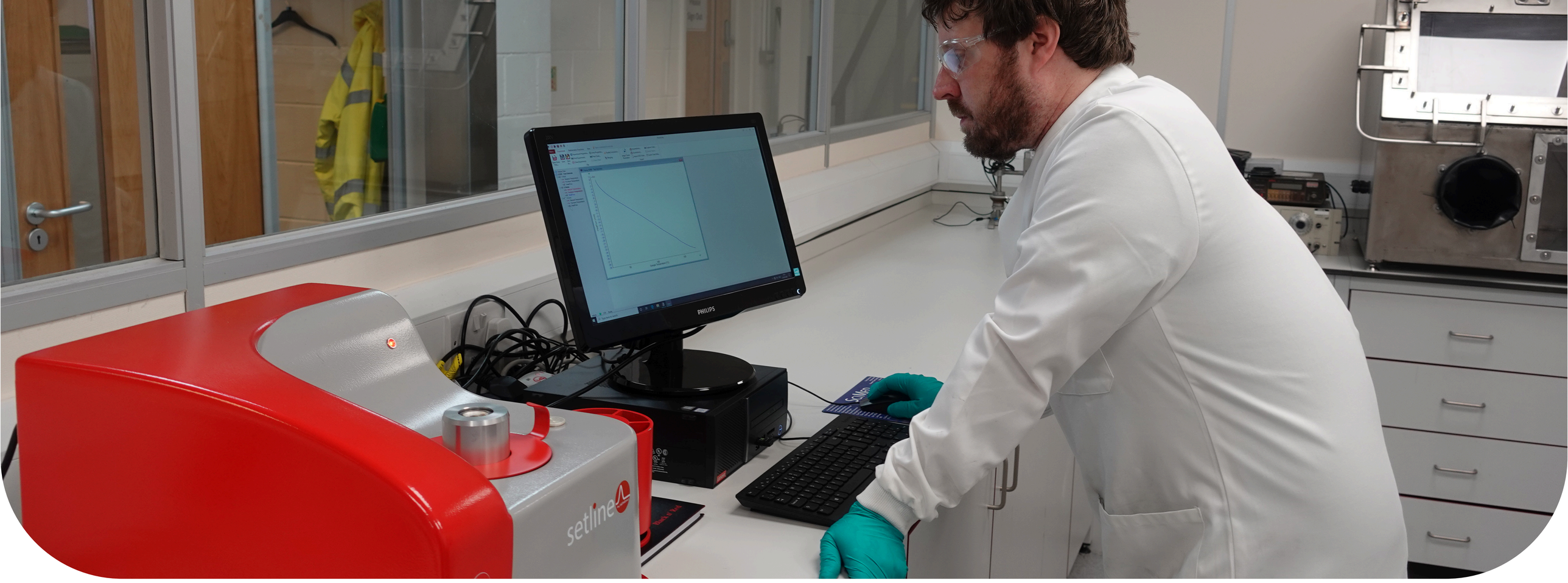
Chemical Reaction Hazards

Sigma-HSE



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Introduction to Chemical Reaction Hazards (CRH)

Reaction hazards remain the most serious concern for various chemical industries, despite continual research and attention devoted to them.

When a new process, material, or procedure is introduced for handling chemicals, the inherent risk of a Chemical Reaction Hazard (CRH) should always be considered.

A hazardous scenario occurs when there is a loss of control in a process in terms of heat, pressure, and undesired by-products.

These hazardous reactions can be categorized in two main forms:

1. Thermal runaway (both endother mic & **exothermic**)
2. Decomposition (i.e. self-reacting, break-down & oxidation, etc.)

Choosing the right screening tools are absolutely essential for the correct design of a safety system, and for ensuring an appropriate Basis of Safety for a process is achieved.

Thermal Runaway Hazard Evaluation

Usually, the following steps are taken to fully understand a CRH thermal runaway type hazard:

1. Initial thermal screening with a small scale tool

   (Thermal Screening)

2. Normal process evaluation within a batch reactor tool

   (Reaction Calorimeter)

3. Runaway reaction simulation within an adiabatic environment

   (Adiabatic Calorimeter)

4. Flow regime evaluation and Vent sizing calculation

   (Vent Sizing Evaluation)

