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Process Safety

NEWSLETTER 2012-03: Assessment of Thermal Stability

The assessment of thermal stability associated with chemical processes is typically based on a cooling failure scenario. For typical process times, the thermal stability assessment is reduced to the determination of the severity and probability of triggering the runaway of a secondary reaction.

Assessment of Severity

The adiabatic temperature rise is a good measure for the severity of a runaway reaction. It can be readily calculated by dividing the specific heat of decomposition Q with the specific heat capacity c_p:

$$\Delta T_{ad} = \frac{Q}{c_p}$$

The adiabatic temperature rise is not only important in determining attainable temperature levels, but also to assess the dynamics of a runaway. As a general rule, high energies result in fast runaways often with gas generation, while smaller energies result in slower temperature increase rates. The assessment criteria:

$\Delta T_{ad} > 200$ K	High severity
$50 < \Delta T_{ad} < 200$ K	Medium severity
$\Delta T_{ad} < 50$ K and no pressure build up	Low severity

Other factors (e.g. release of flammable or toxic gases, foaming, material compatibility issues) should be considered in the assessment. With regard to gas generation hazards, it should be emphasised that especially organic chemicals at higher temperatures generally tend to decompose to smaller fragments that are often volatile or even gases. Thus, gas generation or pressure build up due decomposition reactions are more likely for highly energetic decomposition reactions.

Assessment of Probability

The probability of the hazards due to decomposition reactions can be evaluated using the time scale: In truly adiabatic systems, heat generations will always cause self-heating and only the self-heating time gives an indication whether a heat generation should be regarded as hazardous. E.g. after a cooling failure, if there is enough time left to take emergency measures before the runaway becomes too fast, the probability of the runaway will remain low. For this purpose, the concept of Time to Maximum Rate under adiabatic conditions (TMR_{ad}) has been proven to be very useful. TMR_{ad} represents the time remaining until the self-heating rate reaches its maximum. TMR_{ad} can be approximated for a given starting temperature T_0, knowing the specific heat capacity c_p of the mixture or material, the activation energy E of the decomposition and the specific heat release rate $q(T_0)$ at the starting temperature:

$$TMR_{ad}(T_0) = \frac{R \cdot T_0^2 \cdot c_p}{E \cdot q(T_0)}$$

This equation assumes a 0^{th} order reaction kinetics, which is generally conservative.

The assessment criteria:

TMRad < 8h	High probability
24h < TMRad < 8h	Medium probability
TMRad > 24h	Low probability

The assessment of probability using TMR_{ad} should be seen in context with the severity of the runaway and the implemented countermeasures.

Runaway Risk Assessment

Since risk is defined as a combination of severity with probability, the risk due to decomposition reactions can be expressed as below:

		Probability		
	Risk	high	medium	low
Severity	high	high	high	medium
	medium	high	medium	low
	low	low	low	low

Heat dissipation to the environment

If the generated heat of a decomposition can be dissipated to the environment via heat transfer through the material and the natural cooling capacity at the material surface, only limited low hazard self-heating can occur and hence the risk due to decomposition will be low. For viscous liquids or solids this heat dissipation model is typically described by the Thomas thermal explosion model or its extension by Boddington et al. and is among other things based on a given material geometry, a heat conduction in the material according to the Fourier law, constant physical and heat transfer parameters and a constant exposure temperature.

Even for this line of safety rational, TMR_{ad} plays a vital role as it characterises the self-heating kinetics of the decomposition. With some conservative assumptions regarding the heat transfer and surface cooling properties of the material, the following can be shown:

- Layers of solid material with the ambient temperature that yields a TMR_{ad} of 24h will only show limited low hazard self-heating and consequently a low risk due to decompositions, if the layer thickness is less than 10cm.
- Solid material in standard 55 US gallon (208L) drums (height-diameter-ratio=1.5) will only show limited low hazard self-heating and consequently a low risk, if the TMR_{ad} of the ambient temperature is in excess of 240h or 10 days.

Further reading:

1. Gygax R. Fact-finding and basic data, Part II Desired chemical reactions. in 1st IUPAC-Workshop on Safety in Chemical Production. 1991. Basel: Blackwell Scientific publication.
2. Townsend D.I. and J.C. Tou, Thermal Hazard evaluation by an accelerating rate calorimeter. Thermochimica Acta, 1980. 37: p. 1-30.
3. Gygax R., Thermal Process Safety, Data Assessment, criteria, measures, ed. ESCIS. Vol. 8. 1993, Lucerne: ESCIS.
4. Stoessel F., Thermal Safety of Chemical Processes, Risk Assessment and Process Design. 2008, Weinheim: Wiley-VCH. 374.
5. Thomas P.H., Trans. Faraday Soc., 1958, 54, 60
6. Boddington T., Gray P. and Harvey D.I., Phil. Trans. R. Soc. London. A270, p.467 (1971)

Our services for you:

- Training on Chemical Reaction Hazards
- Assessments Chemical Reaction Hazards of reactions and processes:
  - Support in the design of a safe process
  - Calculation, estimation and assessment of thermokinetic data and the physico-chemical properties of substances
  - Engineering of safety measures (processes, operating procedures, etc.) to keep chemical reactions under control and prevent exothermic decomposition (runaway reactions)
  - Engineering of mitigating measures to limit damage (e.g. decompression)
- Risk analysis:
  - moderation, preparation and actualisation of risk analyses of chemical processes
- Design of pressure relief systems
- Incident investigations

If you have further question or just want to discuss, please do not hesitate to get in touch with us.

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With best regards
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