Visualising the dangers of the chemical reaction steps

Wat are the dangers with chemical reaction steps? The cause of loss of a hazardous substance from a chemical reactor is complex and always consists of a combination of characteristics that come from different risk areas. Figure 1 shows the «and-shortcuts» of the prerequisites for an out of control reaction.
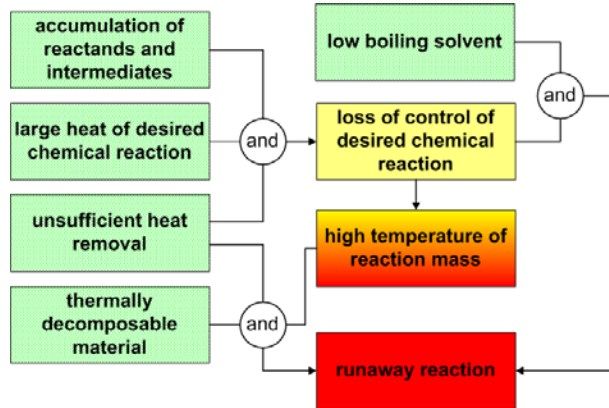

Figure 1

Reasons for accumulation of reagents or intermediates	**Reasons for insufficient heat removal**	**Reasons for elevated temperature**
• Wrong assumptions on reaction kinetics • Feed rate too high • Temperature too low • Inadequate mixing • Initiation wrong or omitted inhibiting impurities	• Inadequate cooling capacity • Excessive thermal insulation • Wrong assumptions on heat transfer • Cooling system failure • Stirrer failure	• Wrong choice of temperature • Unintentional heating • Energy introduced by stirring • Coolant flow failure • Catalysing impurities

How to visualise the Risk module of the chemical reaction step?

The stability of the reaction systems will be visualised based on the defined operating conditions, of the calorimetric data of the desired reactions and of the decomposition reactions as well. On this base, the influence of process changes on the stability of the reaction systems will be visible. The risk of a thermal explosion will be assessed by the scenario of a runaway reaction due to a cooling failure followed by a decomposition reaction (figure 2).

Defining severity, probability and risk of a runaway of a chemical reaction step
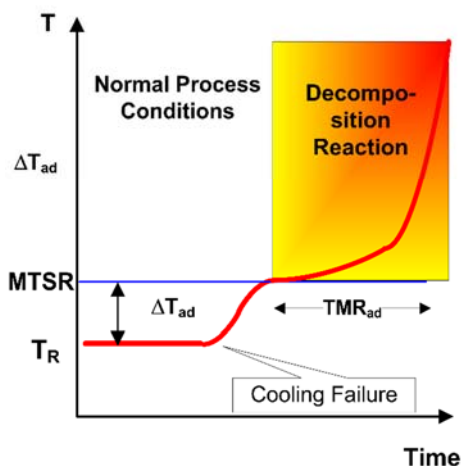
risk = severity ● probability

Figure 2

	severity	probability
high	$\Delta T_{ad} > 200K$	$TMR_{ad} < 8h$
medium	$50K < \Delta T_{ad} < 200K$	$8h < TMR_{ad} < 24h$
low	$\Delta T_{ad} < 50K$	$TMR_{ad} > 24h$

The runaway scenario is based on adiabatic conditions, because

- if a cooling failure occurs the heat removal is limited to a minimum;

- the adiabatic system is independent from technical parameters.

Therefore, the adiabatic system is a safe approach to judge the chemical process safety on big scale.

The following questions will help us to build up the runaway scenario and to provide data for the risk assessment.

Thermodynamic questions:

1. Can the process temperature be controlled by the cooling system? (Method: reaction calorimetry)

2. What temperature can the runaway of the desired reaction reach? For that purpose, we use the concept of Maximal Temperature of the Synthesis Reaction (MTSR). (Method: reaction calorimetry)

3. What is the boiling temperature T_b of the reaction mass in relation to MTSR?

4. What amount of the reaction mass can evaporate when MTSR is reached?

5. What temperature T_{end} and what pressure $P(T_{end})$ can the runaway of the decomposition reaction reach? (Method: DSC, RADEX, SEDEX).

Kinetic questions:

6. At what moment does the cooling failure has the most serious consequences? (Method: reaction calorimetry)

7. Of what speed is the runaway of the desired reaction? (Method: reaction calorimetry)

8. Of what speed is the evaporation of the reaction mass?

9. Of what speed is the runaway of the decomposition reaction starting at MTSR? (Method: DSC, RADEX, SEDEX)

The energy of reaction or of decomposition is a direct measure of the severity of a runaway. So the severity of the runaway can be evaluated using the levels of temperature attained if the desired reaction (question 2) and the decomposition reactions (question 5) proceed under adiabatic conditions. The probability can be evaluated using the time scale: If there is enough time left (questions 5 and 6) after the cooling failure (question 4) to take emergency measures before the runaway becomes uncontrollable, the probability of the runaway will remain low. The probability that at process deviation a runaway reaction starts is much bigger when the time frame—that is left to take countermeasures—gets smaller. The thermodynamic value ΔT_{ad} and the kinetic value Time to Maximum Rate at adiabatic conditions (TMR_{ad}) determines the thermal risk of a runaway. The experience shows that three levels of severity and probability are sufficient for the risk assessment: high, medium and low (figure 2).

For a deeper analysis of the reaction process see MORE