

Evaluation of the validity of the UN SADT H.4 test for solid organic peroxides and self-reactive substances

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Received 14 May 2004; received in revised form 13 September 2004; accepted 13 September 2004

Available online 8 December 2004

Abstract

Many self-accelerating decomposition temperatures (SADTs) of solid organic peroxides and self-reactive substances have been determined with the UN test method H.4, which is a scaled down test in a small Dewar vessel. For solid organic peroxides and solid self-reactive substances Fierz has questioned this procedure in a recent paper. Fierz concluded that the Dewar test results should not be extrapolated to beyond 81 packages, owing to the thermal insulation value of solids. On the other hand, long term experience with the test, with a great variety of solid organic peroxides and self-reactive substances show about equal critical temperatures in the small Dewar vessel and on 50 kg scale. In the present work, we first checked, by numerical simulations, the Dewar scale versus the larger scale, in a way comparable with Fierz' method: both scales are simulated by spheres, consisting of a number of annular layers, for the large scale the usual external heat loss term is used but for the small scale the outside heat transfer is strongly limited. The outcome of these simulations, covering a variety of physical parameters, supports the concerns expressed by Fierz. After this, we performed accurate cooling and heating experiments with solid organic peroxide in the usual Dewar vessel, provided with a large set of thermocouples. The results of these experiments showed that the simulation model for the Dewar vessel has to be changed from a spherical analogue to a short cylinder of solid material with heat exchange mainly via its top ($U_{\text{top}} \sim 3.5 \text{ W}/(\text{m}^2 \text{ K})$), overall heat transfer coefficient) and some heat exchange ($U_{\text{side}} \sim 0.29 \text{ W}/(\text{m}^2 \text{ K})$) through its cylindrical and bottom part. With this “modified cylinder” model (being neither an infinitely long cylinder nor a slab) of the Dewar vessel, we found that the UN method H.4 enables an accurate prediction of the SADT, with small deviations of $0 \pm 2.5 \text{ }^\circ\text{C}$. Further, by performing a truly three-dimensional (3D) finite element calculation in FEMLAB, the new heat characteristics of the Dewar vessel as well as a 50 kg package of dilauroyl peroxide, a solid organic peroxide, were checked. The outcome was compared with the critical ambient temperatures known for various package sizes, which agreed well.

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Keywords: SADT of solids; Transport regulations; UN H.4 test (HAST); Numerical simulations; Scale-up procedure

1. Introduction

1.1. Determination of the Self-Accelerating Decomposition Temperature (SADT) by UN tests

The UN has published recommendations concerning the safe transport of dangerous goods in order to avoid incidents

[1]. Specific testing schemes are described there, in order to achieve the identification and classification of dangerous goods of different classes and divisions. One safety parameter is the Self-Accelerating Decomposition Temperature. The UN manual [2] recommends several test methods for the determination of the SADT. These tests are numbered from H.1 to H.4. The *H.1 test*, also called the US-SADT test, is a full-scale test. That means that volumes up to 220 l may be tested by this method. The temperature of the substance as well as the surrounding temperature in the test chamber is measured.

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Nomenclature

A	area exposed to cooling or heating (m^2)
c	dimensionless concentration (auto-catalysis theory)
c_p	specific heat at constant pressure ($\text{J}/(\text{kg K})$)
conv	conversion
D	diameter (m)
E	energy of activation (kJ/mol)
H	height (m)
HPR	heat production rate (equal to q) (W/kg)
k_a	reaction rate constant (first order), for auto-catalytical reaction (s^{-1})
k_i	reaction rate constant (first order), for initiation (s^{-1})
m	mass (kg)
n	order of reaction
q	heat production rate (W/kg)
r	radius (m)
R	gas constant = $8.314 \text{ J}/(\text{g mol K})$
t	time (s)
T	temperature (K or $^{\circ}\text{C}$)
U	overall heat transfer coefficient ($\text{W}/(\text{m}^2 \text{ K})$)
V	volume (m^3)

Greek letters

α	conversion
β	acceleration of reaction rate due to auto-catalysis, $\beta = k_i/k_a$
Δ	difference, usually in ΔT , temperature difference
λ	heat (or: thermal) conductivity ($\text{W}/(\text{m K})$)
ρ	density (kg/m^3)

Subscripts

ad	adiabatic, usually in ΔT_{ad} , adiabatic temperature rise
amb	ambient
cr	critical
eff	effective
max	maximum
non-sph	non-spherical
sph	spherical
0	at the start
1	in scale-up problems: refers to the smaller scale
2	in scale-up problems: refers to the larger scale
1/2	halving period, usually in $t_{1/2}$, half-life time of temperature equilibration

If, within 7 days from the start of the storage time (the time at which the sample temperature reaches a temperature of 2 K below the test chamber temperature), a temperature increase of at least 6 K is measured, the SADT for that substance is

reached. In general, a temperature increment of 5 K is sufficient for the determination of the SADT. As the packaging forms an essential part of this method, the test substance and the packaging should represent the sample intended for commercial use. Besides, the high costs the potential reaction hazards for these large amounts of substance should be taken into account. Therefore, this method is not very popular and not commonly used in practice. Nevertheless the results obtained are most precise because of the one-to-one scale testing.

The H.2 (Adiabatic storage test) and the H.3 (Isothermal storage test) are also test procedures recommended by the UN. As these are not of main interest here they will not be discussed in detail.

But by far the most popular method is the *H.4 test*, the Heat Accumulation Storage Test (HAST), which is also called the BAM–Dewar test. Briefly explained, a small (usually 500 cm^3) Dewar vessel is filled with 400 cm^3 of the substance to be tested. The Dewar is closed with an appropriate closure system and heated to the desired storage temperature in a suitable test chamber. The test criteria for the determination of the SADT are comparable to those in the H.1 test. The pivotal point is that the heat loss of the Dewar should be representative of the package filled with the substance.

1.2. Recent comments on the UN SADT H.4 test

In an article by Fierz [3], the validity and limitations of the UN H.4 test for solid materials were discussed. By the approach taken by Fierz, the H.4 test seems to be valid up to approximately 8 l of a solid organic peroxide or self-reactive substance. However, practical measurements performed in the past showed that on the average the measured SADTs determined in a 0.5 l Dewar vessel and at 50 kg scale did not differ, which implies that the H.4 test is at least valid for packages of $\leq 50 \text{ kg}$. Malow, Krause and Wehrstedt commented recently upon the concerns of Fierz [4] and the response of Fierz is given in [5].

Table 1 shows the comparison of the experimental results obtained by the two test methods. This table is taken from [4] and was slightly modified. For the substances listed the data show nice agreement. The temperature differences are in the order of about 5 K (to both sides), which is the typical temperature increment for the H.4 test.

2. Conditions for having SADT similarity between two scales, for liquids

The fate of a self-reactive mass is determined by the heat balance between heat production due to decomposition and cooling by the ambient. This balance is critical if the thermal condition is on the borderline between sub-critical (eventually the mass cools) and super-critical (eventually the mass shows a thermal runaway). In practice, an easier criterion for criticality can be used, such as in the UN SADT test.

Table 1
Comparison of test results of the UN tests H.1 and H.4 for solids and pastes

Substance	Test H.1 (US-SADT)			Test H.4 (Heat accumulation storage test)				Remarks
	Sample mass in kg	Packaging	SADT (°C)	Sample mass in kg	Dewar heat loss in mW/(kg K)	Half-time of cooling (H ₂ O) $t_{1/2}$ in hrs	SADT (°C)	
Di-(4- <i>tert</i> -butylcyclohexyl)-peroxydicarbonate	43	1G	40	0.19	79	10.2	45 ^a	UN Manual
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (66%)	30	1G (501)	50	0.25	58	13.9	45	UN Manual
Didecanoyl peroxide, 97%	45.4		35	0.17	75	10.7	40	Technical pure
2,4-Dichlorobenzoyl peroxide, 50% in dibutylphthalate (as a paste)	15.9–34		43	0.535	75	10.7	40	
Dibenzoyl peroxide, 50% in tricresylphosphate (as a paste)	15.9–34		54	0.50	75	10.7	60	50% in a Phthalic acid ester
Dilauroyl peroxide	15.9–34		49	0.25	80	10.0	45	
2,2'-azodiiso-Butyronitrile (AIBN)	50		50	0.18	62	13	50	UN Manual; Whitmore et al. [6]

^a Note that the result of the product reported under test H.4 in [1], is valid for recrystallized material only.

