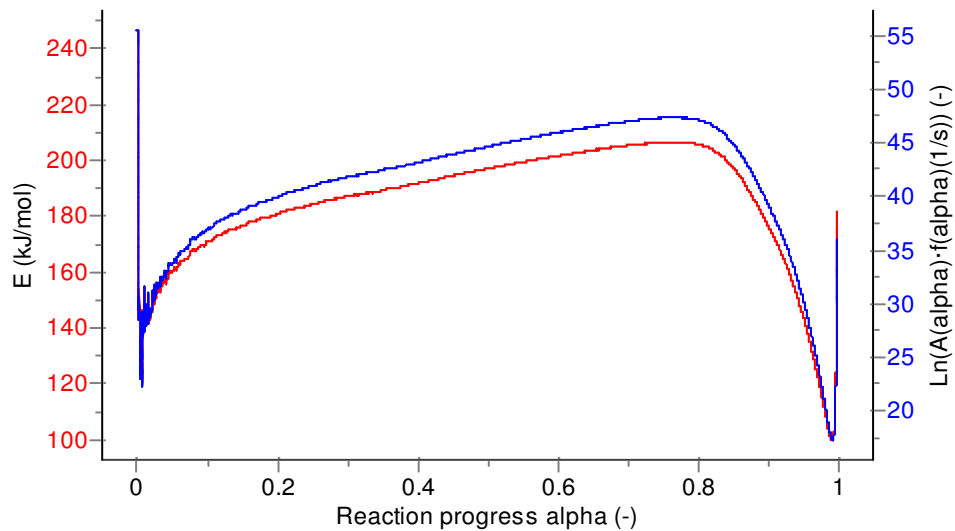


Figure 3 Apparent Activation Energy and Pre-exponential Factor as a Function of Reaction Progress

Using the conversion dependent kinetic parameters, the reaction progress and reaction rate can be calculated for comparison to the experimental signals by numerical integration

$$t_a = \int_0^t dt = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{A'(\alpha) \exp\left(-\frac{E(\alpha)}{RT(t)}\right)} \quad (7)$$

with  $T(t) = T_0 + \beta \cdot t$  where  $\beta$  corresponds to the heating rate applied in the DSC experiment. The results of such comparison of the dependence of the reaction progress and reaction rate on the temperature (ramp experiments) and time (isothermal runs)

are displayed in Figures 4-7. The experimental traces are displayed in color, the calculated dependences are displayed in black.

