Calorimetry at large scale – Monitor critical reactions on-line for a safe operation

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Reaction calorimetry is a common and widely used tool to determine thermal behaviour of chemical reactions. Highly exothermic reactions require special attention for a safe operation to avoid runaways.

Grignard reactions are widely used in the chemical industry to prepare a large variety of interesting intermediates and products. The synthesis of Grignard reagents from alkyl or aryl halides and metallic magnesium is known to be highly exothermic (enthalpy of reaction typically around 300 $kJ \cdot mol_{Mg}^{-1}$). Due to sluggish reaction start and potentially deactivated (oxidised) magnesium large accumulation of unreacted halide components may occur. When the reaction suddenly starts with a lot of accumulated raw material, the evacuation of heat cannot be handled anymore. Consequently, a large temperature increase results capable to trigger the decomposition of the already formed Grignard reagent that leads finally to a disastrous thermal runaway.

The synthesis of methylmagnesium chloride starting from metallic magnesium and methyl chloride gas in an ether as solvent is chosen as the Grignard model reaction to exemplify the procedure. Having a three-phase system consisting of solid magnesium, liquid solvent and a gaseous halide component presents an additional challenge.

The reaction calorimeter RC1 is a widely used tool in the safety and development labs to determine the thermal data (heat capacities, enthalpies of reaction) and additional potential dangers of exothermic reactions such as accumulation. The effects of various process parameters can be tested and safe conditions defined. Measurement of the heat flow gives thereby on-line information about the advancement of the chemical reaction.

Applying the same heat balance methodology at a larger scale such as in a pilot facility or even a production plant is a way to monitor critical reactions and maintain safe conditions at all times. The concept of a heat balance is applied here to the production of methyl-magnesium chloride in a pilot scale reactor where the accumulation of methyl chloride is calculated and monitored on-line. The necessary technical requirements and possible pitfalls are shown and recommendations are given to obtain meaningful results.