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An Alternative Way to Determine the Self-Accelerating Decomposition Temperature by Using the Adiabatic Heat-Pressure Accumulation Test

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In the paper presented investigations concerning the measuring sensibility of the adiabatic heat-pressure accumulation test are performed by using a well-known decomposition kinetic of a reference substance. The accuracy of the method has been proven by comparison with literature values for different substances.
In summary, the Self-Accelerating Decomposition Temperature (hereinafter SADT) values obtained from the adiabatic heat-pressure accumulation are consistent with those of other methods and literature values. Therefore, the adiabatic heat-pressure accumulation can be used for the determination of the SADT.

1. Introduction

According to the UN Recommendation on the Transport of Dangerous Goods (hereinafter UN Transport Regulation), the self-reactive behaviour is an important substance property when dealing with transport and safe handling. The SADT is the main parameter for classification according to the mentioned Regulations. This temperature describes the ambient temperature at which a substance in the package in which it is transported can undergo a critical self-heating. There exist two threshold values:

- SADT≤ 75 °C: for classification into class 4 division 4.1 as self-reactive substance
- SADT≤ 55 °C: for classification into class 4 division 4.1 as self-reactive substances with temperature control

Four different methods are described in the UN Transport Regulation and summarised in Table 1.

Table 1: Short overview of the tests defined for the determination of the SADT according to the UN Transport Regulation

Test code	Name of test
H.1	United States SADT test
H.2	Adiabatic storage test
H.3	Isothermal storage test
H.4	Heat accumulation storage test

This study will present the well-known and accepted experimental setup according to Grewer and Klais (1987) and VDI-Guideline 2263 Page 1 (Y) also as a tool to determine the SADT as well. For more than 20 years, Hoechst AG and companies that emerged after its realignment have been using Dewar tests in a pressure autoclave and with adiabatic shielding for the determination of e.g. ΔT_{ad}, ADT24 or the heat generation rate of a decomposition. The basic test set-up is similar to that of the UN test H.2. Compared to UN test H.2 the method presented here displays the following advantages:

- Only a small amount of the sample (normally approx. 100 g) is needed.
- The test is non time-consuming compared to the tests H.1 and H.4 (for example).
- Is provides additional information regarding the pressure build-up during storage or decomposition
- It is possible to investigate pressurised systems or systems containing volatile compounds with high vapour pressure / low boiling point.

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2. Testing in the closed autoclave

The test set-up present here for determination of the SADT is based on a test setup according to Grewer and Klais (1987).

The test setup consists of a pressure vessel with a volume of approx. 0.75 L. In this autoclave, a Dewar vessel with a capacity of approximately 0.2 L is placed. The Dewar-vessel is thermally isolated from its surroundings by a double walled vacuum jacket with a reflective coating. The autoclave is closed, put into an oven and heated up. After a reaction starts the temperature of the oven is regulated to track the sample temperature. Therefore reactions or decompositions above the start temperature can be investigated under adiabatic conditions. The sample temperature is measured with a thermocouple, which is placed in the centre of the sample and surrounded by a glass cover; hence the sample is only in contact with glass. Additionally, the pressure in the headspace is measured and recorded.

The time resolved courses of the temperature and the pressure during the experiment are recorded.

From the course of the temperature dependent on time, the temperature rise rate can be derived. For the calculation of temperature rise rate, the Phi-factor of the complete measuring system is taken into account.