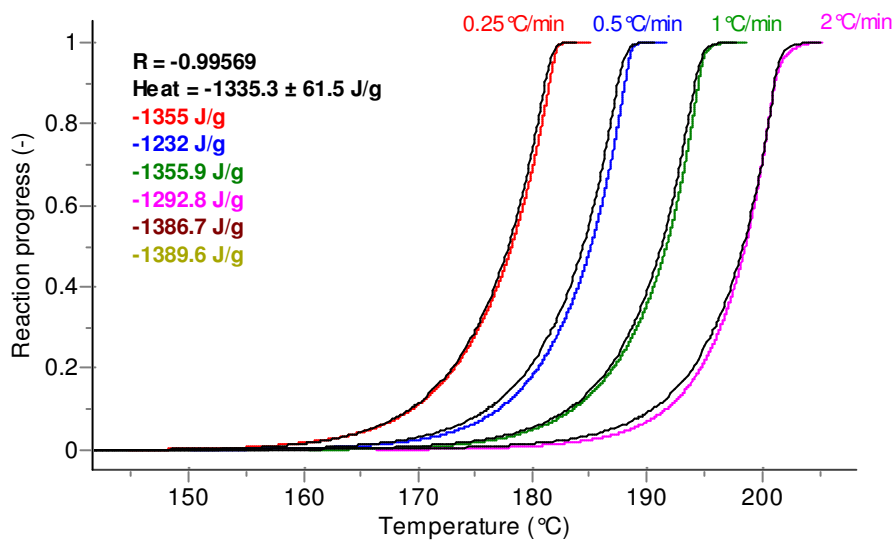


Figure 4 Reaction Progress as a Function of Temperature for DSC Ramp Experiments

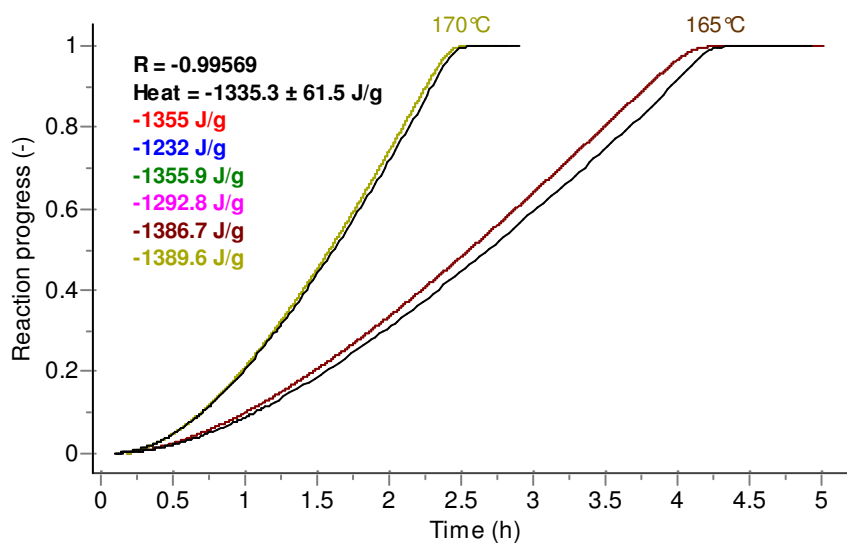


Figure 5 Reaction Progress as a Function of Time for DSC Isothermal Experiments

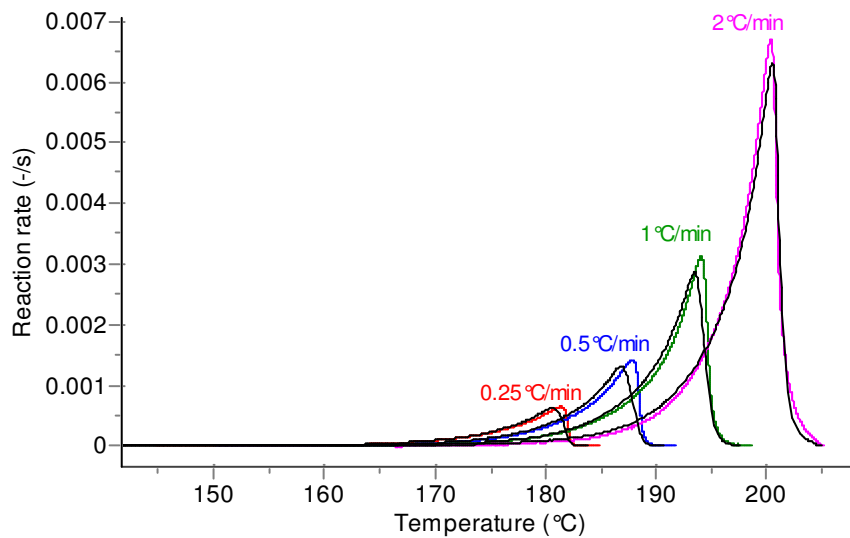


Figure 6 Reaction Rate as a Function of Temperature for DSC Ramp Experiments

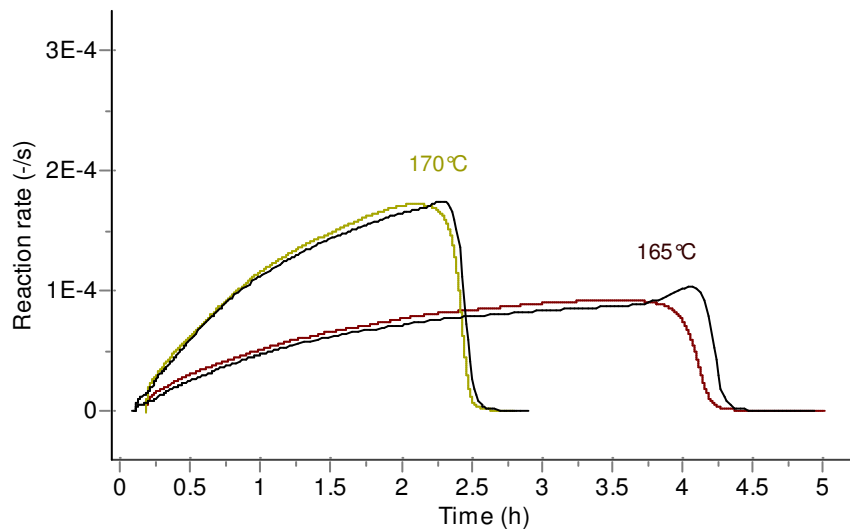


Figure 7 Reaction Rate as a Function of Time for DSC Isothermal Experiments

Figures 4 through 7 show that very good agreement exists between the measured and the calculated results.