Similarity between two scales is possible for liquids, as long there is sufficient internal heat exchange to consider the liquid as one thermally homogeneous mass, subjected to external cooling. This thermal process is only characterised by two parameters: the ratio of volume to area, V/A , and the external heat transfer coefficient, U . The equation for the heat balance of a mass reads, for the liquid case:

$$c_p \frac{dT}{dt} = q_{T=\infty} \exp\left(-\frac{E}{RT}\right) - \frac{UA}{\rho V}(T - T_0) \quad (1)$$

The solution in the form $T=f(t)$ for equation (1) is only possible under certain simplifying conditions, namely if $(T - T_0) \ll T_0$, and if adiabatic temperature rise is infinite, equivalent to having no influence of conversion. A complicated, but still approximate solution is derived in [7], from which the following expression for the critical condition can be derived:

$$\frac{\rho V}{UA} \frac{E}{RT_{cr}^2} q_{T=\infty} \exp\left(-\frac{E}{RT_{cr}}\right) = \frac{1}{e} \quad (2)$$

The resulting T_{cr} from equation (2) is *rather insensitive*, at most a few degrees K, to factors such as varying specific heat, order of the reaction, total heat of reaction and activation energy, according to [7]. Surprisingly, equation (2) does not contain the parameter time, but by calculation the practical definition of the criticality in the UN SADT test (temperature excursion of 6 K after 7 days) gives a T_{cr} very close to the outcome of equation (2). From equation (2), it can readily be observed that tests on two scales called 2 (“large”) and 1 (“small”) give the same critical ambient temperature, for the same material, if the following simple condition is met:

$$\frac{(UA)_2}{m_2} = \frac{(UA)_1}{m_1} \quad (\text{as } \rho V \text{ equals mass, } m) \quad (3)$$

Instead of the usually unknown UA -value of the Dewar vessel, the thermal half-life time of it, $t_{1/2}$, is usually applied.

The heating of a mass (*without self-reactive decomposition*), starting at a low temperature T_0 by a constant ambient temperature T_{amb} is given by an exponential expression:

$$\ln \left[\frac{T - T_{amb}}{T_0 - T_{amb}} \right] = -\frac{UA}{mc_p} t \quad (3a)$$

By definition, 50% of the starting temperature difference $T_0 - T_{amb}$ is left if $t = t_{1/2}$:

$$t_{1/2} = \frac{mc_p}{UA} \ln(2) \quad (4)$$

Combining equations (3) and (4) teaches that keeping constant the half-life times of cooling/heating for the two scales is the necessary and sufficient condition, to get the same critical ambient temperature.

The critical temperature of a *liquid* self-reactive material at larger scale can reliably be based upon a simpler test in a small Dewar vessel with the same heat loss per unit mass.

3. Conditions for having SADT similarity between two scales, for solids

The UN H.4 test is also permitted for solid self-reactive materials in packages up to 50 kg, which is supported by many experimental data, but it is difficult to see why the small test works so well.

Intuitively, any large-scale criticality problem can be tested in a small Dewar vessel *if it has the correct thermal insulation value*. The limiting case is perfect insulation, which simulates an infinite mass of solid, and the only problem is which heat transfer value must be taken on the small scale to simulate the larger scale. This problem is caused by the in-

insulating properties of the solid material. At larger scales, the heat resistance of the solid material itself adds appreciably to the total resistance to heat transfer. Tackling the problem analytically (in analogy to liquids) seems difficult, because of the following complications:

- Larger packages are mutually not geometrically similar (e.g. a box versus a cylindrical drum) and they are *certainly not similar to a small Dewar vessel* with its usual size $H=0.18$ m and $D=0.0572$ m.
- The starting moment $t=0$ begins if the centre temperature is 2 K below the oven temperature, but the starting temperature difference in the warming-up period (no self-heating yet) is not described in the H.4 test. It can be between 10 and 40 K and has an influence.

Instead of trying to find an analytical solution, we carried out a fair number of numerical simulations to reach general conclusions.

3.1. Use of the spherical analogue, to deal with various geometries and scales

The spherical analogue is introduced, in which a non-spherical with a certain V/A ratio is remodelled to a sphere, with a radius r_{sph} according to:

$$r_{\text{sph}} = \frac{3V_{\text{non-sph}}}{A_{\text{non-sph}}} \quad (5)$$

Mathematically, the spherical analogue can easily be modelled and evaluated. The mass in a spherical analogue is always less than in the original non-spherical package. At most, it is 2/3 of the mass of the package, in case of a cylindrical drum, or $\pi/6$ in case of a block. The advantage of the above definition is that *for liquids* the half-lifetime of cooling for two scales is the same, which can easily be proven by elaborating $t_{1/2}$ according to equation (4). Hence, introduction of the spherical analogue for the solving of the scale-up problem for solids makes sense. However, it is realised that the half-life time concept is not strictly applicable to a solid mass, as it does not cool or heat according to equation (3a). The Dewar vessel ($H/D=3.15$, an area of 375 cm² and a volume of 0.463 l) filled with solid material can in this approach be simulated by a sphere with radius $r_{\text{sph}}=0.037$ m, while the larger scale can be simulated by a sphere with a radius of approximately $r_{\text{sph}}=0.2425$ m. The latter is derived for an average cylindrical package, with $H/D=1.5$ to 1.6, of about 90 l, containing approximately 50 kg, the spherical equivalent volume is nearly 60 l.

In all our calculations for solids, the spherical analogue will be divided into a large number of annular layers in thermal contact with each other. Only the outside layer is cooled by the ambient. This model will be referred to as “the onion model”.

3.2. Approach by Fierz

Fierz (Ref. [3]) combined the concept of the spherical analogue with parts from the existing runaway theories, and therefore as a start, in our simulations also the spherical analogue was applied. The “onion” model uses a large number of annular shells (layers), for which the self-reactive heating, the heat exchange with the adjacent layers, and at the edge cooling/heating by the ambient air, are elaborated, and the resulting set of differential equations are solved numerically. Number of layers taken is usually 16. Auto-catalysis can be taken into account.

4. Results from the first series of calculations

4.1. Both scales simulated by spherical analogue (series 1, summarised in Appendix A)

The aim of these calculations is to vary the external heat transfer of the Dewar vessel (“small scale”), such that the same critical ambient temperature is obtained as for the large scale. The large scale uses a fixed value for the external heat transfer coefficient, between 4 and 8 W/(m² K), which describes the normal heat exchange with the ambient air due to radiation and free convection. The exact value of U for the large scale was found to be rather irrelevant. The runaway criterion according to UN SADT test H.4 was used and the relevant parameters (density, E/R , heat conductivity, radius, degree of auto-catalysis, order of auto-catalytic reaction, etc.) were varied over a wide range.

