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Safe process development from reaction hazards testing

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Abstract

A thorough, in-depth understanding of the reactive nature of chemical processing operations is the first step to accomplishing the reduction of risks of these operations to a tolerable level. This understanding may be obtained through a laboratory evaluation using recognized and accepted process safety testing technologies as well as the conventional process hazards analysis. A systematic process safety testing program characterizes the reactive nature of both the desired and undesired chemistry. These data are needed to define the critical limits of temperature, pressure, power output, concentration, and dosing rates of processes involving reactive chemicals. The minimum basic data are the variation of energy (or power), temperature and pressure as a function of time, and reaction mass composition. The realistic use of these data requires an understanding of both the limitations of some laboratory data for scale-up and acceptable safety margins for industrial size operations. This paper will briefly review the current regulatory environment for chemical process safety, describe the integration of various calorimetric test techniques, and illustrate the use of data from isothermal differential scanning, and adiabatic calorimetry for improving process safety. An example, taken from the investigation of an accident involving the reaction between an amine and chlorine-substituted derivative, demonstrates the use of calorimetric data in understanding the origin and progress of the accident. Suggestions for how to improve process safety, based on the calorimetric information are also presented. © 2001 Published by Elsevier Science B.V.

Keywords: Safe process development; Process hazards analysis; Energy

1. Introduction

Chemical reactions, typical of the polymer, resin, fine chemical, and pharmaceutical industries, are frequently exothermic [1–4]. The uncontrolled release of this energy has been the cause of many serious industrial accidents. Another potential hazard is that some of the feeds, products, or intermediates involved in a manufacturing process may be highly unstable and, under the wrong conditions of processing or even storage, could lead to fire and explosion hazards [5].

Experienced chemists are often aware of potential problems because of their knowledge of the chemical species involved; but frequently this knowledge alone is insufficient to ensure safe operation of the process facilities. It is now widely accepted that the chemist's experience must be supplemented by bench scale testing, using suitable test procedures, to evaluate all steps in a chemical process for their potential hazard and to test the various feeds, products and intermediates [6].

Over the last 15 years several calorimeters have been commercially produced to provide much of the data required for hazard evaluation. Adiabatic and the

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other commonly used calorimetric techniques will be discussed later in this paper. Additionally, an application of calorimetry will be presented that helped explain the circumstances and causes of a chemical processing accident.

First, the links between federal legislation standards, product maturity, and required information about potentially hazardous scenarios will be briefly discussed.

2. Process safety management

The chemical process industry (CPI) is governed by legislation, in the form of standards and rules that cover the day-to-day, year-to-year, and cradle-to-grave operations for projects. The standard of particular relevance to process safety (in USA) was promulgated in 1992 by the Occupational Safety and Health Administration (OSHA) 29CFR 1910.119, Process Safety Management (PSM) of Highly Hazardous Chemicals [7].

The environmental protection agency (EPA) has a rule, "Risk Management Program", 40 CFR 68. This rule is similar to OSHA's PSM standard from a technical viewpoint, but there are administrative differences with additional sections to address worst-case scenarios (WCSs) for major events and community right-to-know requirements. EPA uses a tier approach that distinguishes company size and quantities handled into three levels of rule compliance. OSHA does not make this distinction — if a company is covered by the standard, then full compliance is required.

Table 1 lists the titles of each section, or element, of OSHA's process safety management standard. Of these 14 elements, five address aspects of the standard that require the employer to have reliable and pertinent process safety hazards data. Table 2 provides brief description of the intent of the five elements highlighted in Table 1.

A full assessment of the safety of a chemical process should be founded on specific hazards test data for the desired, and undesired, chemistry and process operations [1–6]. The OSHA standard, process hazards analysis (PHA) (paragraph (e)), lists six methodologies that may be used, together with the category "other appropriate methods". PHA meth-

Table 1
Fourteen elements of OSHA's PSM rule

Employee participation: (c)
Process safety information: (d)
Process hazards analysis: (e)
Operating procedures: (f)
Training: (g)
Contractors: (h)
Pre-startup safety review: (i)
Mechanical integrity: (j)
Hot work permit: (k)
Management of change: (l)
Incident investigation: (m)
Emergency plan and response: (n)
Compliance audits: (o)
Trade secrets: (p)

odologies are well described in several references [7–10]. There is no one method that is required and the choice is left to the process owner and the type of manufacturing process being assessed. However, regardless of the hazard analysis technique chosen, the need for accurate and reliable process safety data is unavoidable. Data for the reactants may be available from the open literature, MSD sheets, or company records. However, hazards data for the process including intermediates and product(s) will not usually be found in the open literature due to the proprietary nature of the manufacturing process. These data can only be obtained from appropriately designed experiments using the correct testing techniques [3,4,6,10].

The majority of these test techniques are calorimetric generating data that are transformed into relevant process safety information by expert interpretation. Ultimately, the *basis of safety* and the *window of safe operations* are obtained from the combined hazards test data. The *basis of safety*, derived from the WCS analysis, defines specific operating conditions that must be adhered to in order to ensure that the WCS is not realized. The *window of safe operations* defines the ranges for each operating condition (temperature, pressure, feed rates, hold times, etc.) within which process deviations are considered as normal and acceptable.