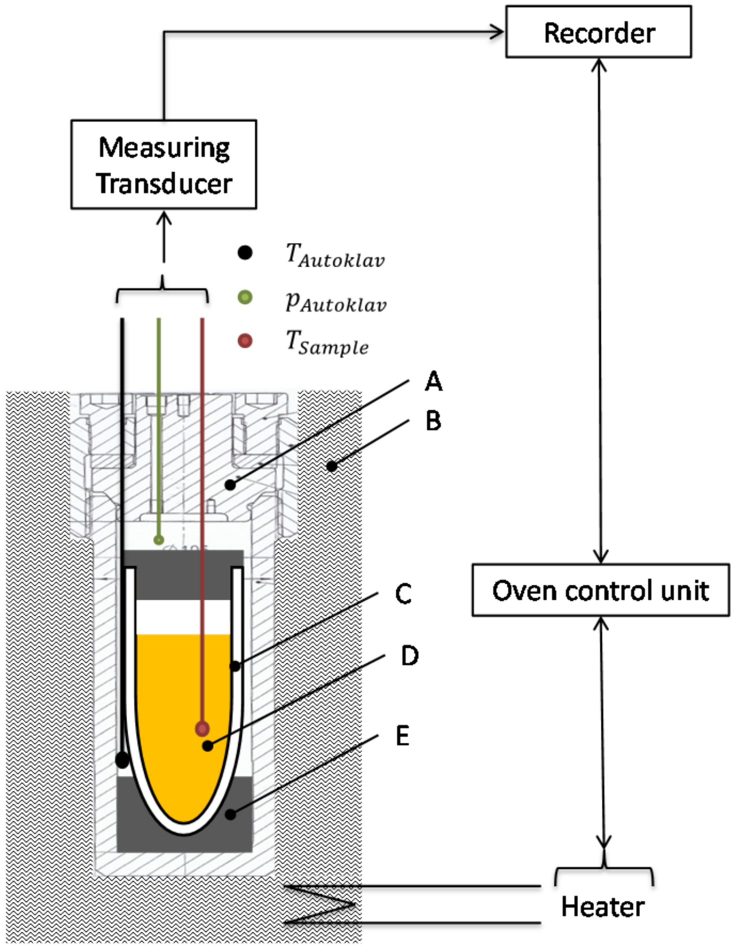


Figure 1: Schematic drawing of the test set-up, with A) autoclave, B) block furnace, C) Dewar vessel, D) test item, E) insulation material

3. Experimental investigations

3.1 Aim of the experimental investigations

There are normally two ways of performing experiments in the described set-up. One possible way is to store the sample at a defined temperature (e.g. 75 °C) and start the adiabatic tracking when a thermal runaway is detected by a rise of the sample temperature. The second possible way is to start at a lower storage temperature and use a slow heating-up rate to detect the onset of the thermal runaway and start the adiabatic tracking. The different thermal pre-treatments of the sample before a significant exothermic reaction is detected by the described operation modes, raises the question of whether these thermal pre-treatments have any effect on the determination of the SADT.

Another question to be answered concerns the regulation of the oven temperature during the adiabatic tracking, since it affects the thermal inertia of the adiabatic system. Obviously, an oven temperature too low compared to that of the sample will lead to a dramatic heat loss and therefore to an underestimation or even a cooling of the reaction system. On the contrary, an oven temperature slightly above that of the sample during the tracking leads to an additional heat input.

3.2 Characterisation of the reaction system

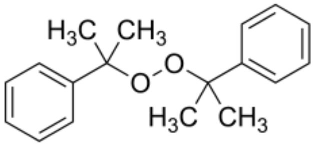
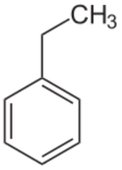
The reaction system used in the present study is the decomposition reaction of Dicumyl peroxide (DCPO) in the solvent Ethylbenzene (EB). The used ratio of DCPO to EB is 40/60 wt.-%. The chemicals used for the experiments are summarized in Table 2.

According to the UN Transport Regulation Dicumyl peroxide is classified as an organic peroxide in class 5, divison 5.2 type F (UN no. 3110) i.e. as “thermally unstable substance which may undergo exothermic self-accelerating decomposition” (UN Transport Regulation, 2013). Dicumyl peroxide can be transported with a maximum quantity per portable tank of 2000 kg. No control or emergency temperature is required.

