Safe Storage of Highly Energetic Materials

When predicting about the storage or transportation of highly energetic materials in the chemical industry, the temperature gradients in the reacting medium must be considered. For highly exothermal reactions, areas with higher temperature and faster reactions feature more intensive heat production and self-heating. Such local areas then become hotspots where runaway or thermal explosions can begin.

Accelerating Decomposition Temperature (SADT) – AIBN

The Self-Accelerating Decomposition Temperature (SADT) is the lowest ambient temperature at which a self-reactive substance will decompose in a specified commercial package within a week or even less. Above SADT, the reaction rate becomes so rapid that the heat generated outpaces the heat removal rate from the package, leading to a self-sustaining reaction. Specifically, SADT is defined as the lowest ambient temperature at which the material temperature exceeds the ambient temperature by 6K after 7 days, after having started 2K below ambient temperature.

The NETZSCH software Termica Neo provides time-dependent and temperature-dependent results for the temperature, the concentration of all reactants and the reaction rate in 2D and 3D view. It is also possible to search for the self-accelerating decomposition temperature (SADT) as well as simulate adiabatic condi- tions and infinite heat transfer to the surroundings. The following example demon- strates the simulation of a 50-kg cylindrical package of azobisisobu- tyronitrile (AIBN) in air.

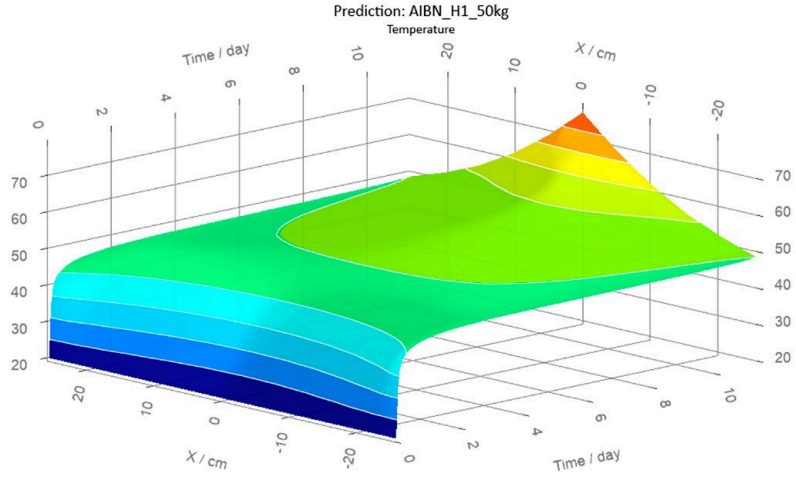


Figure 1: SADT calculation for the decomposition of the package of 50 kg of AIBN.

Simulation Results: Temperature The temperature (x,t) is shown for the decomposition of the package of 50 kg of AIBN. A cylindrical package (room temperature in air) with an initial diameter of 50 cm is placed under storage at a tempe- rature of 48°C (figures 1 and 2). Verification of this simulation can be found in Thermochimica Acta 621(2015) 25-35.

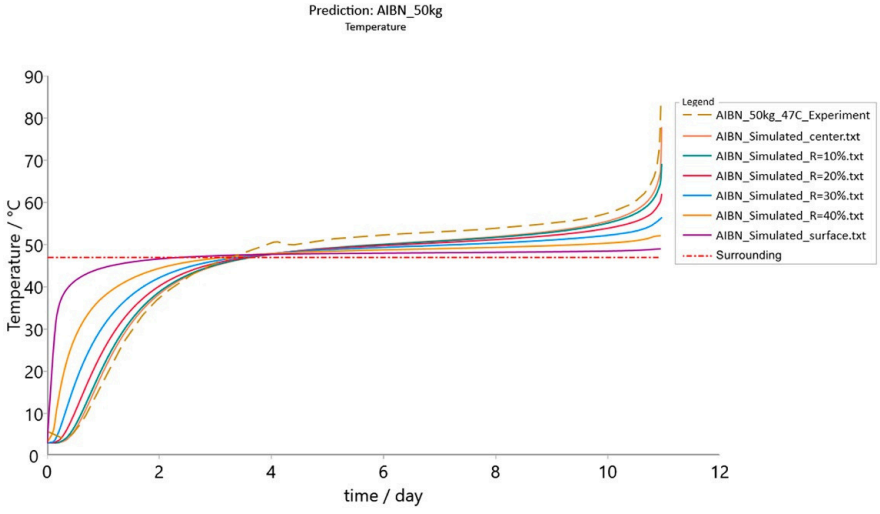
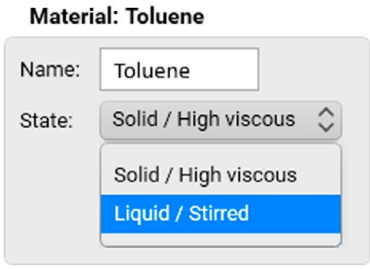