Conclusions, for series 1 calculations (Appendix A)

1. The external heat transfer coefficient, U , of the Dewar vessel wall must vary largely to cover all kinds of solids. Simulating the thermal behaviour of the 50 kg scale seems possible as long as a U -value of 0.1–0.6 W/m² K for the Dewar vessel can be achieved, which still seems feasible. To simulate larger scales, e.g. $r=0.5$ m, equivalent to approximately 400 kg, the required U -value of <0.01 to 0.05 W/m² K can probably no longer be realised for a 0.51 Dewar vessel.
2. Until scale $r=0.2425$ m, the following correlation is approximately valid:

$$\frac{r_2^2/\lambda_{\text{eff}}}{r_1/U_{\text{eff}}} \approx 2.5 \pm 0.2. \quad (6)$$

According to theory, the ratio, r_2^2/λ to r_1/U should be 3 for spherical masses, but this supposes infinite cooling rate at the outside for the larger scale, and infinite conduction rate at the inside for the smaller scale, which is not the case for our simulations. Equation (6) is based on taking the effective values λ_{eff} and U_{eff} , according to:

$$\lambda_{\text{eff}} = \frac{r_2\lambda U}{Ur_2 + \lambda},$$

all heat flow is due to the thermal conductivity λ (large scale).

$$U_{\text{eff}} = \frac{\lambda U}{Ur_1 + \lambda},$$

all heat flow is due to heat transfer coefficient U (small scale).

3. There is a large influence of auto-catalysis, but both scales show approximately the same effect. The decrease of the critical temperature is not as large as predicted by the literature [8].
4. There is practically no influence (at most 0.1 K) on the critical temperature if we start counting the time when $T_{\text{centre}} = T_{\text{ambient}} - 2 \text{ K}$, instead of when $T_{\text{centre}} = T_{\text{ambient}}$.

4.2. Application of the main result, given by equation (6), to the example of Fierz (ref. [3])

Equation (6) is applied to the calculation example used by Fierz, characterised by:

- small scale: Dewar 0.51, simulated by $r_{1,\text{sph}} = 0.05 \text{ m}$, $U = 0.6 \text{ W/m}^2 \text{ K}$;
- large scale: solid heat conductivity $\lambda = 0.1 \text{ W/m K}$.

It is found that $r_{2,\text{sph}}$ should be no more than 0.147 m, implying that the package should be no larger than 13.51. Due to a

slightly other approach, Fierz arrives at a somewhat smaller volume, but it looks as if the concerns of Fierz are realistic. Basic assumption of Fierz was that the Dewar is simulated by a solid sphere, which is strongly insulated at the outside, and hence practically homogeneous inside.

5. Practical experiments on the thermal behaviour of the Dewar vessel and related calculations

A number of experiments with a standard Dewar vessel as prescribed in UN H.4 test were performed. In these experiments, 400 ml solid technically pure di-(4-tert-butylcyclohexyl) peroxydicarbonate (4-tBCHP) was used in such a low temperature range that no decomposition of the organic peroxide could take place. The Dewar vessel was provided with a large number of thermocouples to record the temperature at various locations in the Dewar. The location of the calibrated thermocouples is given in Fig. 1. An example of a heating experiment is given in Fig. 2.

Two large deviations were found between simulations and experiments in a Dewar vessel:

1. The ‘‘onion’’ model predicts that the temperatures within the Dewar vessel during a heating or cooling test, conducted in a temperature region with practically no self-

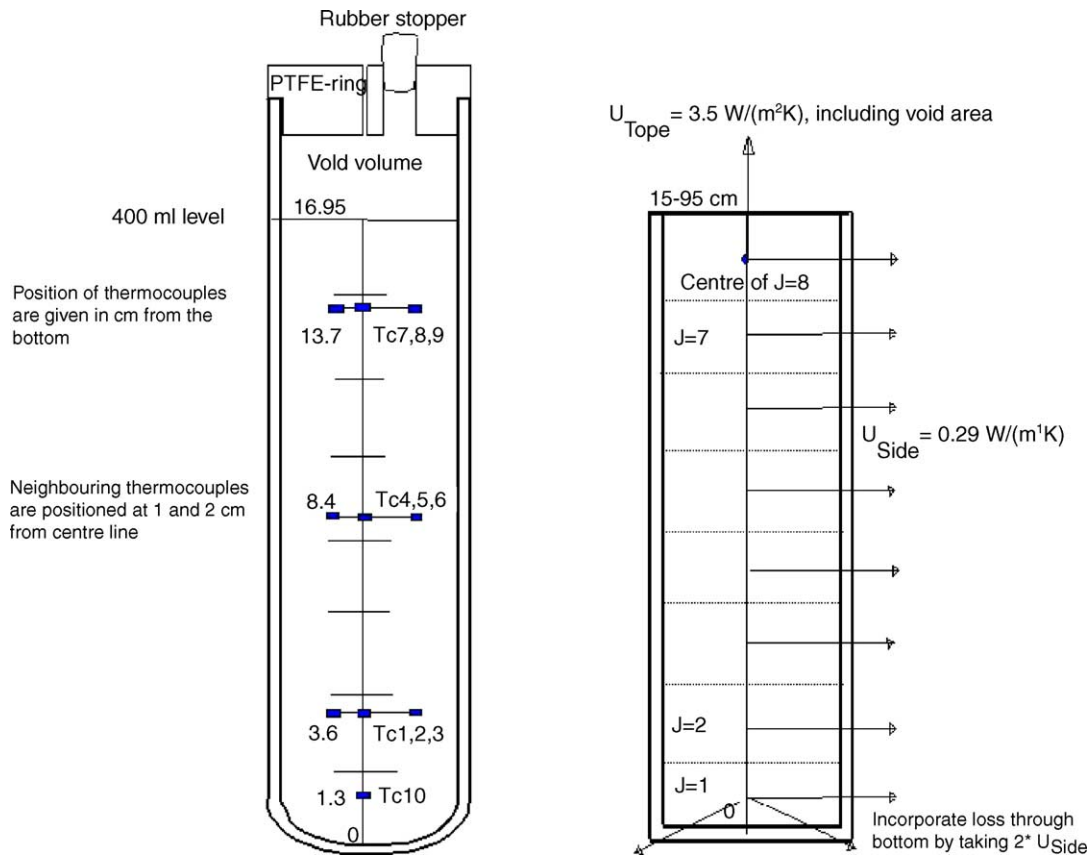


Fig. 1. Set-up of the modified cylinder model of the Dewar vessel, closely following the actual dimensions of the laboratory scale. The model uses eight layers. For the laboratory test thermocouples were placed in (about) the centres of layers 1, 2, 5 and 7, both in the middle, and at 1 and 2 cm from the centre line.

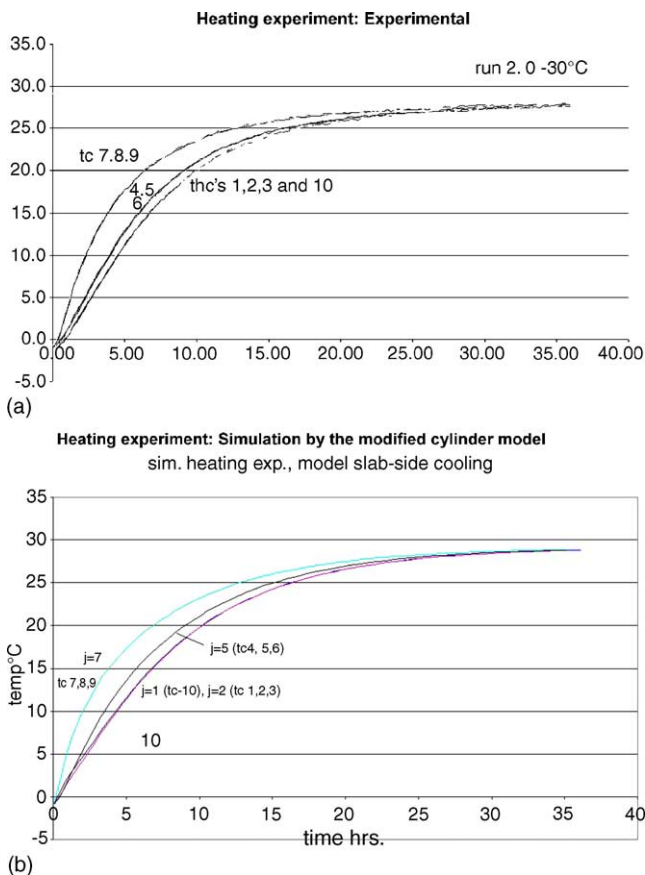


Fig. 2. Comparison of a heating experiment in the Dewar vessel (first graph) and its simulation (second graph). Same drawing scale. $t_{1/2}$ of this Dewar vessel was 7–7.5 h, measured with 400 ml dimethylphthalate (DMP).

heating, are almost equal between centre and near the edge, with a typical difference of only 0.1 K in the initial phase, later on practically nihil. However, the measurements showed that the temperature distribution within the Dewar is heterogeneous in vertical sense, with every height coordinate having a different apparent $t_{1/2}$, but nearly homogeneous in radial sense.