Testing for operational hazards (gas, vapor, and dust explosivity; impact and shock sensitivity; electrostatic generation and accumulation potential) will not be

Table 2
OSHA PSM abstract for selected elements of Table 1

Section/paragraph	Intent of paragraph
Process safety information: (d)	To provide complete and accurate information concerning the process which is essential for an effective process safety management program
Process hazards analysis: (e)	To develop a thorough, orderly, systematic approach for identifying, evaluating, and controlling the hazards of processes involving highly hazardous chemicals
Operating procedures: (f)	To develop and implement written operating procedures that provide clear instructions for safely conducting activities in each process consistent with the process safety information. Operating procedures shall address at least the following: initial startup, normal operations, temporary operations, emergency shutdown including the conditions under which emergency shutdown is required, emergency operations, normal shutdown, and startup following a turnaround, or after an emergency shutdown
Pre-startup safety review: (i)	To make sure that for new facilities and significantly modified facilities, a pre-startup safety review is completed before introduction of chemicals. The pre-startup safety review will assure that: construction is in accordance with design specifications; safety, operating, maintenance, and emergency procedures are in place; process hazards analysis recommendations have been resolved; training of operating employees is completed
Incident investigation: (m)	To require the employer to investigate all incidents that result, or that could reasonably result, in the catastrophic workplace release of highly hazardous chemicals. The employer must establish a system to promptly address, resolve and document the report findings; resolutions and corrective actions, communicate this information to appropriate personnel

covered in this paper, but is an integral part of process safety evaluations.

“Identifying, evaluating, and controlling chemical process hazards” (paragraph (e) of 29CFR1910.119; see Table 2) is accomplished in a practical sense by:

- establishing the worst-case scenario(s) (WCS);
- defining the most severe credible worst-case scenario(s) (MSC WCS);
- developing the appropriate lines of defense for MSC WCS;
- defining the basis of safety;
- setting the envelope or window of safe operations.

The first two actions require direct and indirect information generated by hazards testing designed to closely mimic the target chemical process. In turn, these data are then used to evaluate the WCSs, consequences of process deviations and hence, lines of defense [9]. Further data assessment and considerations lead to the basis of safety and window of safe operation for the process. The test data not only apply to WCSs but are also one of the basis used to develop the operating procedures for the process.

3. Hazards testing and process safety — how much and when

As suggested in the previous section, an entirely adequate and cost effective hazards analysis for the five OSHA PSM elements, identified in Table 1, may be gained through a diligent examination of the safety and potential hazards of the process. A “diligent examination” implies that the desired (intended or primary) process chemistry and unit operations, and the undesired events (mal-operations) are examined in sufficient detail to provide at least quantitative limits on process variables, such as, maximum or minimum temperatures and pressures, feed rates, and temperature and pressure rise rates. Within these limits the process may be thought of as “safe”; or more accurately phrased, “the risk of the process has been reduced to a tolerable level”. Included in this examination is hazard testing for the raw materials, intermediates, final product and perhaps, secondary product(s). Simply put, the “desired reaction” is what you planned to happen and have designed for; the “undesired event(s)” is any process deviation or upset that is not part of the desired manufacturing process. Fig. 1 provides a schematic

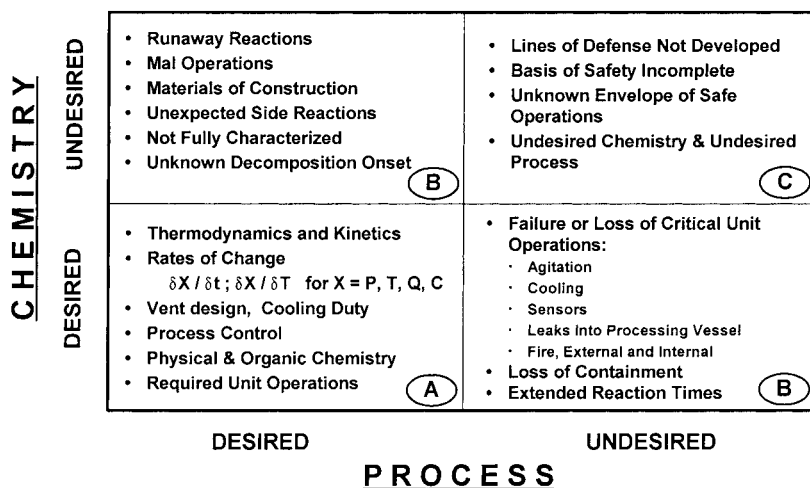


Fig. 1. Relationship between desired and undesired processes and chemistry. P = pressure, T = temperature, Q = reaction power, C = material quantity, t = time.

overview of desired and undesired chemistries and processes.

3.1. Desired and undesired processes and chemistries; levels of hazard evaluation

There are three levels of hazard evaluation that pertain to an assessment of the desired and undesired processes and chemistries.

3.1.1. Level A hazard evaluation

Box A, Fig. 1, suggests that during the course of developing a manufacturing process for a chemical product, the topics shown in this box are generally understood and quantified to a reasonable level of detail through normal process development activities. Most of these data are also applicable to hazard evaluation of the process.

The data obtained from this level are directly related to the range of operating conditions, and design options considered, and may be summarized as follows:

- for raw materials, intermediates, and products:
 - thermal stability; deflagration and detonation;
 - reactivity to common process materials;
 - reactivity towards water, moisture, and air;
 - flammability (gases, vapors and mists, liquids, and solids);

- impact and friction sensitivity;
- inter-reactivity of process materials that are unintended;
- specific, fixed values for temperature, pressure, time, and concentrations;
- variations in operating parameters for normal process are also considered;
- temperature, $\pm 10^\circ\text{C}$;
- feed order of reactants;
- feed rate at higher/lower than planned levels;
- hold time variations;
- specific, allowed process variations.

Level A hazard analysis provides an adequate assessment for processes *operating normally* (the desired reaction) and is therefore a major source of process safety information, paragraph (d) of Table 2.

3.1.2. Level B hazard analysis

Box B, Fig. 1, is the consideration of known failure situations or WCSs *that are credible* for the target process. Examples of typical WCSs are the following:

- loss of, or inadequate, cooling;
- high local temperature caused by loss of, or inadequate, stirring;
- fire or external heating of the vessel or storage tank;
- lack of adequate heat conduction;
- pressurization of an enclosure by an oxidizing gaseous intermediate;

- phase separation of a previously homogenous mixture;
- sudden, or rapid, mixing of previously separate phases;
- extended reaction and/or cycle time favoring autocatalytic reactions;
- the unexpected introduction of a reactant, catalyst, or other material;
- the unexpected depletion of an inhibitor or other chemically stabilizing material;
- accumulation of reactants because reaction is rate limited.