Figure 2: Prediction of the temperature progression for a cylindrical package at different radial distances, depending on time; the dashed curve is the experimental data measured in the center.

Decomposition of 20% DTBP in Toluene

In chemistry, DTBP (di-tert-butyl peroxide) in toluene refers to a solution of di-tert-butyl peroxide, a reactive organic peroxide, dissolved in the solvent toluene. DTBP is a radical initiator, meaning it generates free radicals upon thermal decomposition, making it useful in various chemical reactions and processes like polymerization. Simulations in Termica Neo can be carried out for both solid and liquid materials. Liquids are assumed here to have high convection or stirring. Therefore, liquids have a uniform temperature without gradients.



Simulation in Liquids The simulation was calculated for a liquid solution of 20% di-tert-butyl peroxide (DTBP) in toluene in an 8.5-ml titanium container with a radius of R = 2.5 cm and a wall thickness of 0.89 mm (figure 1).

The simulation results were confirmed by accelerating rate calorimetry measurements using the NETZSCH ARC 244 (figure 2).

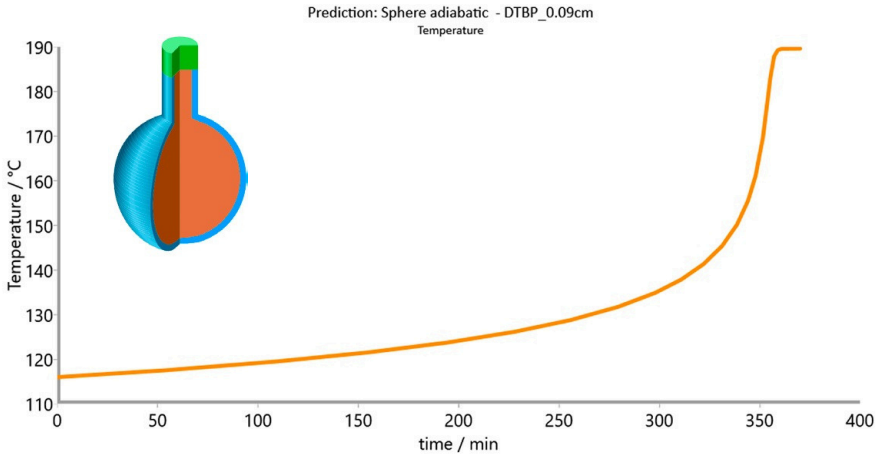


Figure 1: Prediction of the temperature progression.

