

Advanced Kinetics-based simulation method for determination of the Time To Maximum Rate under Adiabatic conditions (TMRad)

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ABSTRACT

To investigate runaway exothermic reactions an adiabatic calorimeter is very often used. However the adiabatic environment is a theoretical state, in laboratory scale testing this cannot be obtained but may only be approached. Deviation from the fully adiabatic state comes from (i) the thermal inertia of the test system or heat lost into the sample container and (ii) the loss of heat from the container itself to the environment that reflects the 'operational adiabaticity' of the instrument. In addition to adiabatic testing, advanced kinetics determination from DSC data performed under different heating rates can be applied to simulate what may happen on a large scale by testing a small amount of sample [1-3]. For the 'up-scaling' of DSC data, two important factors have to be considered (i) the application of advanced kinetics, which properly describes the complicated, multistage course of the decomposition process (ii) and the effect of heat balance in the energetic system to generate the adiabatic conditions, as the sample mass is increased by a few order of magnitude compared to the thermoanalytical experiments. The validity of the obtained kinetic description can be checked by comparing the predicted adiabatic runaway profiles with experiments in the adiabatic calorimeters. Moreover, accurate kinetic description and reliable enthalpy of reaction gathered from DSC data enable to mimic the behavior in an adiabatic reaction calorimeter. Thus, advanced kinetics-based simulation methods can be used to evaluate the impact of different thermal conditions such as various phi-factors and process temperature on the decomposition behaviour. The variation in the runaway time for any phi-factor can then be plotted as a function of any initial process temperature in a thermal safety diagram. Commonly accepted as the safety limit on the industrial scale, the critical temperature corresponding to a Time To Maximum Rate under adiabatic conditions of 24 hours (TMRad = 24 hours) can then be easily determined. Before carrying out a thermal hazard evaluation experiment with an adiabatic calorimeter, therefore, the reactivity of the sample can be assessed using DSC data and advanced kinetics. This approach leads to proper selection of experimental conditions and the versatility of the adiabatic calorimeters can be better exploited.

REFERENCES

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