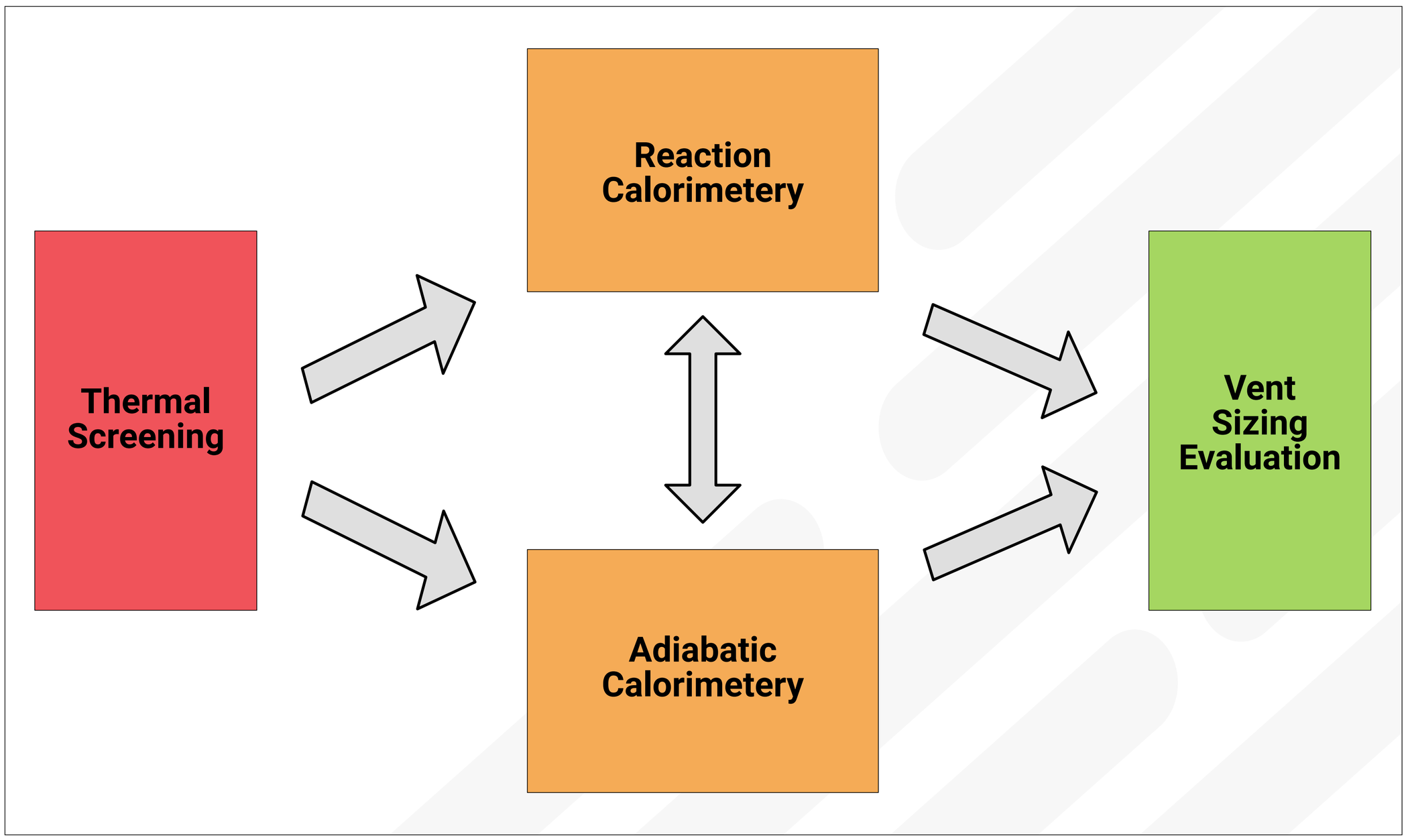

Figure 1: Typical stages of a CRH Thermal Runaway Evaluation Process

Typically, at each stage in the evaluation process, the sample size is increased and tested in more representative conditions. As a result, more accurate data is ascertained.

With this data, a protection system and a Basis of Safety can be developed with confidence.

At Sigma-HSE, we are passionate about process safety, especially in the exciting and technically challenging field of Chemical Reaction Hazards.

Our knowledgeable team of industry experts can assist you with full life cycle assessment of reaction hazards, from the preliminary design stages and testing through to the practical application of data to your production plant.

Beginning the CRH Evaluation Journey

The following flow chart outlines a typical selection procedure for CRH testing and evaluation process:

Step	Customer CRH Requirements	Test Type	CRH Test	Use When Requirements Are:	Stage in New Process
1	Screen for Highly Energetic Materials	Thermal Screening	DSC • 100 °C safety factor	• Use of Small sample (10-20mg) • Suspected high energetic materials • Sampling not an issue (i.e. non heterogenous) • Onset and quantitative heat measurement • No pressure data required • *Initial screening - may have lots of samples*	**Product Identified**
2	Screen for Thermal Decomposition limits		Carius Tube • 60 °C safety factor	• Sample size of 10g available • All sample types solids, liquids, Heterogeneous mixtures • Onset and non-adiabatic temperature rise (indication) • Pressure/Gas data required • *Initial screening - may have lots of samples*	
3	Accurate Determination of Thermal Decomposition Limits	Adiabatic Calorimetry	ARC • 30 °C safety factor	• Sample size of 5-10g available • Accurate onset and adiabatic temperature rise • Pressure/Gas data required • Estimate of TMR required • Not a tool for screening lots of samples as test is slow.	**Synthetic Routes Identified**
4	Heat of Reaction Data	Reaction Calorimetry	RC • 30 °C safety factor	• Close simulation of process chemistry (agitation, temperatures, feed rates etc) • Desired output is heat of reaction, heat flow, accumulation, gas flow etc.	**Chosen Synthetic Route Optimisation**
5		Adiabatic Calorimetry	ARSST • 30 °C safety factor	• Low Phi data – T and P • Energetic materials • Data for relief sizing (screening) • SADT studies • Open cell testing (good for gassy reactions) • Tempered reactions require two tests • Heats of Mixing (Simple)	**Scale-up to Pilot Plant**
6	Data for Relief Sizing (Low Phi)		VSP • 30 °C safety factor	• Low Phi data – T and P • Data for relief sizing (detailed) • Vapour pressure systems • Mixing critical systems (i.e. emulsions, polymers) • Gas additions e.g. hydrogenation • Controlled/metered additions • SADT studies • Open and closed cell testing • Heats of Mixing	**Scale-up to Production**

Figure 2: Flow path for choosing the appropriate CRH testing

What Can you do with CRH Testing Data?

With CRH testing data, a variety of aspects can be examined for a production plant process. Key areas to assess based on CRH data include: process scale-up, design of emergency relief systems (ERS), aspects of Process Safety Management (PSM), design cooling systems, process controls, human factors, and Layers of Protection Analysis (LOPA).