Level B hazard analysis is the minimum standard that can lead to acceptable levels of safety for most processes and becomes the basis for providing the information and data for PHA (paragraph (e)) and operating and procedures (paragraph (f)).

3.1.3. Level C hazard evaluation

This level, box C of Fig. 1, is concerned with the consideration of specific, abnormal conditions leading to unwanted exothermic activity not covered in level B. For example:

- cross contamination from adjacent processes, including inter-reactivity;
- variations in raw material quality;
- failure of inerting system, or vacuum, in reactor or storage vessel;
- self-polymerization of monomers in storage.

Level C concentrates on specific situations revealed by PHA such as What-If or HAZOP procedures [8] that probably require specific testing strategies. The information obtained at this level provides additional information for PHA and operating procedures.

3.2. Process safety and product life cycle

The products that are manufactured by a chemical company have reached commercial status by a number of routes. The three most common situations are the following:

- Product and process development, from conceptual R&D through pilot scale to full scale manufacturing, is performed entirely by the company.

- License, or purchase technology, from another company — the product is close to commercialization.
- Toll manufacturing of an intermediate or final product for another chemical company.

The absolute life cycle of the product is the same for all three situations. However, the relative life cycle, from the viewpoint of the current process owner, starts at different points along the absolute time line. Each commercial development route presents a different set of challenges to providing a safe working environment free of unacceptable process and chemical hazards.

3.2.1. From R&D to manufacturing

In this situation the manufacturer will likely design a molecule of interest that may be a variant within an existing molecular family, or is a new family. The molecule must be prepared, at the lab scale, in sufficient quantities to perform trials and applications testing to satisfy any number of commercial suitability screens. Although quantities handled are small (typically less than 500 g or 5 l), potential hazards to personnel exist and need to be identified and evaluated. If successful at the lab bench then scale-up to pilot and manufacturing scales normally follows. A hazards testing protocol, which follows the life cycle of a process, is shown in Table 3.

Two key features of Table 3 are worth noting. First, the testing is closely tied to the scale of the operation and the three hazard evaluation levels A, B, and C. For example, it is important to know the flammability of the materials and the shock or friction sensitivity of any newly synthesized chemicals, as well as reactants. Differential scanning calorimetry (DSC) and adiabatic calorimetry provide valuable information about the desired and undesired reactions and some WCSs that are relevant even at the lab scale. On the other hand, emergency relief design is normally of little concern at the R&D (bench scale), but is often appropriate at the pilot scale, and is critically important at the manufacturing scale.

Second, personnel responsible for the next step in product development can expect a full process safety package to be available from the previous level of operations. Hazards information is added to the package relevant to the new scale of operation. In other words, process safety management, and its

Table 3

Degree of hazards testing and assessment through product life cycle (1. Process hazard evaluation, including ranking assessments: F&EI, CEI, Mond indices; 2. Checklist; 3. What-If, What-If/checklist; 4. HAZOP; 5. Fault tree; 6. QRA, FMEA, etc.)

Life cycle stage	Hazard test technique	Hazard level	New product	New formulation	Process modifications
R&D bench	Calculations/books; flammability; DSC/DTA; adiabatic high ϕ ; impact/friction sensitivity	A	2 ^c	1/2 ^b	1 ^a
R&D pilot	Reaction calorimetry; adiabatic low ϕ ; venting requirements, if needed; flammability/explosion; friction sensitivity	B	3 ^{c,d}	2/3 ^d	2 ^{c,d}
Pilot/trial	Reaction calorimetry; adiabatic low ϕ ; venting requirements, if needed; flammability/explosion; friction and dust explosion potential	B	3/4 ^{e,f}	3 ^e	3 ^d
Manufacture	Dust explosion; adiabatic low ϕ ; venting requirements; flammability/explosion	C	4–6 ^g	4–6 ^g	4/5 ^{f,g}

^a Within R&D group: researcher + 1 other.

^b Within R&D group: researcher + process engineer.

^c Within R&D group: researcher, R&D supervisor + 1 other.

^d Within R&D department: researcher, R&D supervisor, hazard evaluation team.

^e Within R&D pilot: researcher, R&D supervisor, pilot plant supervisor, hazard evaluation team.

^f Within pilot/trial: project or process engineer, pilot plant supervisor, hazard evaluation team.

^g Within manufacture: process and project engineer, pilot plant supervisor, hazard evaluation team, SHE.

documentation, is an evolving and on-going activity integrated into product life cycle.

3.2.2. License or purchase technology

Companies license or purchase technology in order to shorten product development cycle times. Evaluation of the process safety information, which is part of the technology transfer package, is necessary in order to safely integrate the new product with company standards. This evaluation process may start, for the process of interest, at any point within the overall life cycle.

3.2.3. Custom manufacturing

In this situation the toll manufacturer frequently relies on the client to provide the process safety information. Rapid manufacture of the product is the hallmark of a successful toll manufacturer. Therefore, the need to reduce cycle time to the minimum while appropriately addressing the potential risks of the process presents a dilemma to the toll manufacturer. Recent accidents in this segment of the CPI indicate that potential hazards, arising from the process chemistry, may have been unidentified or unknown with (potentially) tragic consequences. An appropriate level of preliminary hazards testing, recommended from an effective process hazard evaluation,

is often all that is required to demonstrate the level of risk associated with the new chemical to be manufactured [11]. The required hazards testing may need to focus on verifying that the chemistry of the new process fits into the custom manufacturer's in-place process equipment with regard to cooling duty requirements and emergency relief system (ERS) for the reactor(s), storage and day tank(s).

