

CHEMICAL REACTION HAZARDS : AN INTEGRATED APPROACH

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A procedure is presented that integrates process design, hazard evaluation and safety measure specification and implementation into a comprehensive system for the avoidance of chemical reaction hazards.

KEY WORDS: Chemical Reaction Hazards, Reactor Safety, Vents, Process Control.

1. INTRODUCTION

The manufacture of chemicals can produce hazardous situations if chemical reactions are uncontrolled (1).

Although the number of major incidents arising from uncontrolled runaway reactions is small relative to the number of process operations carried out in the chemical industry, they do indicate the need for constant vigilance and the adoption of systematic procedures to maintain a safe manufacturing situation.

The essential stages of the procedure are

- (1) Definition of the process/operating conditions/plant design.
- (2) Characterisation of the process with respect to chemical reaction hazards.
- (3) Selection and specification of safety measures.
- (4) Implementation and maintenance of safety measures.

It is an oversimplification to consider that the evaluation procedure can be based solely on some sequence of chemical testing. The characterisation of the process must take account of the other three considerations and interact with them.

Furthermore the procedure must be applicable to hazard assessments carried out (a) during initial (research) development work, (b) prior to transfer to pilot plant scale (c) before full scale manufacturing is established and (d) when modifications to the process/plant are undertaken. Factors important at each stage are shown in Figure 1.

This review considers the interaction between process/plant design, process characteristics, identification of risk and the specification of safety measures to produce a procedure that will ensure safety in manufacture.

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2. FACTORS INFLUENCING THE PROCEDURE

The procedure must take account of:

- (1) evidence from previous incidents - their cause and means of preventing them.
- (2) the intrinsic link between process definition and the validity of hazard evaluation.
- (3) the options that are available in the design of safety measures.

The chemical industry uses a diverse range of chemical reactions in a multiplicity of plant types. Uncritical evaluation procedures can lead to an open-ended commitment to process testing - an impractical situation that does not serve the cause of operating safety. Each of the above must be examined to establish the boundaries to an investigation that will lead to safe manufacture without unnecessary constraints on operating conditions, plant design or production.

2.1. Evidence from Incidents

Incidents occur when uncontrolled or runaway exothermic reactions are allowed to develop. The factors leading to this situation vary from incident to incident and the kinetics of the runaway reaction depend very much on the chemistry of the particular process.⁽²⁵⁾ It is however possible to identify general trends that highlight the essential features of a chemical reaction hazard testing procedure.

Once the details of the exothermic activity have been identified, it is rarely, if ever, found to involve novel, hitherto unknown, chemistry. Frequently however it is a "side reaction" that does not play a significant role in the normal process but that has been accelerated by the attainment of temperature, time or concentration conditions outside the values present in the normal process. The test procedure must be capable of detecting and quantifying not only the main reactions, but also any side reactions that could develop under all expected process conditions. This in turn demands that the process description specifies the normal variations in process conditions that can be expected in full scale manufacture. Furthermore the plant manager must recognise that both the process specification and the hazard evaluation have boundaries, if operating conditions move outside these limits then hazardous situations may develop that have not been identified in the hazard evaluation.

Although certain chemicals and reaction types (e.g. nitrations, diazotisations) are recognised as generally more dangerous than others (e.g. sulphonations) there are exceptions, it is necessary therefore to examine every process under development. The testing procedure must be sufficiently simple for a large number of processes to be assessed.

Once the sources of risk have been identified their quantification must provide data that enable safety measures to be specified. Furthermore these must be compatible with the engineering, production, economic and commercial criteria for the process.

The last, but not least important lesson to be learned from the incidents is that the basis of safety must be recognised by the plant operators, and must be implemented and maintained.

2.2. Process Definition and Hazard Evaluation

The degree of safety achieved from a hazard assessment is directly related to the range of process operating conditions and plant design features considered in its preparation. It is important therefore that the process definition be sufficient to produce the desired level of safe operation.

Four levels of process definition can be identified.

Level 1: Process Definition with Fixed Parameters

Process descriptions, particularly at early stages of development, often include specific values for such parameters as temperature, reactant concentrations, time, etc. The hazard assessment can only cover a process operating with these fixed values.