- It was also striking that an apparent $t_{1/2}$ value of 6 h (maximum value, about 1/3 of the height from the bottom of the Dewar vessel) was measured for the light powder 4-*t*BCHP, which should have given a $t_{1/2}$ value of approximately 2 h, according to equation (4), which was derived for homogeneous liquids.

Therefore, the onion model and the spherical analogue of the Dewar vessel were abandoned, and a modified cylinder model was developed, with heat exchange via the top but also some heat exchange via the sides. However, the spherical analogue for the large-scale package was maintained. The modified cylinder model for the Dewar is outlined in Fig. 1. The best-fit parameters for the heat transfer were determined by analysing the just mentioned heating experiment in the Dewar test with technically pure 4-*t*BCHP with well-known physical parameters (bulk density 464 kg/m³, specific heat

1450 J/(kg K), heat conductivity 0.16 W/(m K), determined for a thin layer of powder).

The results are:

$U_{top} = 3.5 \text{ W}/(\text{m}^2 \text{ K})$. This overall heat transfer coefficient acts on the centre of the mass of the top layer, with number $j = 8$, and is applied to the *top area* of $\pi/4 D_{inside}^2$. It, hence, includes

- the heat resistance of a length of solid of $1/2 H_{solid}/8$ or about 1 cm solid;
- the heat exchange through the vessel wall not covered by solid; and
- the insulation value of the rubber stopper.

$U_{side} = 0.29 \text{ W}/(\text{m}^2 \text{ K})$. This value acts on the centres of all cylindrical “slices”, numbered $j = 1–8$ in Fig. 1, and is applied to their *circumferential areas* $\pi D_{inside} H_{solid}/8$. It, hence, includes the heat resistance of a solid thickness of $D_{inside}/2$. To include the effects of the round bottom, the heat loss of the bottom layer $j = 1$ is taken double, in case of eight numerical slices.

Varying the solid thermal resistances (within the expectable limits) does not change the values U_{top} and U_{side} much, and therefore, these will be taken for all simulations. Performing the heat balance with these U -values yields that the top accounts for 49% of the heat loss and the side/bottom for 51%, *at least at the start when we have equal temperatures in the solid mass.*

Fig. 2 shows the good agreement between model calculation and experiment: the differences in (apparent) $t_{1/2}$ values are less than 4% for the top part and less than 1.5% for the rest of the Dewar vessel.

Assigning a $t_{1/2}$ to a Dewar vessel filled with solid self-reactive material is regarded to be erroneous or at least risky as $t_{1/2}$ depends strongly on the position of the thermocouple, but more importantly, the temperature versus time plot at a specified position does not closely follow equation (3a). In Fig. 3, the heating curves are plotted as $\ln((T - T_{amb})/(T_0 - T_{amb}))$ versus time, which should give a straight line through the origin, but actually a straight line is only achieved after a few hours. Hence, if it is required to thermally specify a Dewar

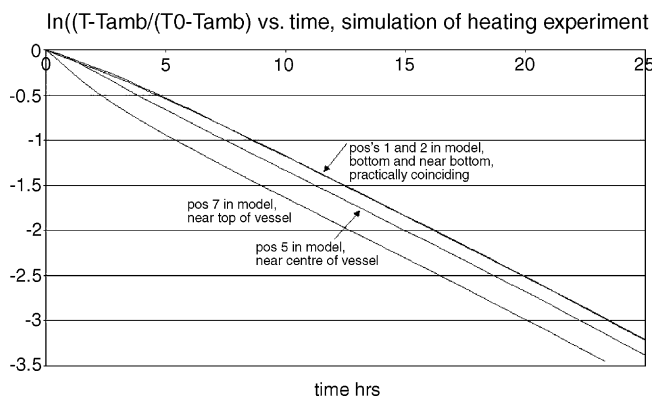


Fig. 3. Logarithmical analysis of temperature differences vs. time, for the heating experiment (simulation) given in the second figure in Fig. 2.

filled with solid, it is more precise to define the $t_{1/2}$ as the half of the time at which the original temperature difference has decreased with a factor four.

6. Results of the second series of numerical calculations

6.1. Dewar vessel modelled as a modified cylinder

Appendix B gives a survey of all numerical experiments for the “modified cylinder” model of the Dewar vessel, with the optimised values of U_{top} and U_{side} . Again, the runaway criterion according to UN SADT H.4 test is used, and the relevant parameters are widely varied. The main goal is now to compare the critical ambient temperatures for both scales, because with a perfect model they should be the same.

The model gives excellent agreement in critical ambient temperatures, with deviations from -0.6 (Dewar vessel outcome too low) to $+2.75$ K (opposite). As soon as smaller or larger packages are taken than the assumed 50 kg, the deviations between the calculated critical ambient temperatures increase sharply.

It is postulated that the modified cylinder model of the Dewar vessel gives a good agreement because it resembles a conical “pie” from the spherical analogue of the 50 kg package, as sketched in Fig. 4.

The filled solid height in the Dewar vessel is 0.16 m, not 0.2425 m (the radius of the spherical analogue) but its solid height should be increased with the effect of the rubber stopper (a few cm’s). There is compared to a cone much more mass in the well-insulated bottom section of the Dewar vessel, which is also equivalent to a certain extra length. The

weak cooling via the side of the Dewar vessel must be considered as a tuning of the model to the actually measured half-life times along the height of the Dewar vessel.

6.2. Finite element computations on self-accelerating decomposition in Dewar vessel and packaging

The apparently best way to apply data from lab-scale tests to facilities of technical size is to use a validated and reliable mathematical model. Advanced multi-dimensional models allow taking into account any geometry and any thermal boundary condition. The main criticism about the scale-up of Dewar vessel tests is focused on the negligence of the temperature distribution within the self-decomposing solid material. A computational model solving the heat balance equations with respect to position and time can smooth out this disadvantage.

Self-accelerating decomposition of solid materials in transport packagings can be modelled as a set of equations describing the time-dependent, three-dimensional (3D) energy flows. The following assumptions were made:

- Heat is transferred throughout the solid bulk material only by diffusion.
- The influences of moisture and particle size distribution are not considered.
- A zero-order reaction is assumed valid enough to reflect the decomposition.
- No heat loss due to gas release.