Despite the obvious differences between cradle-to-grave product development, technology acquisitions, and toll manufacturing, the underlying principle of tying the nature and extent of hazards testing to the product life cycle is a key concern. Several benefits accrue by coupling testing with product and process development:

- ensures on-going personnel safety at all developmental stages of the product;
- provides up-to-date and relevant process safety that is available to all personnel;
- does not generate more information than is needed at the current stage (e.g. reactor vent sizing considerations are not a primary concern at the lab scale, unless the reaction generates a gaseous product);
- lessens the process safety hazards testing and assessment work-load for the latter stages of product life cycle;

- provides valuable information that will influence process development, at the design phase, rather than requiring last-minute process design change(s).

3.3. Process safety and hazards test data

Table 3 presents the link between product life cycle and hazards testing tied to progress through the cycle. The linkage of common hazards testing techniques with the five process safety elements is shown in Table 4.

Table 4 makes the point that for a typical process a *thorough* examination of the process, yielding process safety information in compliance with section (d), also serves to provide most of the data for PSM sections (e), (f), and (l). The assumption is that as the PHA turns up questions about WCSs, they can usually be answered from the data and analyses of the hazard testing indicated in Table 4. In particular, operating procedure limits on temperature, pressures, and other parameters, which are elements of the basis of safety and window of safe operations, are also obtained from the test data. Again, little additional test data may be required if the initial process information and PHA are fully complete. Data requirements for plant pre-startup safety reviews are similar but reduced to those for PHAs.

4. Calorimetric techniques for hazards testing

4.1. Development and evaluation of the desired reactions

4.1.1. Reaction calorimetry

Exothermic chemical reactions in the fine chemical and pharmaceutical industries, commonly carried out in batch multi-purpose chemical reactors, can be conveniently studied in reaction calorimeters. These devices are based around conventional jacketed laboratory reactors often 1 l in volume and can provide much valuable information about the safety and operability of chemical processes. Semi-batch reactions are particularly suited to this type of calorimetric investigation of the desired reaction.

A reaction calorimeter consists of a reaction vessel surrounded by a heating/cooling jacket. Silicone oil is

circulated through this jacket at high velocity. Because of the high mass flow rate of oil, the change in the oil's temperature as it passes through the jacket is small. The jacket is therefore essentially isothermal. The reactor and jacket can be fitted with a number of sensors measuring reactor and oil temperatures, pressures, pH, stirring speed, etc. In addition, feed streams can be pumped to the reactor from vessels on weigh scales at prescribed rates at any stage during the reaction. Operations at sub-ambient temperatures or with a reflux condenser are also possible. A central computer monitors and records the outputs from all sensors as well as controlling the experiment according to a user-defined plan. Fig. 2 shows a schematic of a typical heat flow reaction calorimeter.

The most common calorimetry method is heat flow, where energy output information is obtained from a knowledge of heat transfer through the reactor walls to the coolant circulating through the vessel jacket. Heat flow is calculated from the overall heat transfer coefficient, the wetted area, and the difference in temperature between the reactor and jacket. The desired reactions will be experimentally characterized in terms of:

- reaction enthalpy from the principal reaction, and side reaction(s) if present;
- degree of accumulation of reactant(s) from the desired reaction;
- global reaction kinetics;
- gas production as a function of time and temperature;
- instantaneous heat output from the desired reaction;
- power output and, therefore, full-scale cooling duty needed.

4.1.2. Enthalpy of reaction

Integration of the sum of the reaction and dosing power over the duration of the experiment(s) gives the total enthalpy release. This can be based on the mass of reactants or number of moles of a key component. If the latter option is chosen, then the key component should be a limiting species that is totally consumed in the reaction.

4.1.3. Reactant accumulation

If a reactant is added in a semi-batch fashion for part of an experiment and the kinetics of its consumption

Table 4
Types of hazards test data needed to satisfy five OSHA PSM elements

Hazards testing procedure	PS info (section d)	PHA (section e)	Operating procs (section f)	Pre-start up rev (section i)	Incident invest (section m)
Calculations/books/open literature	●				●
Flammable limits and flash points	●				●
DSC/DTA	●	●			●
Adiabatic high ϕ calorimetry	●	●			●
Reaction calorimetry	●				●
Adiabatic low ϕ calorimetry	●	●			●
Venting requirements	●	●			●
Flammability/deflagration versus detonation	●				●
Impact sensitivity	●				●
Dust explosion potential	●				●

are relatively slow, then its concentration will gradually increase. Conversely, if it is consumed rapidly, then its concentration will, at any point in the addition step, be essentially zero. The potential for an exothermic runaway reaction resulting, for instance, from loss of cooling will be proportional to the build up of this dosed component. The extent of this accumulation, and hence the potential hazard for this mal-operation, can be measured by determining the fraction of the total enthalpy release that occurs after dosing has ceased.

4.2. Development and evaluation of the un-desired reactions

The objective of this part of hazards testing is to determine the nature and extent of the consequences of a mal-operation (WCS) [5–7]. The basic data obtained from the testing will be pressure, temperature and power output as a function of time. These data can be transformed into rates and subsequently specific parameters such as time to maximum rate, t_{MR} , temperature of no return, T_{NR} , adiabatic temperature rise,