The decomposition kinetic of DCPO is part of various articles, like Marco et. al. (2000), Wu et. al. (2009), Di Somma et. al. (2011). This reaction system was mainly chosen because of its decomposition kinetic, which can be described by a 0-order reaction when using the Arrhenius-equation (gl.1). This results in a linear function, when plotting the temperature rise rate as a function of the inverse absolute temperature.

$$\mathrm{dT}/_{dt} \sim Q_0 \times \mathrm{e}^{-\frac{E}{R\times T}} \tag{1}$$

Table 2: Characterisation of the chemicals used for characterisation of the heat pressure accumulation test

Name of the substance	CAS-No.	Molecular Formula	Supplier	Purity
Dicumyl Peroxide (DCPO)	80-43-3		Sigma Aldrich	> 98 %
Ethyl benzene (EB)	100-41-4		Merck	> 99

3.3 Storage Temperature

In order to determine if the differences regarding the starting temperature or the use of a temperature ramp have any influence on the decomposition kinetic and the SADT of the system, different storage temperatures were chosen.

At first, experiments starting at a temperature of 85 °C were performed. Afterwards, experiments were performed at a lower storage temperature of and 80 °C.

In order to determine the effect of the ramp on the decomposition of the reaction, experiments were performed starting at a storage temperature of 40 °C and using a heat-up ramp of 0.5 K/h.

With the purpose of checking the effect of too high an oven temperature during the adiabatic tracking, some of the tests at a storage temperature of 80 °C were performed setting a difference of +1 K between sample and oven temperature. The experiments performed are summarised in Table 3.

Table 3: Short overview of the defined tests for the determination of the SADT according to UN Transport Regulation

Test no,.	Starting temperature	Adiabtic tracking mode	Thermal pre-treatment by using the heat-up ramp
1	85	adiabatic	No
2	80	adiabatic	No
3	80	oven temperature in tracking method = Sample Temperature + 1 K	No
4	40	adiabatic	yes (0.5 K/h)

3.4 Results

The plots of the temperature dependent on the time of the above mentioned experiments are shown in Figure 1.

Based on the measured temperature courses the first derivative of the temperature dependent on the time ("temperature rise rate") is calculated and plotted as a function of the reciprocal, absolute temperature. This temperature rise rate can be plotted in a logarithmic graph as shown in Figure 2. When using a zero order kinetic (see (Eq1)), the slope of the temperature rise rate can be easily used to calculate the activation energy EA and the y-Axis intercept results in the Arrhenius pre-factor Q0. In Table 4, the results of the five tests are summarised.

The plot of the temperature rise rates as function of the temperature shows that the starting temperature, the thermal pre-treatment by the temperature ramp as well as a too high oven temperature during the adiabatic tracking have no major influence on the kinetic. Therefore in all performed tests the activation energy can be calculated to 137 kJ/mol ± 4 kJ/mol (see also Table 4). The values obtained for the kinetic parameters therefore stay in a very good accordance with the literature values, which are declared to be between 130 kJ/mol and 150 kJ/mol, when assuming a zero-order kinetic.