The design process for reactive systems is complex because of the reaction dynamics that take place. These are affected by multiple parameters such as time, temperature, concentration, contaminants, transport properties and the possibility of secondary reactions. As a result, it is rarely feasible to design a proper relief system encompassing runaway reactions without dynamic simulation tools and/or adiabatic calorimetry testing.

The following section outlines typical questions that plant designers, project teams and operators face when dealing with reaction hazards; and how CRH test data can provide valuable answers.

Effect on Process Plant Design & Process Control:

- Can modifications be made to a plant to satisfy the cooling requirements for a new process in a reactor? i.e. using another heat transfer fluid in the cooling system, modifying the heat exchange networks, vessel heat transfer jackets, refractory lining, vessel insulation, agitation mechanism.

- Is there adequate control, alarms and instrumentation to detect the onset of a potential thermal runaway? i.e. the cooling medium temperature could rise before the runaway.

- Has the process control system been calibrated to prevent a runaway scenario from occurring? How is this system introduced? i.e. is it based on trends from a measurement device? Does it account for fluid expansion or equipment efficiency, such as the transfer pumps, the opening of control valves.

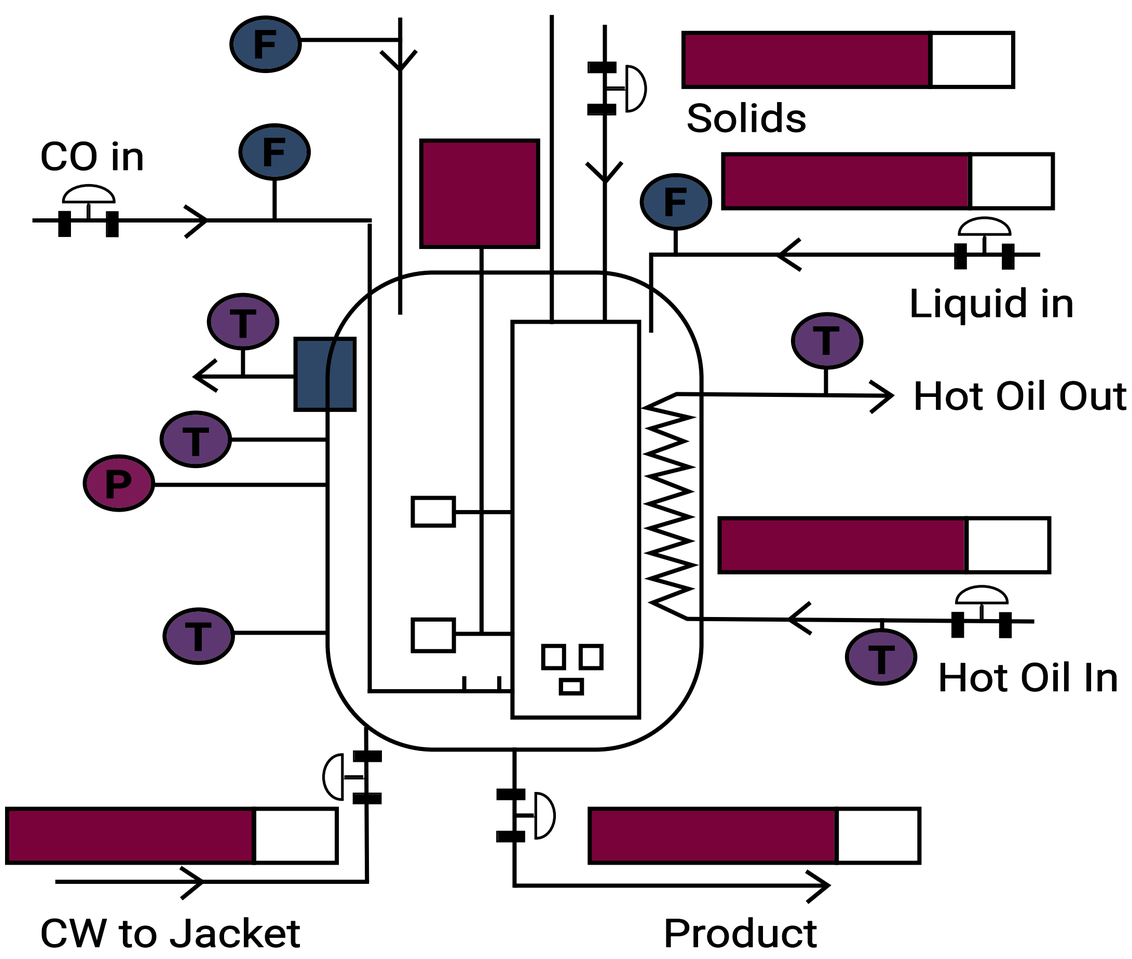

Figure 3: Typical control system for a Reactor

Effect on Emergency Relief System (ERS) Design:

- Can an existing emergency relief system be used for a new reaction process? Can it account for a combined emergency relief system from multiple reactors?

- Will back pressure and vibration be an issue on the relief system? Is two phase flow, high viscosity, solid entrainment or foaming accounted for in the relief system design process?

- Can two-phase flow from a runaway reaction be prevented by changing the inventory, concentration or the physical vapour space (vapour disengagement) within a reactor vessel?

Effect on Operating Procedures and Human Factors:

- Given that agitation malfunctions and the restarting of a stirrer is a very common cause of CRH incidents, are proper training and procedures in place for operators to understand the risk of runaways and how to react to such events?

It should be noted that with colder reactions, reactant accumulation can form, and higher concentrations/amounts can react suddenly to trigger a runaway reaction.

- Can you add reagents/reactants in a different order and in different concentrations? i.e. to remove any rate limiting steps, unwanted products or unexpected runaway reactions.