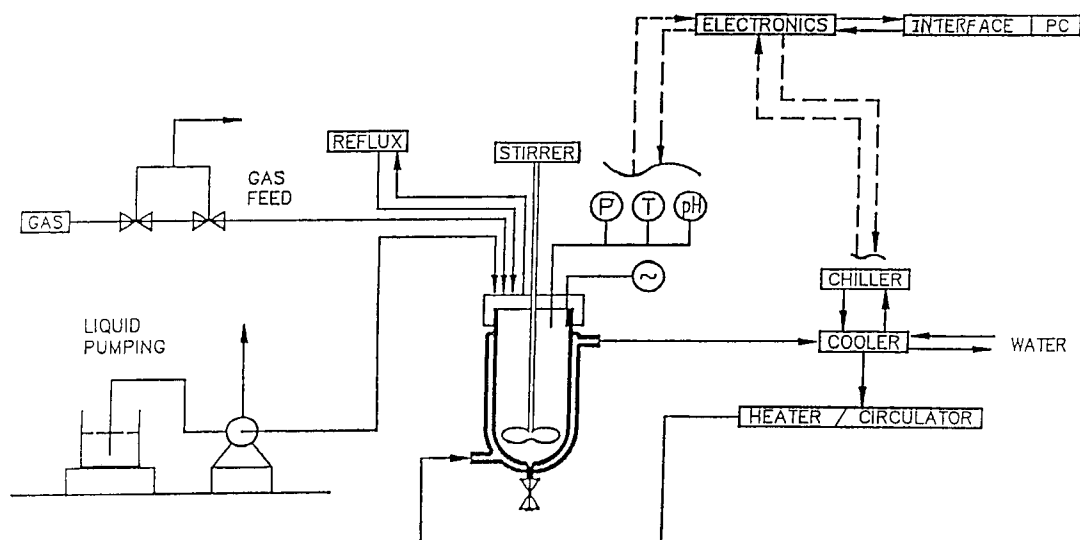


Fig. 2. Schematic representation of a reaction calorimeter (SIMULAR).

ΔT_{ADIAB} , approximate heats of decomposition, self-accelerating decomposition temperatures, T_{SADT} , global kinetics, etc. This information is used in process engineering to design the adequate reserve capacity of the cooling system and adequate ERSs to manage a runaway reaction.

Hazard evaluation is not merely a matter of performing calorimetry testing to determine thermal parameters. In fact, these data are secondary to the more important information — pressure and pressure rise rates as a function of time and temperature [1,6,10]. Fundamentally, the temperature of the reactor and its contents is of interest because this immediately informs those working in and around the vessel about the internal pressure and pressure rise rate. Certainly a detonation leads to catastrophic vessel failure but the unvented pressure rise, due to a runaway reaction, can also lead to major vessel failures. The premise that heat flow reaction calorimetry and DSC, e.g. gives an adequate and thorough hazard evaluation *is without merit* because neither technique provides any pressure data. Therefore, the consequence of pressure changes during the desired or undesired reactions is unknown and potentially hazardous.

At a screening level the Thermal Screening Unit, TS^{U} , and the Reactive Systems Screening Tool, RSST, provide both temperature and pressure information regarding the runaway characteristics of the chemical or mixture under consideration.

4.2.1. DSC

The DSC is a primary screening test. It indicates whether a material undergoes an exothermic or endothermic reaction and a general temperature range in which the reaction occurs. The DSC is often used to determine if further testing is required. The main pros and cons are summarized below:

- This test is often run before an adiabatic calorimetry test, a drop weight test, or when preliminary quantitative data is desired. Heats of reaction, heats of decomposition and heats of fusion can be determined for systems generating up to 100 atm of pressure.
- DSC data should be used with caution, avoiding any inference that the test conditions duplicate those that the material will experience in a plant environment [4,6].

- A typical DSC test uses 1–5 mg of material, sealed in a glass ampoule or crimp-sealed metal pan. The sample is heated from room temperature to an elevated temperature (150–400°C) at a user-selected ramp rate, often 5–20°C min⁻¹. Exotherms are usually detected by the DSC test at temperatures significantly higher than those routinely seen in plant equipment that are more adiabatic [4].
- Small changes in the composition of a material can have a significant effect on its thermal behavior. For example, a material may not decompose in the glass container in which the DSC test is done, but may be catalytically decomposed by the metal container used in plant production.
- No pressure information is available from this technique and consequently hazard evaluation from DSC data is at best incomplete and possibly misleading.

4.2.2. Isoperibolic mixing calorimetry

This test is used to measure the heat associated with the intentional or inadvertent mixing of chemicals. The enthalpy data gathered from this test can be used in the engineering of the reactor system. As an example, the heat measured can be used to size heat exchangers, determine subsequent temperature changes upon mixing and aid in assessing any further potential hazards. Inadvertent mixing situations can arise during loading, shipping, or storage situations, along with leaking reactor jackets or spills.

A variety of specific instruments are utilized depending on the specific mixing scenario of interest. The amount of sample used in a test can range from a few milligrams to a few liters. Temperatures under which mixing calorimetry tests can be performed range from –40 to 300°C.

Heat of mixing experiments are often followed by a DSC or other temperature ramped screening tests. This is done to determine if a secondary decomposition reaction occurs at a higher temperature which operationally may be reached in a system with limited heat loss.

4.2.3. Adiabatic calorimetry

Adiabatic calorimetry is used primarily as an aid in thermal hazard evaluation to measure rates of energy output, temperature, and pressure rises of desired or undesired chemical reactions. Under certain

conditions, the data may be scaled to larger vessels. Two principal types of adiabatic calorimetry are routinely used in the hazard evaluation context.

4.2.4. High thermal inertia adiabatic calorimetry

This type of calorimetric testing provides an opportunity to examine the thermal stability of materials under adiabatic conditions. The sample is brought to the start temperature and evidence for sample self-heating is sought (wait and search phase). If none is seen the sample temperature is rapidly raised by 5 or 10°C (heat mode) and the search for self-heating repeated. Once detected, the calorimeter switches to a tracking mode, also under adiabatic conditions, until the current exotherm is complete. These data, under some circumstances, lead to estimations of heats of reaction for the reaction mixture, onset temperature of exothermic activity and also pressure information, along with temperature and pressure rise rate information. In addition, when the chemistry is not too complicated, Arrhenius-type kinetic analysis may be performed.

The test is conducted in high thermal inertia equipment, using a sample size of 4–10 g and is not suitable for direct use in emergency relief design for reactive systems. The overall mode of operation of the adiabatic calorimeter is known as Heat–Wait–Search (HWS).

4.2.5. Low thermal inertia adiabatic calorimetry

A test similar in overall operation to that described above, i.e. HWS, may be used to determine times to maximum rate, t_{MR} , and give appropriate information about the vessel, temperature of no return, T_{NR} . These data may also be used to estimate the self-accelerating decomposition temperature, T_{SADT} . For low thermal inertia calorimetry the sample size is increased to 40–60 g and the test is conducted in low ϕ -factor (thermal inertia) equipment. The data are directly usable in emergency relief design for reactive systems. Fig. 3 shows a typical low thermal inertia calorimeter.

