Process Safety Information Using Calorimetric Tests and Techniques for Safety, Compliance and Business Purposes

Summary:

Conducting chemical reactions in a safe and compliant manner on a global basis requires process safety information for compliance and risk management purposes. Obtaining this information may in certain cases be perceived as a difficult or complex task. However, our experts at Fauske & Associates, LLC (FAI) successfully deal with these requests by using proven techniques and accepted methodologies on a daily basis. We can use any of the techniques described in this section to meet your requests for a safer scale-up at any stage of development (kilo-lab, pilot-plant and full-scale commercial).

Desired Reaction:

Chemists, engineers, or managers involved in the development or commercialization of batch or continuous chemical processes understand the need for basic thermodynamic and kinetic data for the desired reaction. This information allows in part for the reaction to be optimized.

Worst-Case Scenario:

From a risk management and process safety perspectives, it is critical to understand how robust the desired reaction is to ensure that minor process changes do not result in catastrophic events, e.g., thermal runaway reaction, sudden decomposition reactions, etc. These undesired scenarios can result in a sudden uncontrolled batch temperature and/or pressure, which are significant process safety hazards that can if ignored lead to severe employee(s) injury or even death.

Compliance and Business:

In the United States, United Kingdom, Europe, and many other countries, there are compliance requirements that tend to have a common theme related to the requirement for adequate process safety information. It is requisite that companies have the proper level of this information to ensure these processes can be conducted safely under the desired and worst case scenarios, to ensure in part for worker safety. An added benefit, from a business perspective, is that it reduces the risk of a business interruption.

In the U.S., the Occupational Safety and Health Administration (OSHA) have several compliance standards applicable to all companies. The “general duty clause” (OSHA Act of 1970 Sec. 5 Duties) requires in part an employer provide a workplace free of recognized hazards to all employees. The Hazard Communication Standard (CFR 1910.1200) requires for hazard identification and communication and the specification of safeguards to avoid injury to employees. The Process Safety Management Standard (29CFR 1910.119) requires processes covered under this standard have adequate process safety information. The OSHA PSM Standard also recommends employers follow the guidance in this regulation for processes not direct covered by it. Since 2011, OSHA has had a National Emphasis Program for chemical process, which actively inspections plants to ensure compliance to OSHA Standards.

In order to ensure proper emergency sizing of relief devices for a worst-case scenario, DIERS and API methodologies must be employed, as needed. The tools and expertise to meet these important items are described in this section.

***Process Safety Strategy*:**

The following items should be considered in relation to process safety and can be accomplished using a variety of calorimetric tools and techniques:

Preliminary hazard assessment:

- Determine the thermal stability of all reaction components/mixtures within the minimum and maximum process temperatures attainable under a worst-case scenario
- Identify unwanted interaction between reagents and solvents
- Identify potential reaction contaminants that may have an inhibitory or catalytic effect on the desired reaction.

Quantification of desired reactions:

- Determine the heat of reaction and off-gas rates for the desired and quench reactions, including the heat resulting from accumulation of reagents or slow forming intermediates
- Determine the maximum adiabatic temperature for the reaction, and determine the basis of safety relative to the estimated boiling point of the reaction mixture
- Understand the relative rates of all chemical reactions at different temperatures

Quantification of adverse reactions:

- Assess the thermal stability of the reaction mixture over a wide temperature range
- When optimizing the robustness of the process, consider other reaction variables, such as pH, concentration, conversion rate, off-gas rate, stability of starting and product substrates in solution and as a slurry
- Consider the potential and impact of unwanted vapor-phase reactions
- Develop a chemical-interaction matrix for materials present in the reaction mixture, classify the reactivity and communicate this information to operational personnel
- Emergency relief device sizing for protected plant vessels is essential for reactions that have the potential to become a thermal runaway hazard and/or initiate a thermal decomposition resulting in uncontrolled heat/pressure generation

Plant considerations:

- Conduct a basic energy balance to consider the heats during various additions, heat generated during the chemical reaction, and the heat removal capability of the plant reactor system – remember to include reactor agitation as a source of energy
- Consider the impact of possible deviations from the intended reactant charges and operating conditions
- Identify all heat sources connected to a reaction vessel and assume the maximum possible worst-case scenario
- Determine the effect of the lowest possible temperature to which the reactor heat-transfer fluid could cool the reaction mixture
- Consider the impact of temperature gradients and other issues, such as increased viscosity, freezing at reactor walls, fouling, and so on, in plant-scale equipment

General chemistry and engineering design concepts:

- Design reactions that occur fairly rapidly
- If possible, avoid batch reactions in which all the potential chemical energy is present at the onset of the reaction
- Use semi-batch processes for exothermic reactions in which the batch temperature and any off-gassing can be maintained through controlled addition of the reagent
- For highly exothermic reactions, avoid using temperature control of the reaction mixture as the only means for limiting the reaction rate
- When scaling up a reaction, account for the impact of vessel size on heat generation and heat removal: the volume of the reaction mixture increases by the cube of the vessel radius but the heat-transfer area increases by the square of the radius

A comprehensive hazard evaluation should be conducted using appropriate estimation and experimental techniques to identify potential reaction hazards in materials, as well as the desired and adverse reactions. We use differential scanning calorimetry (DSC), Advanced Reactive System Screening Tool (ARSST) and reaction calorimetry (ChemiSens), as needed. Identify any adverse or thermal runaway reactions and, if needed, characterize them using adiabatic calorimetry, such as ARC (Accelerating Rate Calorimeter) and TAM (Thermal Activity Monitor). When required, the vent size can be determined using Design Institute for Emergency Relief Systems (DIERS, an AIChE industry alliance) methodology with data generated using an ARSST or Vent Sizing Package II and DIERS methodology.

In order to obtain a rapid and meaningfully understanding of a reactive raw material/product in terms of decomposition kinetics, e.g., SADT (Self Accelerating Decomposition Temperature) and TMR (Time to Maximum Rate), we use AKTS-Thermokinetics Software. SADT is commonly used for process and transportation purposes, while TMR is used mainly for process safety determinations.

This section provides more detailed information on each test and technique used for safety, compliance, and business purposes. It is critical to appreciate that data interpretation of the test(s) information is important and it is essential to work with our experts who can provide you with a clear understanding of significant issues.