- Is there potential for the boiling point of a reaction mixture to be reached before the onset of a thermal runaway? This could lead to gas/vapour generation and potential greater likelihood for a loss of control scenario.

- Can pre-heating of feed materials be avoided? Feeding material at higher temperature than boiling points of other reactor contents may result in rapid boiling and vapour generation.

- For a semi/batch process, is additional time needed for the desired products to form at a larger scale? Does transient solid formation or viscosity present a mixing/ agitation challenge? Does the heat transfer property change with time?

Differential Scanning Calorimeter (DSC)

What is the Differential Scanning Calorimetery (DSC) Test?

The Differential Scanning Calorimetery (DSC) test is usually the first step in detecting the onset of an exotherm or thermal instability of a material or mixture.

A sample of around 5-10 mg and a reference material are held in crucibles within a temperature-controlled oven. Both crucibles are heated at a constant rate, typically 2 to 10 °C/min and up to 600 °C. The heating is carried out by a control system that maintains the sample and the reference material at the same temperature.

The variation in the heat that must be supplied to the sample to keep it at the same temperature as the reference material, gives a quantitative measure of any exotherm in the sample. The test result gives the heat flow as a function of sample temperature.

The baseline is then used to integrate the heat flow and thus calculate the energy released by the reaction. Closed-cell high pressure crucibles are typically used to provide a worst case value.

An inlet sample gas line is also present on the DSC, which allows open-cell tests to be performed under air or nitrogen to identify whether a thermal instability is due to oxidation or pure decomposition.

Figure 4: DSC test unit

Thermal Screening | Adiabatic Calorimetery | Reaction Calorimetery

Advantages of DSC Testing:

- Easy setup for fast test turnaround screening
- Small amount of sample needed (10 mg)
- Quantified energy data
- Good for homogenous materials & mixtures

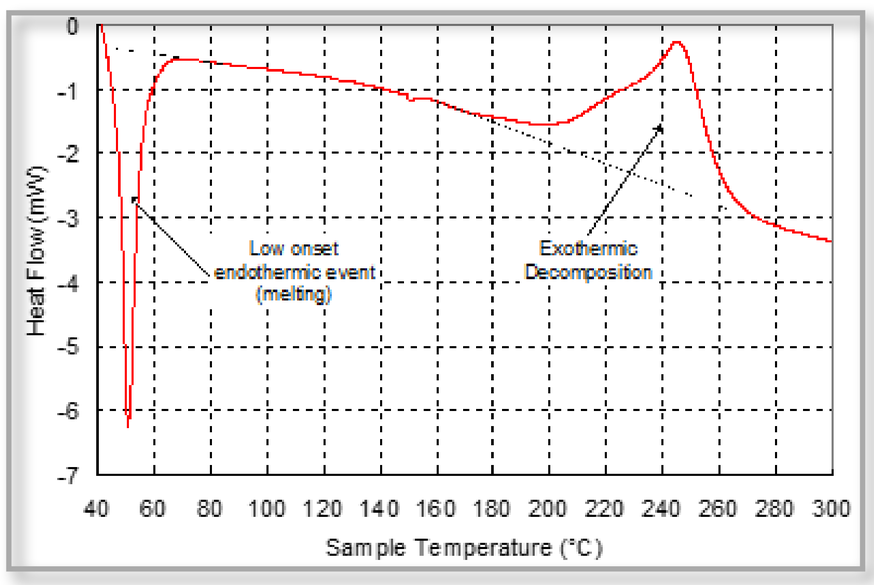

Figure 5: Typical heat flow v temperature profile for a DSC test

Test Summary

- Use of small sample (5-10 mg)
- Suspected high energetic materials
- Sampling not an issue (i.e. non-heterogenous)
- Onset and quantitative heat measurement
- No pressure data required
- *Initial screening - may have lots of samples*

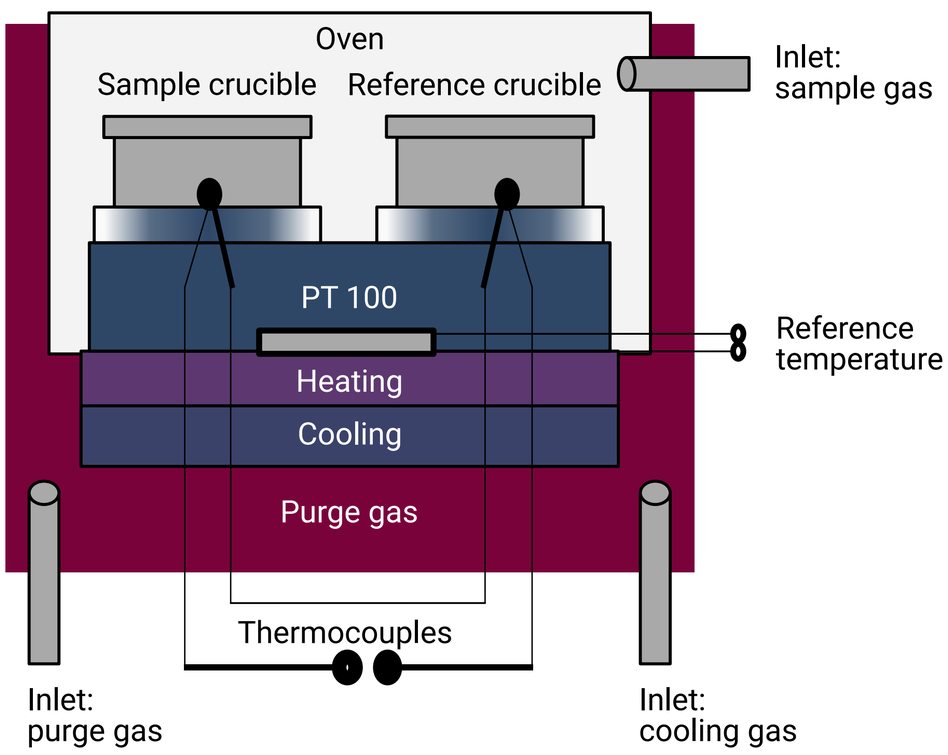

Figure 6: DSC test set up

Why do you need DSC testing?