Low thermal inertia adiabatic devices are used to study the emergency relief need of reactive systems. They simulate real conditions, such that relief areas can be calculated from the data with minimal knowledge of physical properties and kinetics [4,6,8,10]. This reduces the computational effort and uncertainty involved in the interpretation of high thermal inertia data for vent sizing purposes.

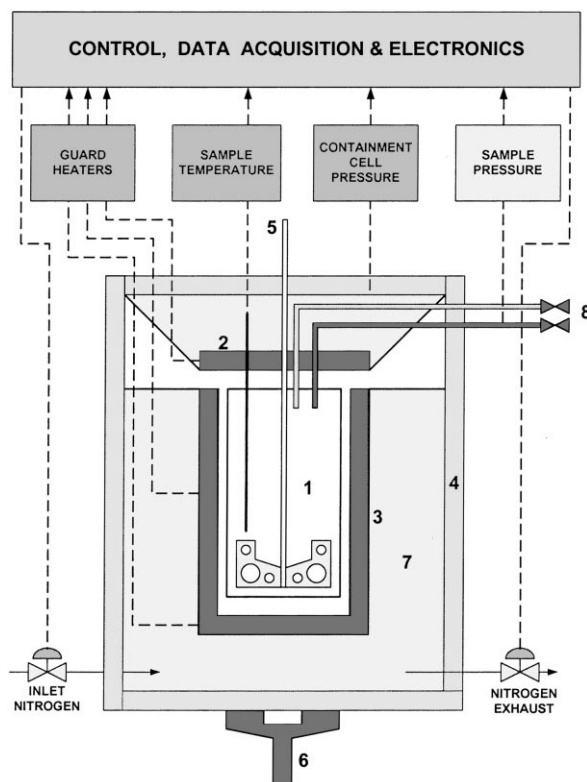


Fig. 3. Schematic representation of a low thermal inertia adiabatic calorimeter (PHI-TEC). Main components are: (1) sample can, 110 ml; (2) top heater; (3) side and bottom heaters; (4) containment vessel; (5) mechanical agitator; (6) magnetic agitator; (7) insulation; (8) feed and nitrogen lines.

Several modes of testing can be used to study different aspects of reactive venting. Some of the conditions that can be simulated are as follows:

- exothermic reactions, with or without external fire, with or without gas generation;
- endothermic reactions with external fire, with or without gas generation;
- degree of disengagement of vapor from the liquid reaction mass relieving through the emergency relief nozzle;
- turbulent or laminar flow;
- area-to-charge venting test (blow-down) or simulation of an existing relief.

Data are obtained in either graphical or tabular forms. Plots of self-heat rate versus temperature, temperature versus time, pressure versus time, log

pressure versus temperature and pressure rate versus temperature are most frequently used to study behavior of the chemical system. If the heat equivalent of the system is known or can be approximated, a measure of the enthalpy of reaction can be obtained.

4.2.6. Other calorimetry

Many process scenarios require more sophisticated measurements of total heat or heat flow. Examples of these include packed-bed, plug-flow reactors, systems where mass transfer may be rate limited and extreme high or low temperatures. Specialized calorimetric experiments can be designed to quantitatively measure the heats and heat rates under these conditions. Further, systems with extremely limited heat transfer, such as large storage vessels (>10,000 gal), powdery solids (e.g. as exists in large drying operations), materials spilled on insulation, may undergo thermal runaways at very low rates of heat generation. These systems require measurement of heat rates in the milliwatt to microwatt range.

4.3. Verification of ERSs for processing reactive materials

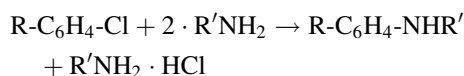
By definition, these systems are reactive and as such the data necessary to validate the ERS must be obtained experimentally. The verification of the ERS for reactive systems is handled as follows:

- Establish the credible worst case for the vessel of interest; this will be at least a fire engulfment scenario. Other WCSs are considered at this point with regard to their potential severity.
- Perform appropriate reaction runaway testing to confirm that the selected worst case is the most severe.
- Perform vent sizing calculations appropriate for reactive systems, using the data generated above, Design Institute for ERSs (DIERSs) design computations.
- Perform vent piping and header calculations, where appropriate.
- Compare with the in-place ERS.
- Offer recommendations regarding adequacy of existing ERS.
- Offer recommendations, if required, concerning alternative strategies for personnel and vessel protection if existing ERS is judged to be inadequate.

For completeness it should be noted that non-reactive vent verifications can be performed, without recourse to experimental work, using DIERS technology [10]. Recent publications by Leung [1] provides an overview of the calculation strategies that will be adopted.

5. Use of calorimetry in an accident investigation

An accident occurred during the manufacture of a secondary amine by mixing an aliphatic primary amine with a chlorine-substituted molecule.



Pilot plant studies had shown that the reaction could be run either in a batch or semi-batch mode. The required cooling duties were significantly different for the two modes. These studies had indicated that the batch additions of the chloro-derivative to the amine, at elevated temperatures, could be difficult to control thermally and so full-scale manufacture was started at ambient temperature with all reactants present in the reactor. The process in question was run several times prior to the incident.

5.1. Incident description

The batch proceeded normally with heat being applied to the reactor after a full charge of reactants had been added and the reaction exotherm led to the expected increase in temperature. However, when operators switched over to cooling the reactor temperature continued to climb. The subsequent runaway reaction was contained within the plant's vent header and catch tank. There was no loss of containment to the outside.

5.2. Available process information

Data from the pilot plant studies provided an indication of the power output of the reaction when performed at elevated temperatures. However, only limited pilot plant information was available that was applicable to the specific process being performed at the manufacturing scale or about the procedures being used at the time of the accident.