### Applying Conversion Dependent Kinetic Parameters to Determine SADT

During the DSC experiments carried out in mg-scale all heat generated during the exothermic reaction can be released from the sample. Due to the small sample sizes the heat balance may not be taken into account in thermoanalytical experiments. It is commonly assumed that the heat accumulation in the sample is negligible because the total amount of heat evolved or consumed during reaction is fully exchanged with an environment, therefore it does not influence the sample temperature in a noticeable extent. However, for larger sample masses during exothermal reactions, the rate of the evolved reaction heat may be greater than the rate of the heat exchanged with an environment what will result in the heat accumulation in the sample increasing in uncontrolled way its temperature. Detailed discussion of this problem is described e.g. in [5] and is out of scope of the present considerations. However, if the self-heating problem occurs, the expression for sample heating rate commonly applied in DSC experiments and in kinetic analysis

$$\frac{dT}{dt} = \beta \quad (8)$$

with respectively  $\beta > 0$  and  $\beta = 0$  for the nonisothermal and isothermal conditions, has to be replaced by a more complicated expression considering the heat balance [5]:

$$\frac{dT}{dt} = \frac{\lambda}{\rho C_p} \left( \frac{\partial^2 T}{\partial r^2} + \frac{g}{r} \frac{\partial T}{\partial r} \right) + \frac{-\Delta H_r}{C_p} \frac{d\alpha}{dt} \quad (9)$$

in which the  $C_p$ ,  $\lambda$ ,  $\rho$ ,  $g$  and  $r$  mean: specific heat, thermal conductivity, density, a geometry factor ( $g=0$  for the infinite plate,  $g=1$  for the infinite cylinder and  $g=2$  for the sphere (as applied in the current study)) and container radius, respectively. The differential isoconversional method (eq.6) can now be applied to accurately predict not only the reaction rate and progress given by the DSC traces in mg-scale but in addition for kilo-scale under any thermal conditions, where  $dT/dt$  and  $T(t)$  are determined by applying appropriate heat balance equation (eq.9). Eq. 9 indicates that the change of the sample temperature for larger sample masses  $dT/dt$  depends among others on the reaction rate  $d\alpha/dt$  and on the container radius  $r$  as well. The temperature of the sample will not be the same in the centre or at the surface of a package and in addition it will depend on its size i.e. on the  $r$  value. In order to determine the SADT of a 50 kg package of azodicarbonamide, the convective heat transfer from the package (the boundary conditions) as well as the conductive heat transfer within the package can now be introduced into calculating procedure. AKTS uses finite element analysis so that the temperature at any location within the package can be predicted at any given time. For the 50 kg package of azodicarbonamide, the following packaging and sample parameters were applied:

$\rho$	=	density (1650 kg/m <sup>3</sup> )
$c_p$	=	specific heat (1.05 J/g/K)
$\lambda$	=	thermal conductivity (0.1 W/m/K)
$h$	=	heat transfer coefficient (5 W/m <sup>2</sup> /K)

Using the criteria set forth by the United States SADT test, the resulting temperature profile (the blue curve represents the surface of the package while the green curve represents the center of the package) for the 50 kg package of azodicarbonamide is provided in Figures 8. AKTS Thermokinetics software predicts an SADT value of 114°C~118°C (depending on the thermal conductivity) which is in very good agreement with literature values [6].

The calculations of the dependence of SADT values of azodicarbonamide on package mass and thermal conductivity  $\lambda$  (usually unknown) are submitted in Tab.1.

Tab.1 Dependence of SADT (°C) of azodicarbonamide on equivalent thermal conductivity  $\lambda_{s,eq}$  and the sample mass.