Typical outputs of a DSC test include the following:

- Onset temperatures, i.e. exothermic / endothermic behaviours, phase transitions, decomposition, etc.
- Heat capacity and its change with time & temperature
- Reaction behaviour – if explosive
- Heat of decomposition

Carius Tube

What is the Carius Tube Test?

The Carius tube test is used to detect the onset of an exothermic event and quantify associated gas evolution.

A roughly 10 g sample is held in a sealed Carius tube within an oven.

The temperature of this oven is then ramped upwards at a typical rate of 0.5-2 °C/min to up to 400 °C, or up to a defined pressure cut-off.

The glass Carius tube is fitted with a thermocouple and pressure transducer to take sample measurements throughout the heating profile.

A differential temperature reading between the sample and baseline of the oven can indicate and quantify energetic events, and whether they are exothermic or endothermic.

A plot of Ln (pressure) versus the reciprocal of temperature can also indicate the onset temperature of gas generation.

Advantages of Carius Tube Testing:

- Easy setup for fast test turnaround screening
- Easy to interpret pressure data available
- Both pressure and temperature parallel data
- Identify energetic event onsets
- Larger sample size (more representative samples for heterogenous mixtures)
- Glass tube (no contamination/observations possible)
- Study pressure effects and gas generation

Thermal Screening | Adiabatic Calorimetery | Reaction Calorimetery

Why do you need Carius Tube Testing?

Typical outputs from a test, include the following data:

- Onset temperatures, i.e. thermal instability or boiling (tempering) temperature
- Rate of temperature & pressure rise
- Onset of gas generation potential
- Reaction behaviour - if it is explosive
- Further analysis can be undertaken to qualify chemical nature of residual gas generated in a test