5.3. Incident investigation results

The exact reaction recipe and the finished product were tested using high thermal inertia adiabatic calorimetry. The results showed that the reaction was exothermic leading to an adiabatic temperature rise of about 218°C. This temperature rise would be sufficient to lead to product decomposition ($T_{\text{ONSET,DECOMP}} = 180^\circ\text{C}$), in the event of a major loss of cooling capability. The decomposition reaction was strongly exothermic and produced significant quantities of non-condensable gaseous decomposition products as evidenced by the pressure of the sample container at the termination of the adiabatic calorimetry tests. As is commonly the case with gross runaway decomposition reactions, a tarry, carbonaceous mass remained accompanied by the evolution of small molecule permanent gases such as CO_2 , CO and fragments of the parent molecules. In this type of calorimetric study, where the objective is to determine the extent of the runaway and its impact on the process equipment, the identity of the decomposition products and reactions is of lesser consequence than the accurate determination of dT/dt and dP/dt .

Fig. 4 illustrates the result of mixing the reactants at ambient temperatures in an adiabatic environment. The mixture exhibits a self-sustaining exotherm beginning at 45°C . The temperature/time plot shows that the desired reaction is nearing completion, under adiabatic conditions, at around $170\text{--}180^\circ\text{C}$. However, the decomposition runaway reaction is well underway at this point, as shown by the saddle point in the temperature/time curve. These deductions were confirmed by performing the same test on the reaction product that showed an identical trace through the $210\text{--}350^\circ\text{C}$ temperature range but without the thermal activity from 45 to 200°C , Fig. 5.

Fig. 6 diagrammatically summarizes the process safety information in terms of the desired and undesired reactions. Once T_{MAX} and T_{S} have been determined from experimental testing (heat flow and adiabatic calorimetry, respectively) the difference ($T_{\text{S}} - T_{\text{MAX}}$) can be evaluated. The numerical difference for low risk operations is usually at least 50°C . This is the “inherently safe” situation as shown in Fig. 6. As ($T_{\text{S}} - T_{\text{MAX}}$) decreases, even becoming negative, the situation becomes progressively more hazardous. If the onset temperature of the desired

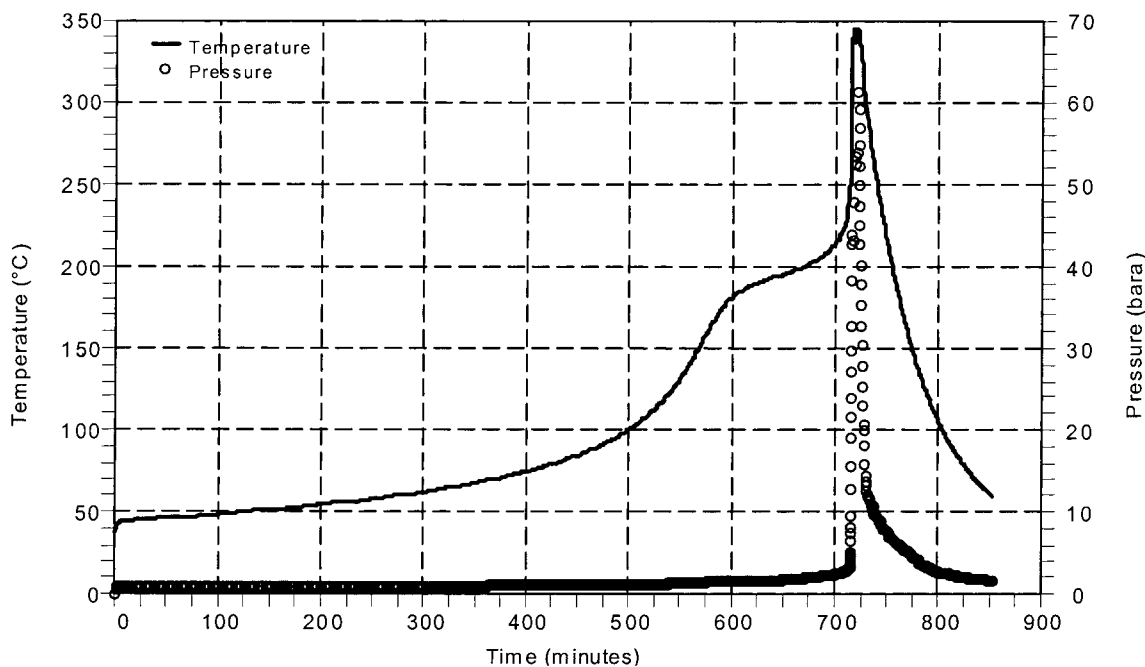


Fig. 4. Temperature and pressure versus time of the reaction mass (high thermal inertia, PHI-TEC).

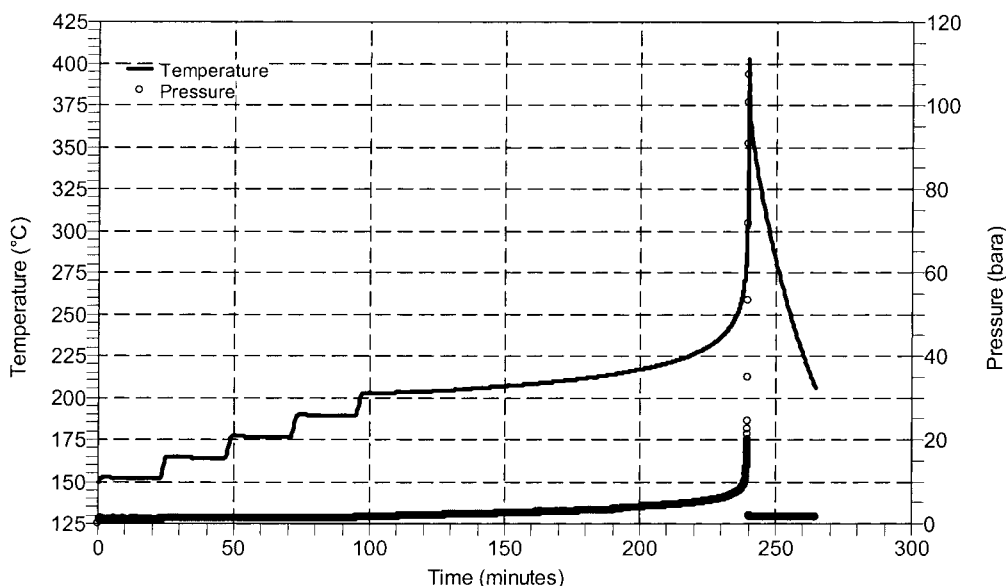


Fig. 5. Temperature and pressure versus time for the isolated product (high thermal inertia, PHI-TEC).

reaction is similar to the onset temperature of the undesired reaction(s) the situation has become inherently hazardous.