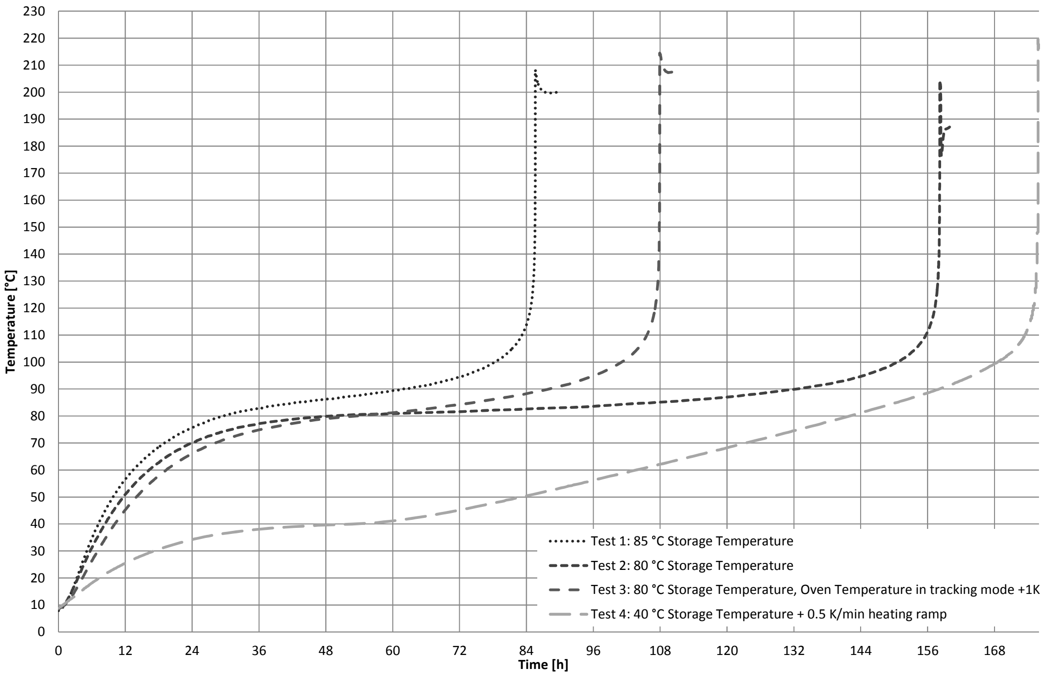


Figure 2: Courses of the temperature dependent on the measuring time for all four experiments.

Table 4: Short overview of the results of the tests performed for the determination of the SADT according to the UN Transport Regulation

Test no.	Starting temperature [°C]	Activation energy [kJ/mol]
1	85	137
2	80	142
3	80	132
4	40	139

The determination of the SADT is performed analogous to the method described in the UN Transport Regulation test H.2 in a Semenoff diagram by plotting the heat production rate and the linear heat loss of the package as a function of the temperature. The slope of the linear function of the package heat loss is defined as the heat loss per unit of mass. This value is specific for every package. Based on the defined or calculated heat loss term per unit mass (unit: mW/(kg•K)) of the package, a straight line is fitted tangential to the heat production rate of the reaction. The corresponding temperature of the tangent point describes the equilibrium temperature of this system. The intersection of the straight line with the x-Axis (Temperature axis) is the SADT and normally rounded up to the next multiple of 5. For comparison of the results, it is only rounded to an accuracy of 1 K, see Figure 4.

Table 5: Calculated SADT of the performed test by using heat loss terms as tabled in the UN transport regulations….

Test no.	Storage temperature [°C]	SADT for 500 L IBC, type 31 HA1, heat loss: 51 mW/(kg•K) [°C]	SADT for 50 L package, type 1A1, heat loss: 63 mW/(kg•K) [°C]	SADT for a 400 mL Dewar, UN Test H.4, heat loss: 100 mW/(kg•K) [°C]
1	85	86	87	91
2	80	87	89	93
3	80	85	87	91
4	40	88	90	93

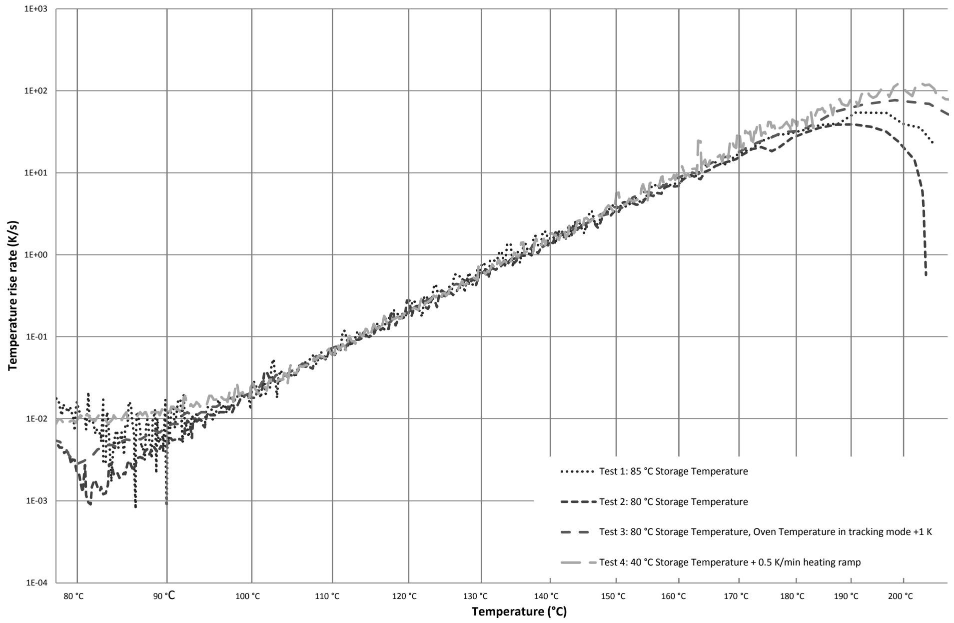


Figure 3: Temperature rise rate as a function of the reciprocal, absolute temperature for all four experiments. For the graphical representation the reciprocal, absolute temperature values of the x-axis are replaced by the corresponding temperatures in degrees Celsius.