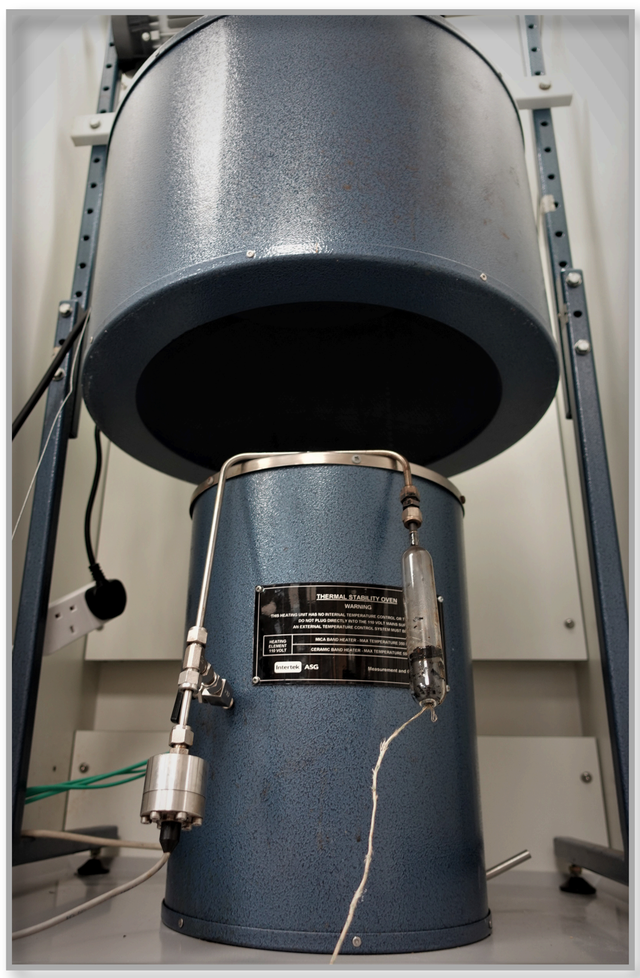

Figure 7: Oven assembly for the Carius Tube Test

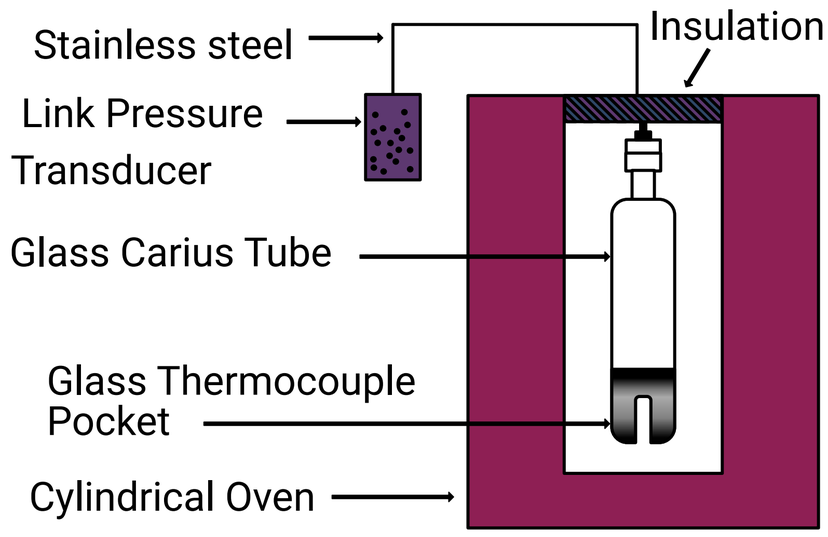

Figure 8: Carius Tube set-up

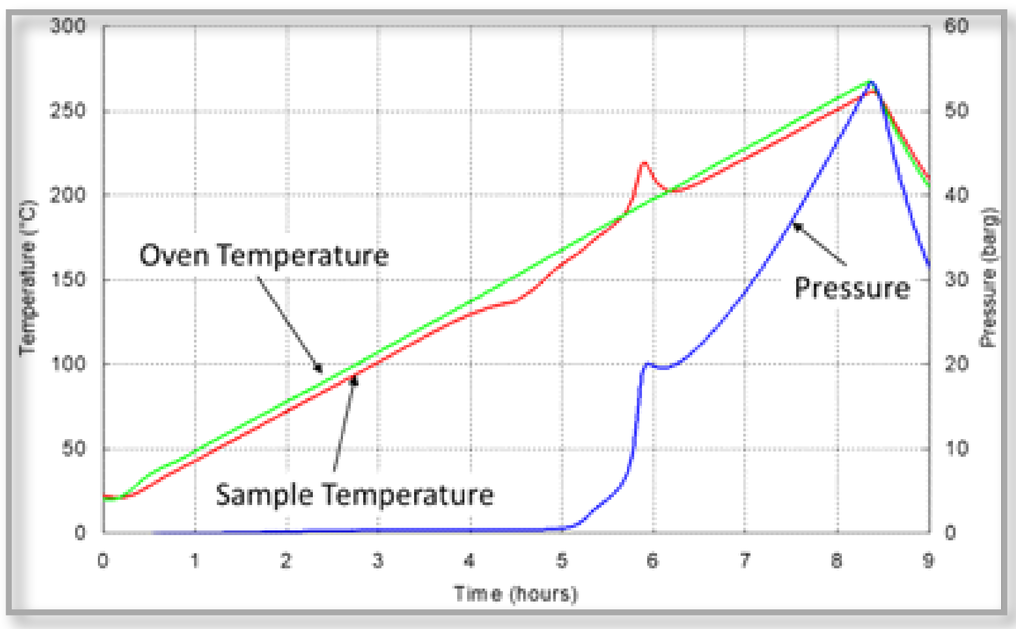

Figure 9: Typical Temperature & Pressure v time profile for a Carius Tube test

Test Summary

- Sample size of 10 g available
- All sample types solids, liquids, Heterogeneous mixtures
- Onset and non-adiabatic temperature rise (indication)
- Pressure/Gas data required
- *Initial screening - may have lots of samples*

Accelerating Rate Calorimeter (ARC)

What is the Accelerating Rate Calorimetery (ARC) Test?

The Accelerating Rate Calorimetery (ARC) test is used for determining potential exothermic reaction of materials, and provides a realistic worst case simulation of runaway conditions.

Samples of up to 10 g are held in typically a titanium spherical cell known as a ‘sample bomb’, and is heated under adiabatic conditions within a containment vessel. Adiabaticity is achieved by heating the surroundings of the sample cell via heaters, so that the temperature outside the cell matches closely the temperature within the cell.

Typically a Heat-Wait-Search mode is used; where the sample temperature is increased in steps, of up to 10 °C increments and is then held for a period at that temperature. The rate of any temperature increase is observed to see if it exceeds a set value, typically about 0.02 °C/min. If it does not, the temperature is raised by the incremental amount and the procedure is repeated until an exotherm is detected. Once detected, the heaters within the vessel are then increased automatically to follow the sample temperature.

This outputs into an adiabatic temperature/pressure vs. time profile for an exothermic reaction, all within a safe and controlled manner. Stirring can also be undertaken in the ARC through the use of a thick-wall sample cell equipped with an internally mounted magnetic stir bar.

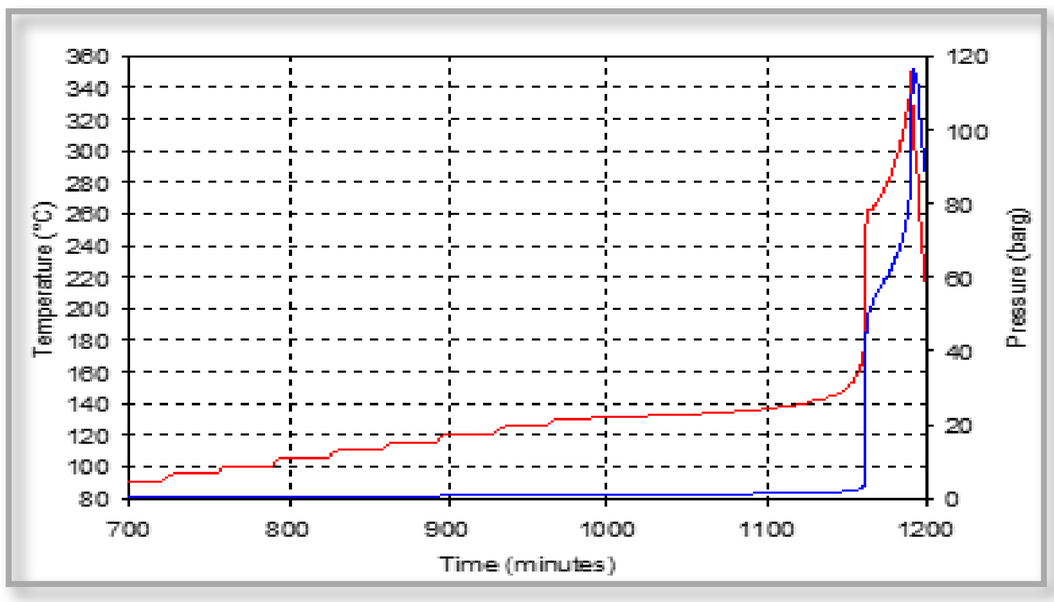

Figure 10: Typical adiabatic temperature and pressure v time profile for an ARC test