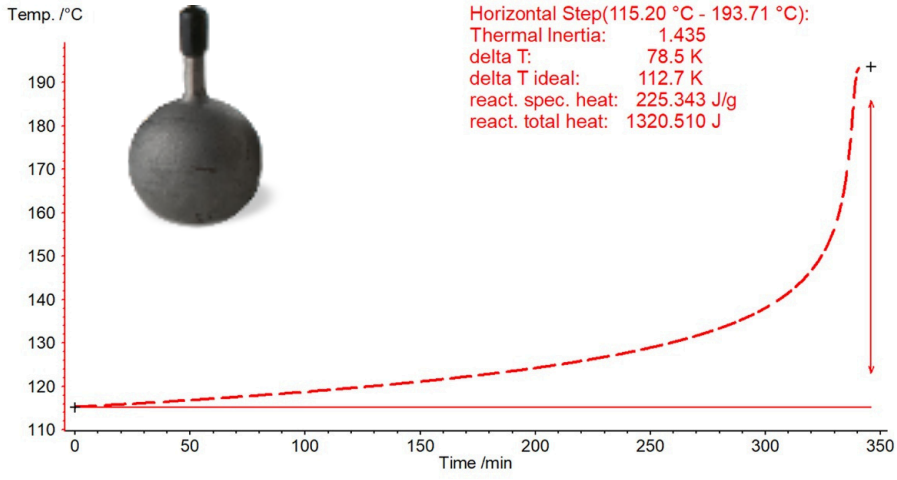
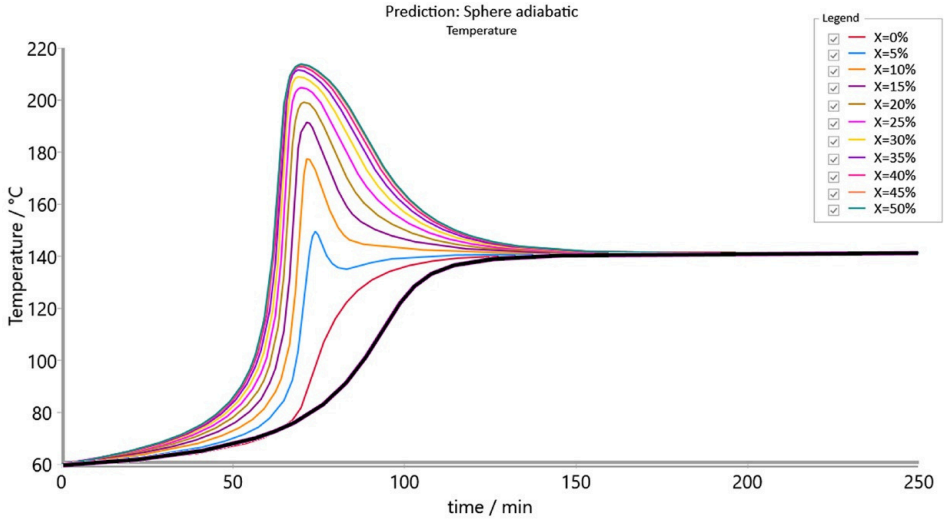


Figure 2: Confirmation of the simulation by means of an ARC 244 measurement.

Reactant in an Adiabatic Container

Adiabatic simulations for liquids and solids involve modeling systems where no heat is exchanged with the surroundings. These simulations are crucial for understanding various phenomena, including phase transitions, material properties, and energy storage. However, these investigations also show that adiabatic simula- tions for liquids and solids yield different results. The temperature of low-viscous liquids with convection or stirring is uniform (black curve). The reactant has no temperature gradients, and it heats up very slowly. It is usually calculated according to the factor of thermal inertia, Phi (see figure below).

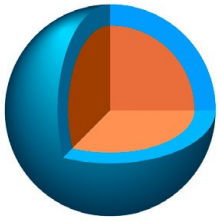
Exothermal reactions in solids lead to temperature gradients and overheating in the center, where heat accumulates. Solids heat up faster, have a lower Time to Maximum Rate (TMR), and have a higher maximum temperature (colored curves in the figure). Therefore, calculation for solids according to the Φ-factor is inaccurate and dangerous. The simulation for solids, here demonstrated as the prediction, clearly shows an earlier reaction at a higher temperature than the calculation according to the Φ-factor. The final temperature for both simulations is the same and corresponds to the heat balance.