Hence, the heat balance equation is written:

$$\frac{\partial T}{\partial t} = a \operatorname{div} \operatorname{grad} T + S_T \quad (7)$$

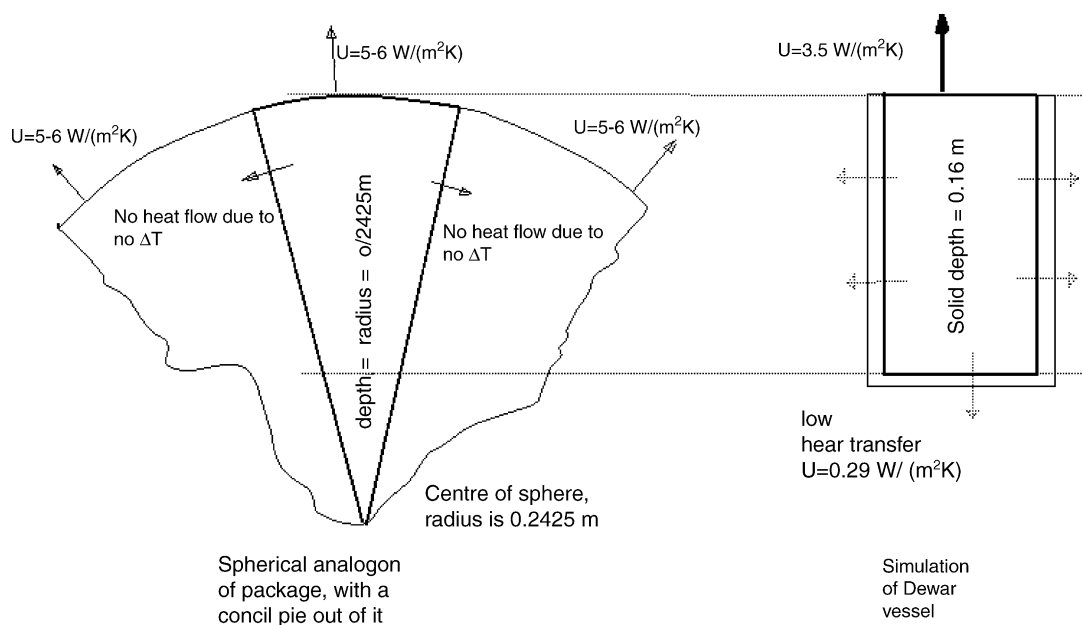


Fig. 4. Possible explanation of the success of the modified cylinder model: Dewar vessel resembles a conical “pie” from the spherical analogue of a 50 l package.

Table 2
Experimental parameters for Dewar tests of dilauroyl peroxide

	Dilauroyl peroxide
Half-life time of cooling in hours (thermocouple position 1.3–3.6 cm above bottom) for H ₂ O	11.0
Sample mass (g)	222
Bulk density (g/cm ³)	0.548
Thermal conductivity (W/(m K))	0.0977
Specific heat capacity (J/(kg K))	3370–4.618T [10]
Heat of reaction (J/kg)	8.23 × 10 ⁵ [10]
Apparent activation energy (J/mol)	1.2337 × 10 ⁵
Pre-exponential factor in (s ⁻¹)	3.92 × 10 ¹³
Induction period in hours (starting temperature 10 °C)	121.5
SADT (°C)	49

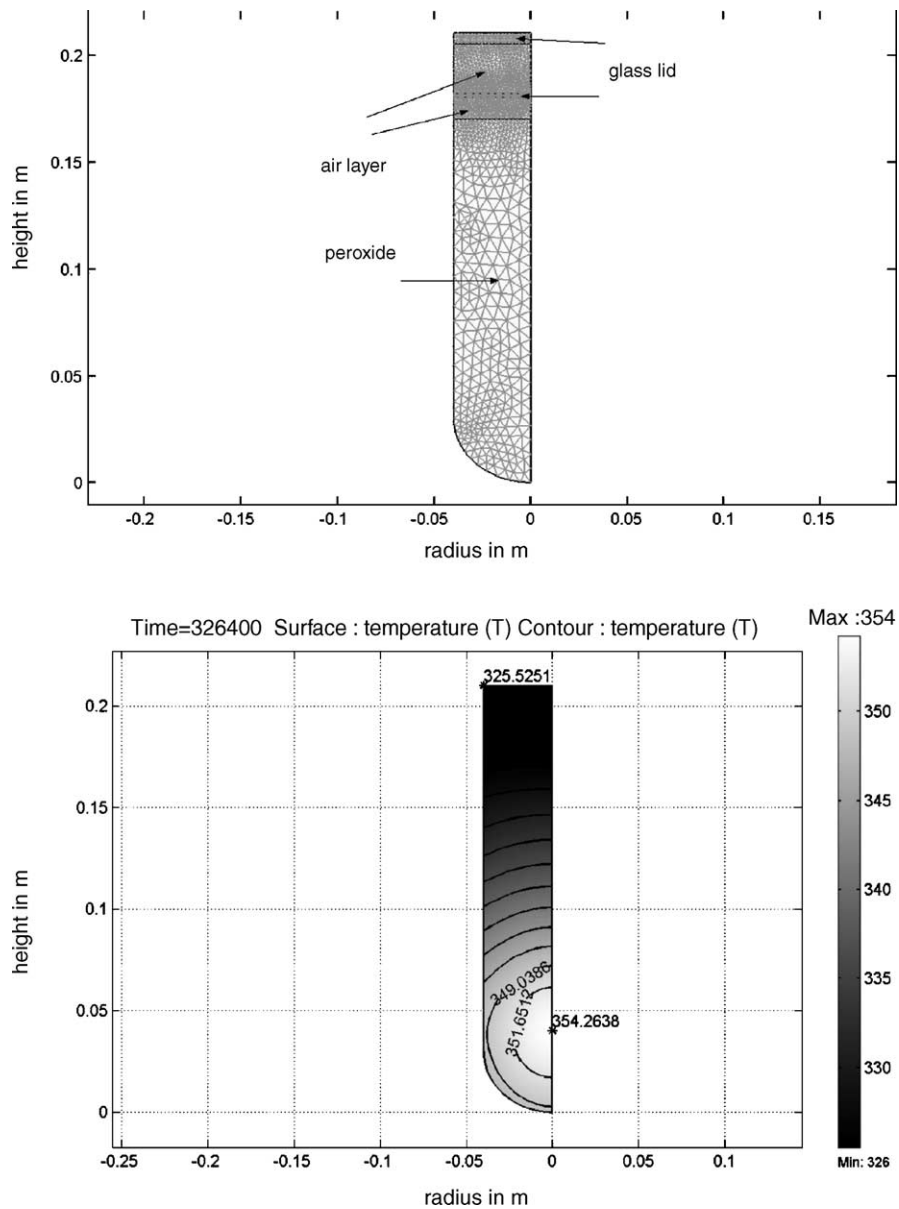


Fig. 5. Computational mesh and temperature distribution in a Dewar flask filled with 222 g of dilauroyl peroxide and stored at 45 °C (storage time 3.8 days).

The term on the left side of equation (7) describes the change of the local temperature with time, while the first term on the right side of equation (7) describes the transport by heat conduction and the second term is a source term.

The latter may be computed by using an Arrhenius-type rate equation

$$S_T = \rho \Delta H_R k_0 \exp\left(-\frac{E}{RT}\right) \quad (8)$$

At the system boundaries, the same conditions were applied as used in Section 5.

For solving the equations numerically, the Finite-Element-Method was applied using the commercial computer code FEMLAB.

As a first step to verify the model, Dewar vessel tests were simulated. The self-decomposing material under investigation was dilauroyl peroxide. This material has excessively been tested on lab-scale. Table 2 shows the experimental parameters of SADT tests. The tests were performed in a Dewar vessel of 500 ml internal volume. The half-life time of cooling of H₂O refers to a location of the thermocouple in the lower third of the Dewar flask where, as experience shows, the self-decomposition starts. The induction period is the time since the sample reached the storage temperature until self-decomposition starts.

A mathematical model of the Dewar test was set up, with the numerical grid as depicted in Fig. 5. The vessel consists of the Dewar flask and a lid especially designed to control heat losses. The lid is equipped with a lead-through for the thermocouple and another one for a capillary tube to allow the release of gases being formed during decomposition.

To model the heat loss through the wall of the Dewar flask the heat transfer coefficients have been adopted according to the measured cooling half time of the Dewar flasks. As explained in Section 5, about 49% of the total heat loss (at least at the start of the experiment) are transferred through the lid and 51% through the walls. Heat transfer coefficients were selected according to Section 5.

Fig. 6 exhibits experimental temperature evolutions with time within the Dewar flask used for cooling experiments with water and dimethyl phthalate. The half-life time of cooling for dimethyl phthalate was 9 h in the experiment as compared to 8.3 h found from the computations. For water, the agreement is still better: 12.5 h in the experiment and 12.3 h from the computations.