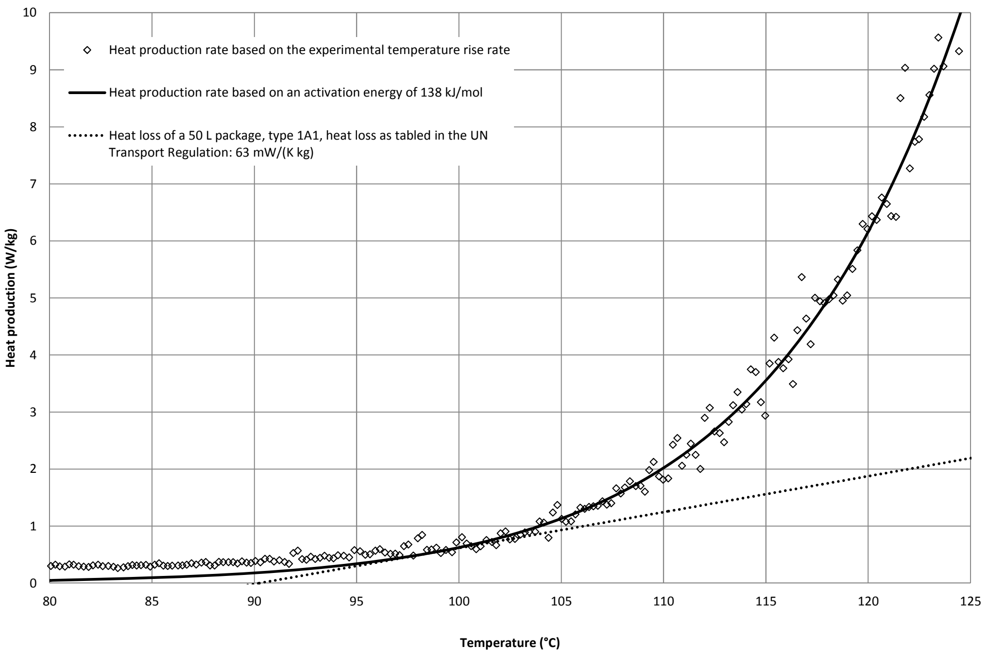


Figure 4: Exemplary determination of the SADT in the Semenoff plot. The heat production rate is calculated by using a heat capacity of the reaction system of 1900 J/(kg•K).

4. Discussion of the results

On the basis of the test results of the adiabatic tests performed it first can be stated, that the obtained decomposition kinetic stays in a very good accordance with the literature values. The used simple Phi-Factor correction by using a constant heat capacity therefore seemed to be applicable.

For the investigated system a SADT rounded up to the next multiple of 5 of 90 °C for a 50 L package (UN code 1A1) can be stated. This SADT value is not influenced by the storage temperature, the thermal pre-treatment of the system or a slightly too high oven temperature during the adiabatic tracking mode.

For a 400 mL Dewar vessel, as used in the UN test H.4 with an assumed heat loss of 100 mW/(kg•K), a SADT of approx. 92 °C is calculated. This means that at 90 °C in the UN test H.4 no significant heat production of the reaction system should be observed, meaning no self-accelerating decomposition. Whereas when storing at 95 °C, a heat production should be observed, meaning that there is a self-accelerating decomposition.

This repeatability of the activation energy and the SADT indicates that the presented adiabatic heat pressure accumulation test is sensitive and stable with respect to the parameters discussed. Therefore the heat pressure accumulation test can be used as an alternative method for the determination of the SADT and classification purposes according to UN Transport Regulation.

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