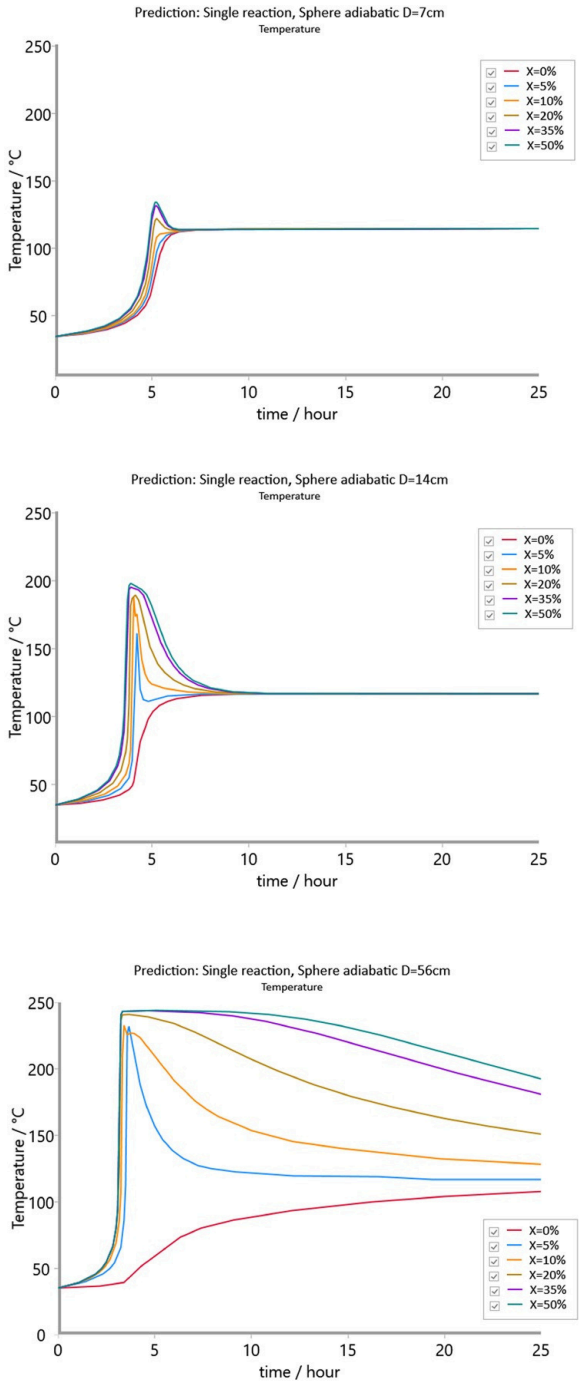
Simulation of the temperature distribution in an adiabatic system: solid reactant (colored curves), and liquid reactant (black curve).

Adiabatic Scale-Up for Single Reaction

The temperature of the material under adiabatic conditions for 24 hours is very important for the safety of industrial reactions with high exothermal effect. For liquid materials with stirring the temperature in the reacting volume is uniform and simulation can be carried out according to the factor of thermal inertia, Phi, which is the ratio of the heat capacity of the material with container to that of the material alone. However, knowledge of the Phi-factor only is not enough for simulation of the correct temperature distribution.



The figure displays the simulations under the assumption of a single reaction for three different diameters. In the first simulation, with D = 7 cm, there are almost no temperature gradients or overheating. The second simulation, with D = 14 cm, exhibits a maximum overheating in the center. The third simulation, with D = 56 cm, has a maximum possible over-heating at the center, which corresponds to an adiabatic temperature increase for a pure material with a Phi-factor of 1. However, the final temperature is the same for all simulations, because of the heat balance with the same Phi-factor.



Simulations for single reaction, with reaction heat 395 J/g, Phi=1.4; diameters 7, 14 and 56 cm.

SIMULATIONS FOR THE DIFFERENT REACTING VOLUMES IN SOLIDS WITH THE SAME Φ-FACTOR LEAD TO DIFFERENT TEMPERATURE DISTRIBUTIONS.

Adiabatic Scale-Up for Primary and Secondary Reactions

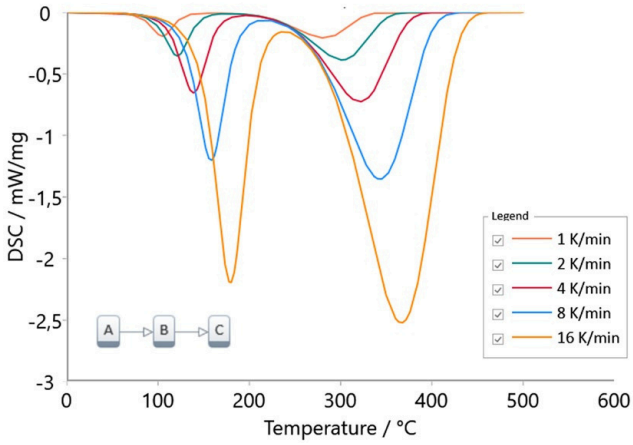


Figure 1: Example of a DSC measurement up to 500°C at different heating rates between 1 K/min and 16 K/min.