The heat loss by the release of gases has not been considered a significant factor, for the computations only the start of the runaway is of interest where the gas release is still negligible.

In a second step, the SADT values were calculated and compared with those observed experimentally. This comparison is shown in Table 3. The induction periods given in Table 3 refer to the SADTs.

Note, that in the experiments a margin in the storage temperature of 5 K is used to distinguish between sub-critical and

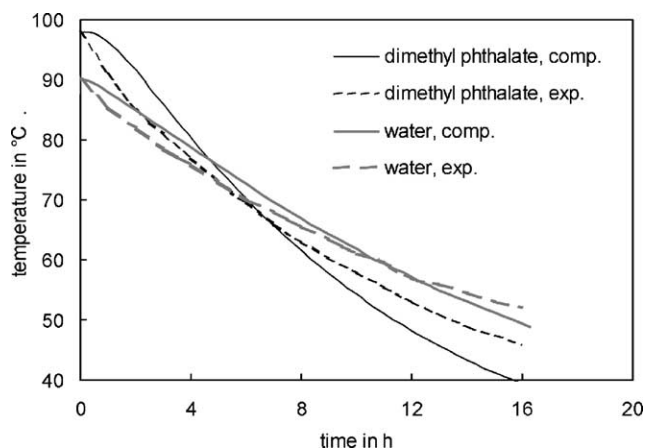


Fig. 6. Comparison of computed and experimental cooling curves for 500 ml Dewar flasks filled with water and with 400 ml dimethyl phthalate, computations with FEMLAB.

super-critical behaviour. In the light of this, the coincidence of the computed results with the experimental SADTs and the induction periods is good and justifies an application of the model to packages of technical size.

In a third step, the model was applied to a 90 l drum container as it is often used for the transportation of solid organic peroxides and self-reactive substances. Two different cases were considered: first, the drum was filled completely with the bulk density being the same as in the Dewar tests, and secondly, when the bulk material was compressed in a way that only about two-third of the drum was filled. Both cases reflect typical situations in practice.

For modelling, the drum container the geometry model was used as exhibited in Fig. 7.

The drum stands on a floor with a constant temperature. At the shell surface, a free convection boundary was supposed as well as at the top surface. The internal boundaries have symmetry boundary conditions (temperature gradient equal to zero). Although the heat transfer problem in the drum container is two-dimensional, a three-dimensional model was applied as a test of the 3D solution algorithm.

Self-decomposition temperatures of dilauroyl peroxide stored in the drum container are given in Table 4.

Fig. 8, as an example, depicts the temperature course in the centre of a 90 l drum container filled with 49 kg dilauroyl peroxide. Being initially at 10 °C, the centre temperature reaches

Table 3
Comparison of experimental and computed SADT values (Dewar test).

	Dilauroyl peroxide
Maximum temperature without self-decomposition (experiment) in °C	45
Maximum temperature without self-decomposition (computed) in °C	40
SADT (experiment) (°C)	49
SADT (computed) (°C)	45
Induction period (experiment) (h)	73
Induction period (computed) (h)	83

Table 4
Initial conditions, boundary conditions and computed SADT values for a 901 drum container with peroxide

	Dilauroyl peroxide		
	Mass of peroxide (kg)	49	15.9
Heat transfer coefficient at the surface ($W/(m^2 K)$)		8	
Bottom temperature	Ambient temperature		
Initial temperature ($^{\circ}C$)		10	
Maximum temperature without self-decomposition (computed) ($^{\circ}C$)	38	40	40
SADT (computed) ($^{\circ}C$)	40	45	45
Induction period (computed) (days)	6.7	3.4	2.5

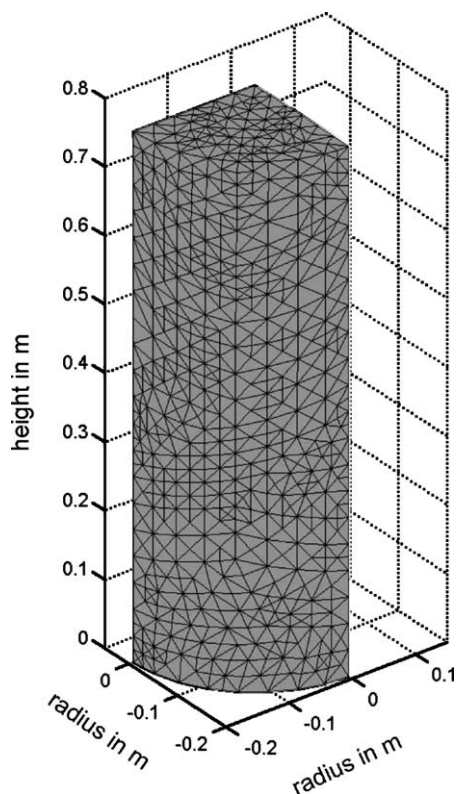


Fig. 7. Finite element mesh of a 901 drum container (27619 elements).

the storage temperature after about 55 h and turns into a runaway after another 160 h.

As Table 6 shows, the computations for 15.9–34 kg dilauroyl peroxide in a 901 drum give only a slightly lower SADT value than measured or calculated in the Dewar flask, and also from the US-SADT test. The difference can be explained from the neglect of reactant consumption, and maybe other factors. Altogether, the 3D calculation for the larger scale seems to produce a result slightly on the safe side, and it

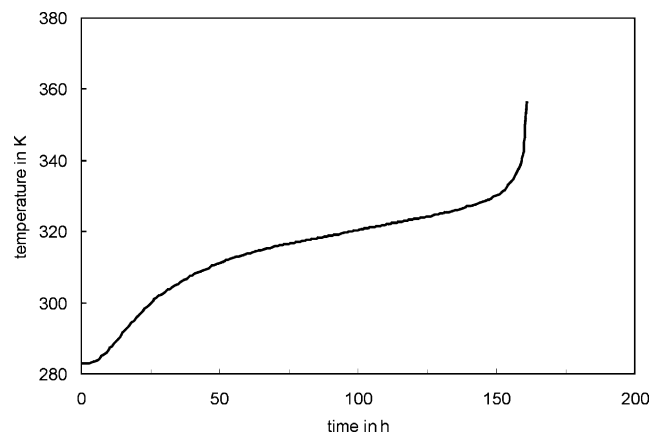


Fig. 8. Computed evolution of temperature with time in the centre of a 901 drum with 49 kg dilauroyl peroxide stored at a constant temperature of $40^{\circ}C$.

Table 5
Initial conditions, boundary conditions and computed SADT values for a 901 drum container partly filled with compressed dilauroyl peroxide

	Dilauroyl peroxide	
	Mass of peroxide (kg)	49
Bulk density (kg/m^3)	750	
Heat transfer coefficient at the surface ($W/(m^2 K)$)	8	
Bottom temperature	Ambient temperature	
Initial temperature ($^{\circ}C$)	10	
Maximum temperature without self-decomposition (computed) ($^{\circ}C$)	38	
SADT (computed) ($^{\circ}C$)	40	
Induction period (computed) (days)	5.5	

is a good supplement to the simpler, but quicker procedure described in Section 5.

In a next step, the influence of the bulk density on the SADT was examined. For this case, the same mass of organic peroxide was assumed to be compressed to a bulk density of $750 kg/m^3$. The results are given in Table 5. Compared to

Table 6
Comparison of the experimental and computed SADT values for dilauroyl peroxide

Substance	Literature values ($^{\circ}C$)		Recent results ($^{\circ}C$)	
	Test H.1 (US-SADT)	Test H.4 (heat accumulation storage test)	Test H.4 (heat accumulation storage test)	FEM-calculations for a 901 package
Dilauroylperoxide (kg)	49 (15.9–34)	45 (0.25)	49 (0.222)	45 (15.9–34), 40 (49)

the measured bulk density of about 500 kg/m^3 , the computed SADT value remained the same, however, the induction periods decreased slightly. This is mainly due to the fact that a compaction of the material increases also the thermal conductivity to a value of about 0.135 W/(m K) , which results in a shorter heating period.