Thermal Screening | Adiabatic Calorimetery | Reaction Calorimetery

Advantages of ARC Testing:

- Adiabatic pressure and temperature profile
- High precision in exotherm detection, thus beneficial for storage conditions analysis i.e. self-accelerated decomposition temperature (SADT)
- Medium phi factor and fast tracking
- Gas collection for further analysis
- Sample addition, mixing and dosing possible
- Analysis of multiphase mixtures including gas/solid phase reaction analysis i.e. decomposition under inert conditions

Test Summary

- Sample size of 5-10 g available
- Accurate onset and adiabatic temperature rise
- Pressure/Gas data required
- Estimate of TMR required
- Not a tool for screening lots of samples as test is slow.

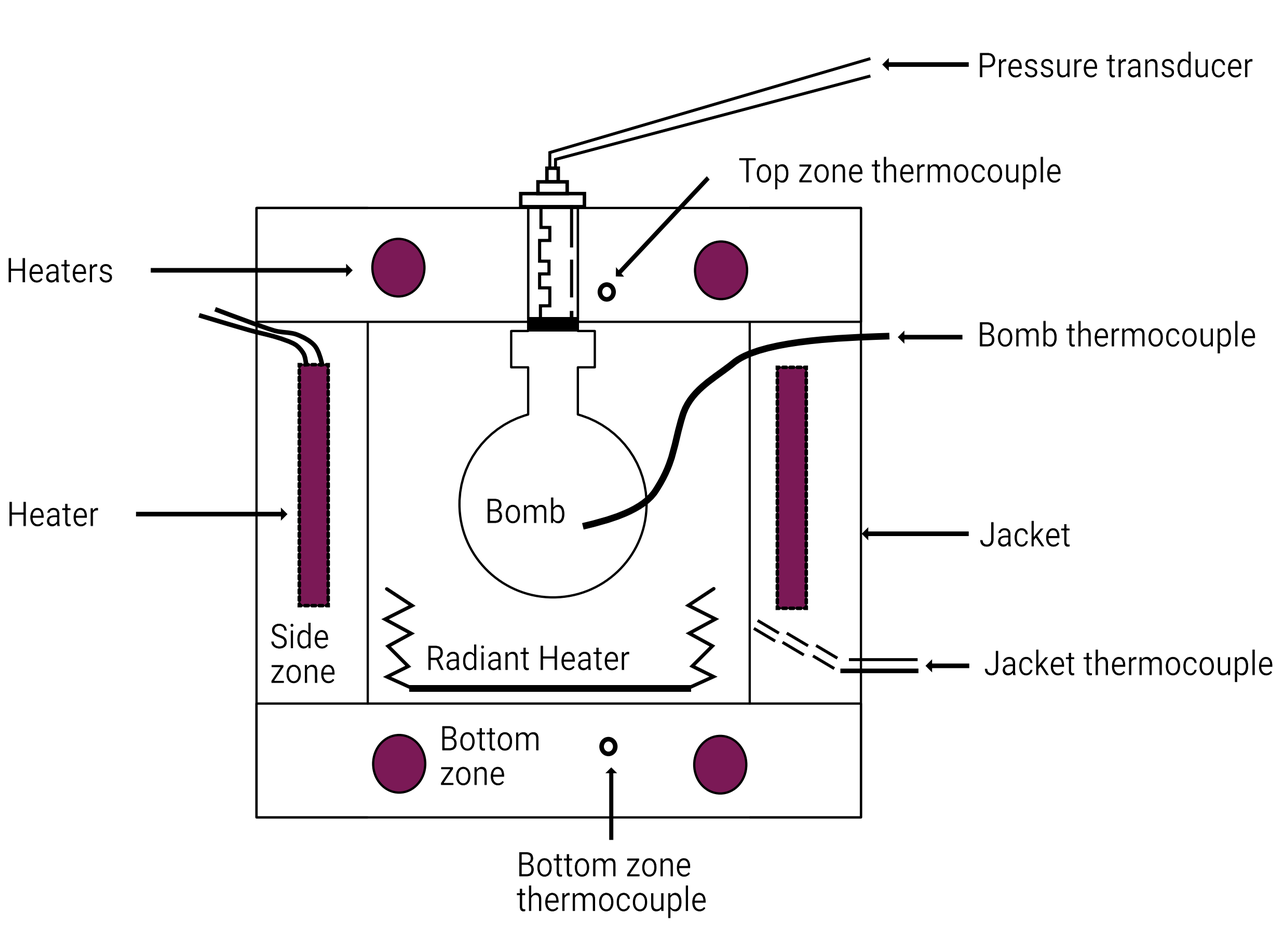

Figure 11: Accelerated Rate Calorimeter (ARC) test setupa Reactor

Why do you need ARC Testing?

Typical outputs from an ARC test include the following data:

- Rate of adiabatic temperature & pressure rise during exothermic reaction
- Adiabatic heat of reaction
- Time to maximum rate (TMR)
- Measure of condensable and non-condensable gas generated

Thermal Screening | **Adiabatic Calorimetery** | **Reaction Calorimetery**

Advanced Reactive System Screening Tool (ARSST)

What is the Advanced Reactive System Screening Tool (ARSST) Test?