Many industrial applications have secondary decomposition reactions, which must be avoided during industrial processes. These highly exothermal secondary reactions may lead to serious damage if they get out of control. Therefore, it is important to know the temperature increase for adiabatic cases.
The current simulation example presents the adiabatic scale-up simulation over a 24-hour period for primary and secondary reactions in solids for the same Phi-factor.

Based on the DSC measurements (figure 1), three simulations are done for a Phi-factor of 1.4 (figure 2). After 24 hours, only the primary reaction is finished for the first two simulations, with D = 7 cm and D = 14 cm. The second simulation exhibits slight overheating in the center. In the third simulation with D = 56 cm, overheating in the primary reaction was too high, triggering the secondary reaction. The simulation shows that the larger the size, the greater the overheating in the center. The simulation helps determine the size at which overheating in the center becomes too high and leads to dangerous triggering of the secondary reaction.

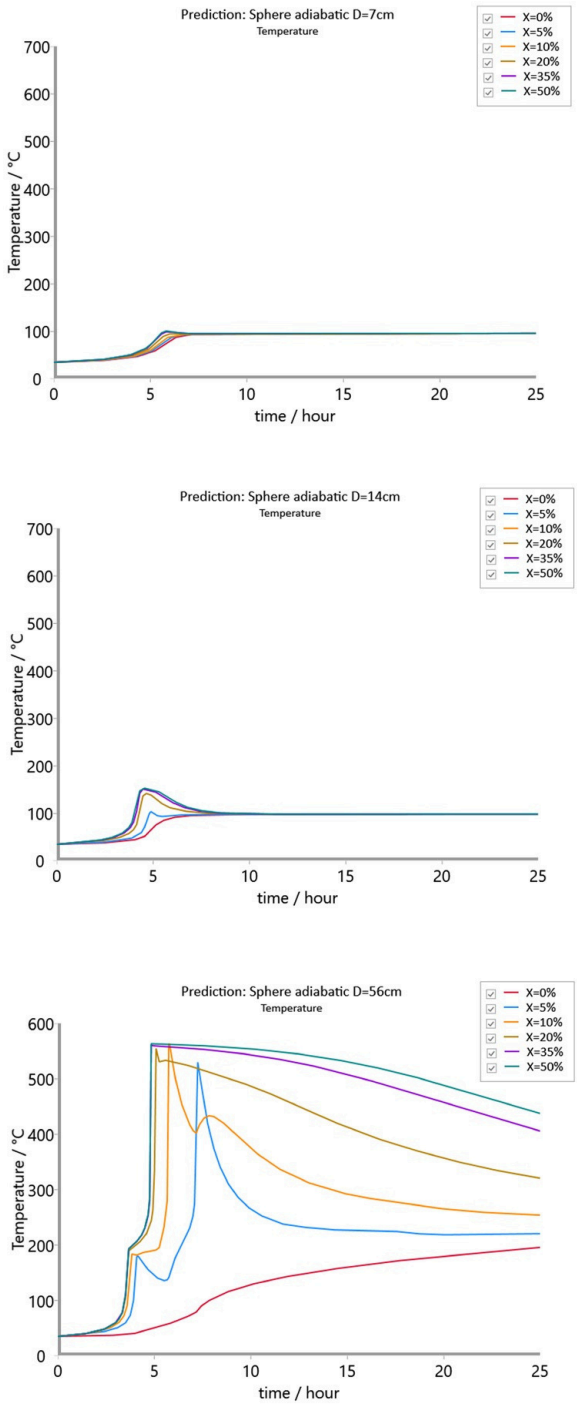


Figure 2: The primary reaction amounts to 300 J/g; the secondary reaction to 700 J/g; the Phi-factor for all simulations amounts to 1.4; diameters 7, 14 and 56 cm.