Summarising the comparison of UN H.1 and H.4 tests according to Table 1 and the results of the computations and adding decades of common practice to it, it may be concluded that the UN H.4 test gives a sufficiently accurate prediction of the SADT of a 90 l package of self-decomposing peroxides.

In Table 6, the recent results and some literature values are summarised for dilauroyl peroxide. We find 49°C in our H.4 test, which is 4 K higher than the literature value but our value agrees well good with the H.1 test. The US-SADT test gives 45°C (for 15.9 and 34 kg) while our calculations yield 45°C for the same amount in a 90 l package.

7. Conclusions

- Simulation of the 0.5 l Dewar vessel, in use for the H.4 test, by a spherical analogue (which is the basic assumption of Fierz) leads to a much too homogeneous temperature distribution within it, as compared to evidence from heating or cooling experiments of solid material in the Dewar vessel.
- A Dewar vessel is far better simulated by a cylinder of self-accelerating decomposing material, which exchanges heat mostly at the top, but also slightly through its walls. The

agreement between measured and calculated $t_{1/2}$ times as a function of the vertical position within the Dewar was found to be excellent.

- The modified cylinder model of the 0.5 l Dewar vessel should be combined with a spherical model of the 50 kg large package. Simulations covering a wide variety in physical and thermo-chemical parameters showed excellent agreement in the SADTs determined, with deviations $\pm 2.5 \text{ K}$.
- All calculations, including the FEMLAB trials, show that the Dewar vessel test (UN H.4 test) can be used to determine SADTs of organic peroxides and self-reactive substances up to 50 kg packagings.
- As soon as a larger package is taken than the assumed 60 l sphere (is equivalent to a 90 l package), the deviations in SADT increase. Consequently the question arises what kind of small-scale vessel is appropriate to describe larger amounts of solid self-reactive substances. We are currently investigating this problem and hope to report on this topic soon.

Acknowledgement

The authors wish to thank Gerard Wolbert, Safety Services, Polymer Chemicals, Deventer, for conducting the precise measurements of the thermal behaviour of the Dewar vessels used for the SADT-determination. These measurements eventually led to a better insight why the BAM–Dewar test works so well.

Appendix A. Datasets used for the numerical experiments, spherical “onion” model for both small and large scale

Sim. no.	Large scale		Calc $T_{a,cr}$	Small scale		Required U for good	Common physical parameters					
	r_2	U_{sph2}		r_1	U_{sph1}		rho	beta	lambda	E/R	k_0	Order of auto-catalytic reaction (n)
1	0.2425	8	313.1	0.037	0.565	464	0.033	0.48	19338	3.68E+19	1	[1]
2	0.2425	4	309.7	0.037	0.166	464	0.033	0.12	19338	3.68E+19	1	[1]
3	0.2425	4	311.2	0.037	0.28	464	0.033	0.24	19338	3.68E+19	1	[1]
4	0.2425	4	314.9	0.037	0.173	464	no	0.12	19338	3.68E+19	n.a.	[1]
5	0.2425	8	312.3	0.037	0.1	464	no	0.06	19338	3.68E+19	n.a.	[1]
6	0.5	6	306.5	0.037	0.054	464	0.033	0.16	19338	3.68E+19	1	[1]
7	0.6	5	304.9	0.03	0.01	1000	0.2	0.1	19338	3.68E+19	1	[1]
8	0.1125	4	316.6	0.025	0.384	700	0.2	0.1	19338	3.68E+19	1	[1]
9	0.6	5	304.9	0.092	0.03	1000	0.2	0.1	19338	3.68E+19	1	[1]
10	0.2425	4	315.4	0.037	0.285	464	0.2	0.24	19338	3.68E+19	1	[1]
11	0.6	5	305.2	0.03	0.005	1000	no	0.1	19338	3.68E+19	n.a.	[1]
12	0.6	5	303	0.03	0.0075	1000	0.033	0.1	19338	3.68E+19	1	[1]
13	0.6	5	305.3	0.03	0.0104	700	0.2	0.1	19338	3.68E+19	1	[1]
14	0.6	5	306.3	0.03	0.015	464	0.2	0.1	19338	3.68E+19	1	[1]
15	0.3658	6	305.5	0.0558	0.083	700	0.033	0.0905	19338	3.68E+19	1	[1]
16	0.2425	8	307.9	0.037	0.17	900	0.033	0.1164	19338	3.68E+19	1	[1]
17	0.2425	8	312.8	0.037	0.54	464	0.033	0.48	13000	7.23E+10	1	[1]
18	0.2425	4	310	0.037	0.263	464	0.033	0.24	13000	7.23E+10	1	[1]
19	0.2425	8	312.1	0.037	0.092	464	no	0.06	13000	7.23E+10	n.a.	[1]
20	0.6	5	300.6	0.03	0.065	1000	0.2	0.1	13000	7.23E+10	1	[1]
21	0.6	5	300.6	0.092	0.02	1000	0.2	0.1	13000	7.23E+10	1	[1]
22	0.6	5	310.3	0.03	0.007	1000	no	0.1	13000	7.23E+10	n.a.	[1]
23	0.6	5	300.7	0.03	0.007	700	0.2	0.1	13000	7.23E+10	1	[1]
24	0.3658	6	310.8	0.0558	0.076	700	0.033	0.0905	13000	7.23E+10	1	[1]
25	0.2425	8	313.05	0.037	0.56	464	0.033	0.48	19338	3.68E+19	1	[2]
26	0.2425	4	309.65	0.037	0.166	464	0.033	0.12	19338	3.68E+19	1	[2]
27	0.2425	4	314.9	0.037	0.174	464	no	0.12	19338	3.68E+19	n.a.	[2]
28	0.2425	8	312.2	0.037	0.096	464	no	0.06	19338	3.68E+19	n.a.	[2]
29	0.1125	4	316.6	0.025	0.383	700	0.2	0.1	19338	3.68E+19	1	[2]
30	0.2425	4	311	0.037	0.273	464	0.033	0.24	19338	3.68E+19	1	[2]
31	0.3658	6	305.4	0.0558	0.055	700	0.033	0.0905	19338	3.68E+19	1	[2]
32	0.2425	8	307.8	0.037	0.167	900	0.033	0.1164	19338	3.68E+19	1	[2]
33	0.2425	8	308.35	0.037	0.22	1032	0.033	0.175	19338	3.68E+19	1	[2]
34	0.2425	8	307.65	0.037	0.146	900	0.033	0.1164	19338	3.68E+19	1	[2]
35	0.2425	8	313	0.037	0.54	464	0.033	0.48	19338	3.68E+19	0.5	[2]
36	0.2425	4	309.5	0.037	0.165	464	0.033	0.12	19338	3.68E+19	0.5	[2]
37	0.2425	4	314.9	0.037	0.174	464	no	0.12	19338	3.68E+19	0.5	[2]
38	0.2425	8	312.2	0.037	0.1	464	no	0.06	19338	3.68E+19	0.5	[2]
39	0.1125	4	316.6	0.025	0.383	700	0.2	0.1	19338	3.68E+19	0.5	[2]
40	0.2425	4	315.4	0.037	0.284	464	0.2	0.24	19338	3.68E+19	0.5	[2]
41	0.3658	6	305.4	0.0558	0.047	700	0.033	0.0905	19338	3.68E+19	0.5	[2]
42	0.2425	8	307.6	0.037	0.156	900	0.033	0.1164	19338	3.68E+19	0.5	[2]

The aim of the numerical experiments was to get insight into possible scale-up correlations, by widely varying the input data. First, for the larger scale (mostly a simulated 50 kg package, taken sometimes intentionally smaller or larger) the critical ambient temperatures are calculated, secondly for the smaller scale (mostly a simulated Dewar vessel, sometimes intentionally taken smaller or larger) the required heat transfer coefficient U to the ambient, to get the same critical ambient temperature, is evaluated. The meaning of the symbols “beta” and (reaction order) “ n ” used to define an auto-catalytic reaction are explained in Appendix C. n.a.: Not applied; r_2 : radius for the larger scale, in m; U_{sph2} : overall heat transfer coefficient for the larger scale, W/(m² K); r_1 : radius for the smaller scale, in m; U_{sph1} : overall heat transfer coefficient for the smaller scale, W/(m² K); calc $T_{a,cr}$: calculated critical ambient temperature, K; rho: bulk density, kg/m³; beta: auto-catalysis factor, according to Appendix C; lambda: solid heat conductivity in W/(m K); c_p : specific heat of solid in J/(kg K); E/R : activation energy/gas constant, K; k_0 : rate constant at infinite temperature, in s⁻¹; [1]: t is set on zero if $T_{centre} = T_{amb}$; [2]: t is set on zero if $T_{centre} = T_{amb} - 2$ K; applied heat of reaction is 8.3E5 J/kg.

