Hazardous-Chemical Reactions

SWATI UMBRAJKAR, PhD

Chemical reactions on an industrial scale are frequently associated with considerable heat exchange. Large amounts of energy can be released when decomposition reactions are unintentionally initiated. The catastrophic effects that are brought about with the release of such energies are well-known. The actual destructive force originates from the rapid release of pressure contained within the process equipment. Hence, the identification, assessment and characterization of both intended and—more importantly—unintended exothermic reactions are critical for ensuring the safe scale-up and operation of a chemical process.

Chemical reactivity hazards can be grouped into general categories, such as:

- Self-reactive materials (polymerizing, decomposing and rearranging).
- Reactive with other materials (oxygen and water).
- Mixing of two or more chemicals in an intentional chemical process.

General situations involving chemical reactivity hazards include:

- Mixing or physical processing (blending, milling and distillation).
- Intentional chemistry (batch, semi-batch or continuous processes).
- Transportation, storage, handling and repackaging (warehousing or tank storage).
- Unintentional reactions.

Safety and environmental regulations require systematic risk analyses to be carried out on potentially hazardous processes in production plants, pilot plants and auxiliary installations. The risk-assessment strategy generally consists of determining reaction/decomposition temperatures, exotherm-initiation (onset) temperatures, pressure generation, water reactivity, sensitivity to light and air, and spontaneous combustion. Additional tests regarding compatibility, pyrophoricity, peroxide formation, thermal stability, and shock and friction sensitivities could also be included as a part of the assessment for chemical reactivity hazards.

Runaway scenario design is a powerful method that can be employed for conducting thermal process safety analysis of a batch, semi-batch or continuous process, taking into account the thermal characteristics of both the desired and undesired reactions. This strategy additionally involves determining the maximum temperature of the desired reaction in case of cooling loss, as well as the maximum temperature of the process due to decomposition reactions. Depending on the energy potential, the severity of the consequences of a runaway reaction can be assessed, and then combined with the likelihoods of various temperature-control failures, to estimate the risks of personnel injury and property loss. This data could

be used to develop and implement process improvements and contingency plans that are both appropriate and economically feasible. For safe self-reactive material storage, the rates of heat production and dissipation as determined by the time to maximum rate and cooling curves should be compared.

Skills & Disciplines

The understanding of thermal hazard potential requires various skills and disciplines, such as process design in which the mode of operation is an important factor. For example, a batch reaction—with all reactants charged initially—could be more difficult to control than a semi-batch operation because one of the reactants charges progressively as the reaction proceeds.

Another critical discipline comes in the form of engineering. Design and layout of the plant/equipment, built-in controls, and heating and cooling system capacities are important in this context. Moreover, the chemical nature of the process and behavior of the product must be known, not only under normal reaction conditions, but also in case of unexpected deviations (side reactions, accumulation and intermediate instability). The thermo-physical properties of the reaction masses and the kinetics of the chemical reaction are also of primary importance (heats of reaction and Arrhenius relationships).

It is critical to obtain chemical reactivity data under both the desired and undesired process conditions via experimental testing to ensure the safety of a chemical process. When processing exothermic chemical reactions—including thermally unstable substances and mixtures—remember that hazards arise from heat and pressure generation. Chilworth Global has the resources to provide assistance in understanding chemical reactivity hazards as listed in the accompanying chart.

Equipment	Scale	Data Recorded
Differential Scanning Calorimetry	2 to 10 mg	Thermal activity, onset temperature, heat release magnitudes
Accelerating Rate Calorimetry	2 to 5 g	Onset temperature, temperature and pressure rise rates, volume of gas generated, heat release magnitudes
Carius Tube	10 to 15 g	Onset temperature, temperature and pressure rise rates, volume of gas generated
Reaction Calorimetry	70 mL to 1.5 L	Reaction heat, adiabatic temperature rise
Micro-Stirred Reaction Calorimetry	1 to 100 mg, µL	Reaction heat, adiabatic temperature rise
Adiabatic Pressure Dewar Calorimetry	800 mL	Onset temperature, temperature and pressure rise rates, volume of gas generated, runaway reaction vent sizing information
Vent Size Package	100 mL	Onset temperature, temperature and pressure rise rates, volume of gas generated, vent sizing information for runaway reactions

For more information, please contact Chilworth Global Chemical Process Evaluation Group Manager Swati Umbrajkar, PhD, by phone at 609.799.4449, by fax at 609.799.5559 or by e-mail at sumbrajkar@chilworth.com [1]*. You may also visit www.chilworth.com* [2]*.*

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