The Advanced Reactive System Screening Tool (ARSST) is an adaptable small scale batch reactor, used to measure the rate of temperature and pressure rise, to allow determinations of the energy and gas release rates during a runaway reaction, reaction calorimetry or fire simulation studies.

This unit consists of a well instrumented pressure vessel that typically holds a spherical glass test cell, where it can heat a 10 ml sample usually at a uniform rate up to 400 °C. The reaction mixture and a magnetic stirrer are introduced into this cell as well as thermocouples. The pressure inside the vessel is measured by a pressure transducer. Due to the unique heating method by a wraparound heater, the sample is kept in a quasi-adiabatic mode and no heat loss to the environment occurs.

A small immersion heater with an attached thermocouple is also present in the upper freeboard space of the test cell. This is used to determine the flow regime of a runaway reaction, for example, if it is foamy or non-foamy. This operates on the simple principle that if the flow regime following the onset of boiling is foamy, then the detector will be wetted and rapidly cooled. If the flow regime is non-foamy, then the detector thermocouple will continue to measure a temperature well in excess of the sample temperature.

Figure 12: Vessel assembly for the ARSST test unit

Thermal Screening

Adiabatic Calorimetery

Reaction Calorimetery

Advantages of ARSST Testing:

- Easy setup for fast test turnaround
- Open or closed cell tests with moderate sample size
- Lightweight glass test cell with good mixing
- Low phi factor, so more reliable for process scale-up
- Used as a simplified method to assess vent requirements
- Flow regime detection (between foamy/non-foamy)
- Scanning and isothermal modes
- Simulation of vessel fire exposure

Test Summary

- Low Phi data – T and P
- Energetic materials
- Data for relief sizing (screening)
- SADT studies
- Open cell testing (good for gassy reactions)
- Tempered reactions require two tests
- Heats of Mixing (Simple)

Why do you need ARSST Testing?

The ARSST provides reliable energy and gas release rates, to determine thermal hazards, runaway reaction evaluations and often the proper sizing of pressure relief vents for a process. Typical outputs from a test include the following data:

- Rate of temperature & pressure rise
- Heat of reaction & mixing
- Total adiabatic temperature rise (ΔTad)
- Onset temperatures, i.e. boiling (tempering) temperature and self-accelerating decomposition temperature
- Time to maximum rate (induction time profile)

Reaction Calorimetry – RC

What is the Reaction Calorimetry (RC) Test?

Reaction Calorimetry is a powerful tool that can be used to simulate a wide variety of synthesis processes and plant conditions. At its core, it is a reaction vessel in which moderate quantities of materials or reagents can be studied for reaction conditions, monitored with high accuracy measurements to quantify heat of reactions, maximum reaction rates, reagent accumulation, and further useful information.

The data can be utilised for proper process design and scale-up, optimisation of the reaction, and to study worst case scenarios of plant faults.

The unit typically consists of a glass jacketed vessel, of around 0.5–1 L volume, cooling fluid and chiller, vessel stirrer and calibrated heater. Periphery monitoring probes can also be used, such as pH, conductivity, FTIR to study reaction progress.

The calibrated heater allows for accurate determination of reaction heats, using one of two methods: Heat-Flow Calorimetry or Power Compensated Calorimetry. Dependent on the reaction being studied the appropriate method will be selected.

These tests are typically isothermal calorimetry where the reaction parameters will be studied at a set reaction temperature to mimic the proposed production synthesis. Multi-stage syntheses can be studied but will require to be studied in separate tests if temperature set-points vary.

The data from calorimetry is crucial to ensure correct cooling capacity for scale-up to a production scale of a syntheses, while the process can also be optimised to produce more efficient outputs and ensure the safest process possible. Optimal reaction set-points such as stirring/agitation, cooling, heat-input, and reactant addition rates can all be inferred from RC data.

This can be interpreted by analysis of the heat of reaction data, rate kinetics of reaction, reagent consumption rates/reagent accumulation and more.

Thermal Screening | Adiabatic Calorimetery | **Reaction Calorimetery**

Advantages of RC Testing:

- Adaptable testing to suite specific reactions
- Large sample size to accurately replicate heterogeneous mixtures and mixing dynamics
- Durable glass test vessel with good mixing
- Useful data for process optimisation
- Easy to compare process variations and effects
- Secondary measurement probes and gas/fluid sampling can quantify and qualify reaction yields

Test Summary

- Close simulation of process chemistry (agitation, temperatures, feed rates etc)
- Desired output is heat of reaction, heat flow, accumulation, gas flow

Why do you need RC Testing?

The RC provides reliable energy data, to determine process heats and kinetics. Typical outputs from a test, include the following data:

- Heat of reaction & mixing
- Reagent consumption/ accumulation potential
- Total adiabatic temperature rise (ΔTad)
- Maximum Temperature of Synthesis Reaction (MTSR)
- Time to maximum rate (induction time profile)

Figure 13: Atlas Reaction Calorimeter

Benefits of Sigma-HSE's Solutions

The solutions offered by our experienced team at Sigma-HSE, is much more than standalone test result.

- Combined testing and consultancy experience to ensure that our accurate and methodically generated test data is applied to your process safety applications correctly to protect your staff, site and your brand reputation.
- Free technical advice to ensure the correct test package is selected for your needs.
- Complementary post-project support, to ensure you are happy with the data and understand the implications for you project.

Sigma-HSE’s testing laboratory has state of the art equipment and is operated by senior laboratory staff with decades of testing knowledge.

Internationally recognised standards are followed such as those adopted by the EU (BS & EN standards) and also ASTM standards as adopted within the USA.

>>> Data alone is only one part of a process safety plan, it must be used with both caution and expertise for it to be effective.

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