Appendix B. Datasets used for spherical “onion” calculations for the 50 kg package, but modified cylinder model for the Dewar vessel

Main goal of these calculations was to find the critical ambient temperatures for both scales, using exactly the same physical parameters, thermal kinetics, heat of reaction, etc.

Sim. no.	Larger scale		Computed data				Common thermo-physical data						
	r_2	U_{sph}	Calc $T_{a,cr}$		delta T	rho	beta	lambda	c_p (Large scale)	c_p (Dewar scale)	E/R	k_0	Order of auto-catalytic reaction
			Larger scale	Dewar vessel									
1	0.2425	8	313.1	312.7	-0.4	464	0.033	0.48	1450	1989	19338	3.68E+19	1
2	0.2425	4	309.7	312.1	2.4	464	0.033	0.12	1450	1989	19338	3.68E+19	1
3	0.2425	4	311.2	312.4	1.2	464	0.033	0.24	1450	1989	19338	3.68E+19	1
4	0.2425	4	318.9	319.8	0.9	464	no	0.24	1450	1989	19338	3.68E+19	n.a.
5	0.2425	4	315.4	317.2	1.8	464	0.2	0.24	1450	1989	19338	3.68E+19	1
6	0.32	6	306.1	310.9	4.8	700	0.033	0.0905	1450	1807	19338	3.68E+19	1
7	0.2425	8	307.9	310.3	2.4	900	0.033	0.1164	1450	1728	19338	3.68E+19	1
8	0.2425	8	312.8	312.4	-0.4	464	0.033	0.48	1450	1989	13000	7.23E+10	1
9	0.2425	4	310	312.1	2.1	464	0.033	0.24	1450	1989	13000	7.23E+10	1
10	0.32	6	302.7	309.8	7.1	700	0.033	0.0905	1450	1807	13000	7.23E+10	1
11	0.16	4	314.1	314.9	0.8	700	0.2	0.1	1450	1807	19338	3.68E+19	1
12	0.2425	8	308.35	310.2	1.85	1032	0.033	0.175	1900	2142	19338	3.68E+19	1
13	0.2425	8	307.65	310.4	2.75	900	0.033	0.1164	1900	2178	19338	3.68E+19	1
14	0.2425	8	310.3	309.7	-0.6	464	0.053	0.48	1450	1989	19338	3.68E+19	0.5
15	0.2425	4	306.4	309	2.6	464	0.053	0.12	1450	1989	19338	3.68E+19	0.5
16	0.16	8	316.2	314.2	-2	700	0.36	0.2	1450	1807	19338	3.68E+19	0.5
17	0.2425	8	313.7	315.9	2.2	464	0.36	0.16	1450	1989	19338	3.68E+19	0.5

The larger scale is sometimes taken intentionally smaller or larger than the simulated 50 kg package, to see the effect. r_2 : radius for the larger scale, in m; U_{sph} : overall heat transfer coefficient for the larger scale W/(m² K); calc $T_{a,cr}$: calculated critical ambient temperature, K; rho: bulk density in kg/m³; beta: auto-catalysis factor, according to Appendix C; lambda: solid heat conductivity in W/(m K); c_p : specific heat of solid in J/(kg K); E/R : activation energy/gas constant, in K; k_0 : rate constant at infinite temperature, in s⁻¹; n.a.: not applied; applied heat of reaction is 8.3E5 J/kg; U_{top} = 3.5 W/(m² K); U_{side} = 0.29 W/(m² K); c_p (Dewar scale) is c_p for solid, but corrected with the heat capacity of Dewar vessel.

Table C.1

Conversion at which Q_{\max}/Q_0 occurs, dependent on order n of auto-catalytic reaction and the auto-catalysis factor β

Order n	$Q_{\max}/Q_0 = 1.5$	Conversion at which $Q_{\max}/Q_0 = 8$
1	Conv = 0.37 at $\beta = 0.27$	Conv = 0.5 at $\beta = 0.033$
2	Conv = 0.56 at $\beta = 0.13$	Conv = 0.68 at $\beta = 0.019$
1/2	Conv = 0.19 at $\beta = 0.51$	Conv = 0.33 at $\beta = 0.053$
1/3	Conv = 0.123 at $\beta = 0.7$	Conv = 0.25 at $\beta = 0.065$

Appendix C. Thermal effects of auto-catalysis

C.1. Heat production rates during auto-catalysis

In the case of auto-catalysis, the reaction rate increases due to the influence of the decomposition products, and this is additional to the usual acceleration caused by temperature increase. The reaction rate for the decomposing component can be given as:

$$-\frac{dc}{dt} = k_i c + \frac{k_j}{\beta} c(1-c)^n$$

(from [9], the authors use the normalised concentration $0 \leq c \leq 1$). The auto-catalytic reaction is characterised by k_a (subscript a from auto-catalysis) while the normal self-heating reaction is described by its kinetic constant k_i (subscript i, probably from “initiator”), and $k_a = k_j/\beta$.

Hence, a small value of β means a large degree of auto-catalysis.

The heat production rate HPR, as a function of conversion α , now becomes:

$$\text{HPR} = \text{HPR}_0(1 - \alpha) \left(1 + \frac{\alpha^n}{\beta} \right)$$

An important aspect of auto-catalysis is the existence of a *maximum* in the heat production rate Q_{\max} during an isothermal measurement. The conversion at which this happens can be numerically calculated, and in some cases analytically derived. The maxima in the ratio Q_{\max}/Q_0 all occur at *about the same value* of the conversion, but are dependent on the order n of the auto-catalytic reaction, see Table C.1.

From Table C.1 it is observed that, if the kinetics is given by a fixed value of n , the maximum rate occurs within a small range of conversions. *Adapting the exponent n* is, hence, a method to utilise the experimentally found value Q_{\max}/Q_0 and the conversion at which this occurs in numerical calculations.

C.2. Theoretical effect of auto-catalysis on criticality

Merzhanov [8] essentially uses the same equation as above to describe the auto-catalysis phenomenon. He presents the

following influence of auto-catalysis (for first order auto-catalytic reaction) on the criticality of a liquid runaway mixture:

$$Se_{\text{cr, autocatalysis}} = \frac{Se_{\text{cr, no autocatalysis}}}{(Q_{\max}/Q_0)}$$

According to the definition of the critical Semenov number Se_{cr} , one gets the following (implicit) correlation describing the decrease of the critical temperature T_{cr} .

$$\exp\left(\frac{E}{R}\left(\frac{1}{T_{\text{cr,noAC}}} - \frac{1}{T_{\text{cr,AC}}}\right)\right) \frac{T_{\text{cr,AC}}^2}{T_{\text{cr,noAC}}^2} = \frac{Q_{\max}}{Q_0}$$

“AC” refers to auto-catalysis, “no AC” refers to no auto-catalysis.

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