5.4. Process improvements

Reaction calorimetry was used to demonstrate that the controlled addition of the chlorinated derivative to

the amine, over a period of about 75 min at 135 °C, produced the correct product (see Fig. 7). Reactant accumulation was found to be 19%. It took about another 2 h to work-off the un-reacted material. Although the ideal situation is zero accumulation at the end of reactant feed, 20% is quite common and presents a minimal hazard compared to the original batch process.

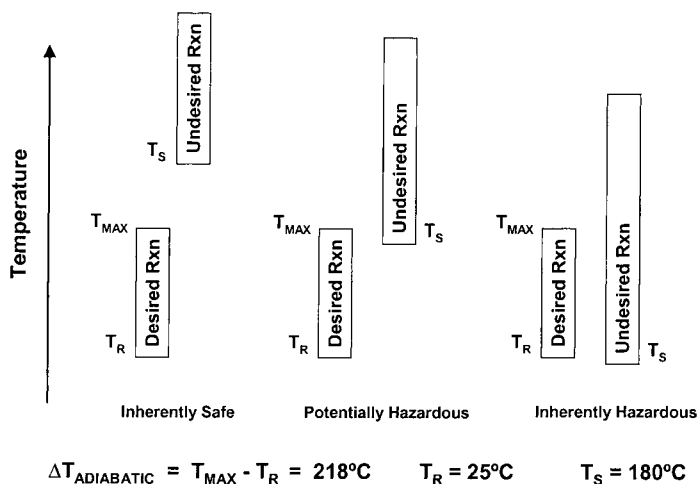


Fig. 6. Temperature relationship between desired and undesired reactions and process safety, where T_{R} = desired reaction temperature, T_{MAX} = maximum attainable adiabatic temperature rise derived from the desired reaction, T_{S} = onset temperature of the undesired reaction(s).

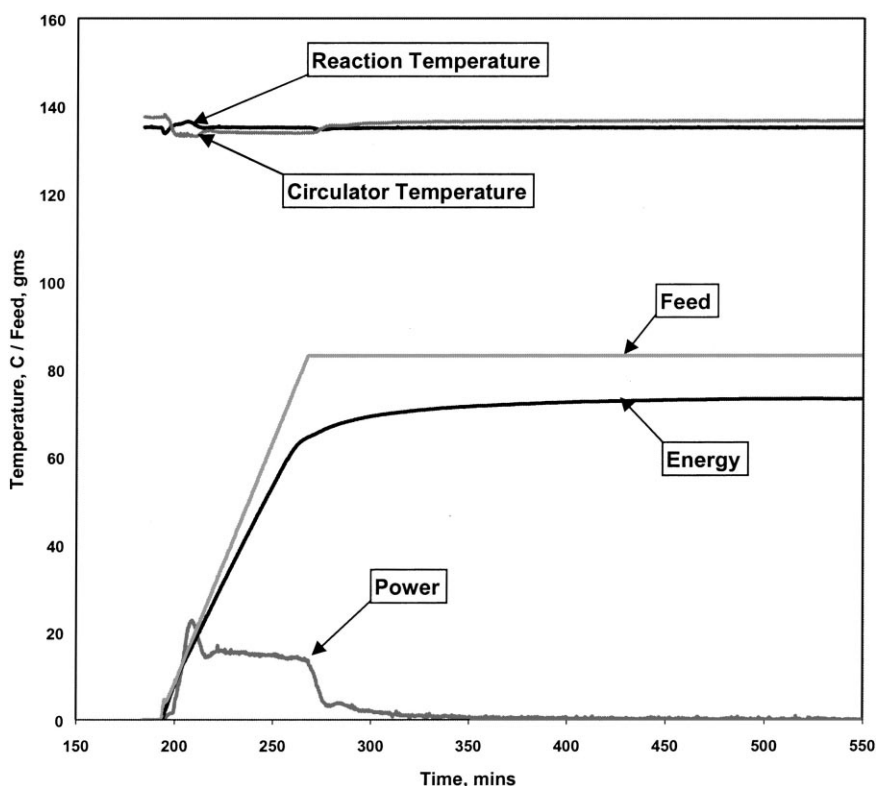


Fig. 7. Reaction calorimetry (SIMULAR) for reaction of primary amine with aromatic chloro compound at 135°C.

In other words, changing the process from batch to semi-batch is a significant move towards an inherently safe system. However, the thermal stability of the finished product remains a hazard potential that must be managed. The margin of safety could be improved by performing the semi-batch reaction at a lower temperature but that led to unacceptably long production cycle time and increased the accumulation.

6. Summary and conclusions

Thermal hazards testing, using a variety of calorimetric techniques, is an invaluable means of identifying, evaluating and assessing the potential hazards of a chemical process. However, hazard evaluation must be tied to the life cycle point of the product. This approach ensures that:

- only testing relevant to the current scale of production is performed;

- the test data from R&D (or pilot) are available to the pilot plant (or manufacturing) stage of product development;
- thermal stability and reactivity information, obtained during the life time of the product, is in compliance with OSHA's PSM standard, 29CFR1910.119.

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