$\lambda_{s,eq}$ W/(m·K)	SADT (°C)						
	Sample mass (kg)						
	5 kg	10 kg	25 kg	50 kg	100 kg	250 kg	500 kg
0.1	118 °C	117 °C	115 °C	114 °C	113 °C	112 °C	111 °C
1	120 °C	119 °C	118 °C	118 °C	117 °C	116 °C	115 °C

Presented results indicate the impact of the sample mass on the SADT values. The one-fold increase of the mass from 5 to 50 kg and from 50 to 500 kg results in the decrease of the SADT value (with  $\lambda = 0.1$  W/m/K) from 118°C to 114°C and 114°C to 111°C, respectively. The largest the mass the higher is the accumulation of the heat in the sample. The change of SADT due to the change of the thermal conductivity value underlines importance of this parameter; the introduction of its incorrect value during the simulations can change the simulation of thermal behavior of the investigated materials.

The simulated SADT values of azodicarbonamide being in very good agreement with those already determined [6] indicate the (i) correct collection of the experimental DSC data, (ii) accurate procedure of the determination of kinetic parameters and (iii) precise evaluation of the thermal safety behavior implemented in AKTS-Thermokinetics software.

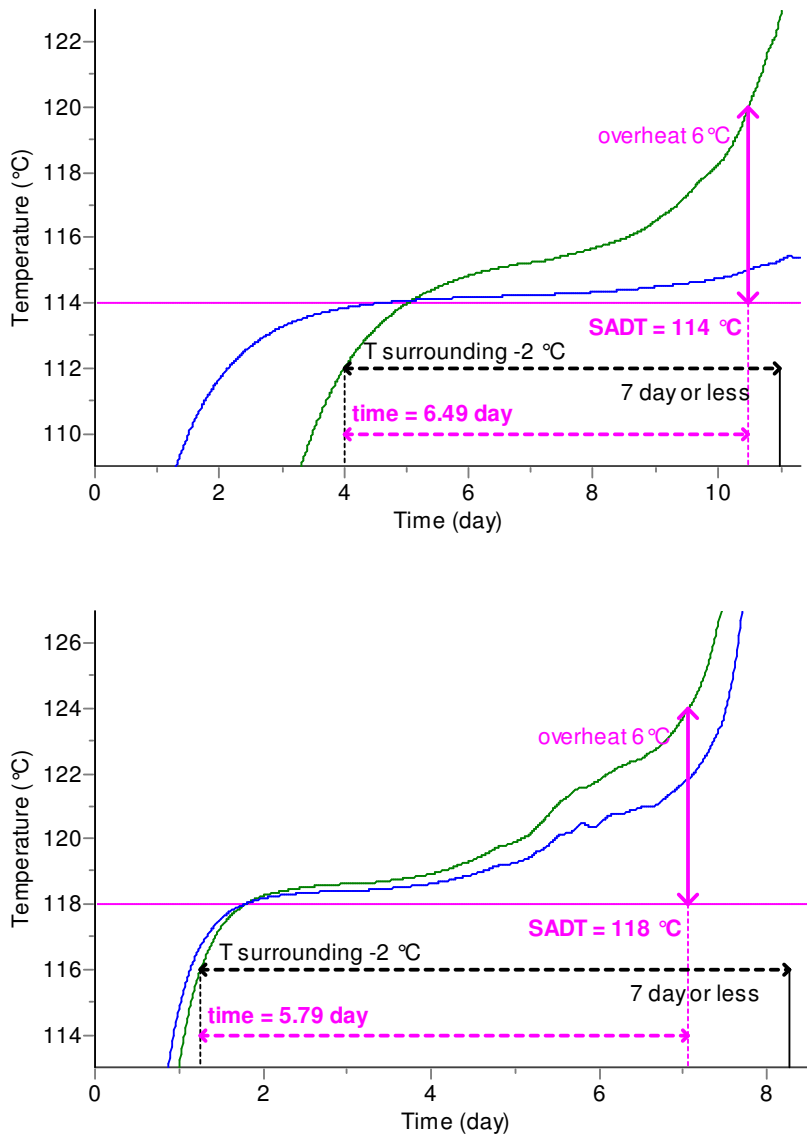


Figure 8 SADT Results for 50 kg Package of azodicarbonamide with  $\lambda = 0.1$  W/m/K (top) and  $\lambda = 1$  W/m/K (bottom), respectively.

### References

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