It will not consider variations in the process conditions that would be allowed to occur in full scale operation and not be considered to be abnormal (e.g. small changes in temperature, concentration, batch hold times). Project definition at this level will rarely produce a hazard assessment giving an acceptable level of safety.

Level 2: Process Definition Including Normal Variations in Operating Parameters

This level of process definition recognises that in actual operation the process conditions will vary. It defines the range of values over which each parameter will be permitted to change without corrective action being taken i.e. the process as normally operated.

Certain of these variations are well recognised e.g. the temperature of a batch varying by $\pm 10^{\circ}\text{C}$. Others are less well recognised and incidents have occurred because the significance of variations in basic parameters that are an accepted part of the manufacture are not included in the process definition and consequently not covered by the hazard evaluation. For example, the hold time at elevated temperature for analysis of product quality that is normally one hour extending to twelve hours at weekends. This is a situation in which "side reactions" virtually dormant over one hour at the elevated temperature can accelerate exponentially to a dangerous level in the increased time.

Hazard assessment based on level 2 process definition should adequately protect a process operating normally.

Level 3: Process Definition Including Non-Specific Fault Conditions

Certain failure situations, although not common, are known to occur in chemical processing. Examples are agitator failure, loss of cooling, fracture of an internal coil. These are not specific to

individual processes and the effect of them can be included in the hazard assessment without additional detailed process definition.

Unless the plant design is such as to eliminate them then the effect of such failures on process stability and the consequences of any subsequent runaway situation has to be included in the hazard evaluation.

Level 4:

Process Definition Including All Conceivable Abnormal Situations

It is possible to postulate a large number of abnormal conditions that could conceivably cause exothermic activity. Examples are: contamination of the batch by a reactive chemical used in a neighbouring process, variations in raw material quality, the possibility of a general fire overheating the reactor. Unconstrained, this approach can lead to an open-ended commitment to testing.

The techniques of Hazard and Operability that can provide guidance as to the probability and consequence of any abnormal situation are a means of determining the additional abnormal situations that need to be considered in the hazard assessment.

It is considered that Level 3 is the minimum standard that leads to an acceptable level of safety in the majority of processes.

The process/plant definition should include

- (a) definition of the process/plant conditions including all known/expected variations in the process parameters (e.g. temperature ranges, concentration variations, hold times, etc.).
- (b) details of operations (e.g. cooling, agitation, pumping, etc.) that are not protected by high integrity trips.

Where necessary this assessment should be expanded to cover the maloperations, etc., that Hazard and Operability Studies indicate could realistically occur in the process.

2.3. Data Required to Design Safe Systems

Safety can be achieved by:

- (a) Preventative Measures: process control, instrumentation, etc., to prevent the initiation of an uncontrolled reaction.
- (b) Protective Measures: containment, reactor venting, crash cooling/drown-out, or reaction inhibition to protect against the consequences of a runaway reaction.

A simplistic representation of chemical activity is shown in Fig.2.

AB : normal process - balance maintained between heat generated by chemical reaction and plant cooling.

B : start of uncontrolled reaction.

BC : runaway reaction - process conditions cannot maintain equilibrium situation.

For safety to be based on process control the reaction condition must remain in AB. A hazardous situation will occur if process conditions (e.g. reactant concentrations, feed rates, temperatures, hold times) are intentionally or unintentionally changed to an extent that condition B is attained and a runaway reaction is initiated.

The procedure must provide information on

- (1) sensitivity of the process to changes in conditions e.g. safety margin between plant operating temperature and exotherm onset temperature.
- (2) minimum temperature under plant conditions at which uncontrolled exothermic activity will start.

Safety based on protection requires data on the "kinetics" of the runaway reaction. Containment requires only the maximum pressure generated by the reaction. For reactor venting, crash cooling and reaction inhibition, both the rate and magnitude of pressure, temperature and gas evolution changes need to be measured. Furthermore they must be measured using techniques that can simulate the worst runaway situation that can occur on the plant. If agitation ceases for example, the reactants layer and then the agitator is restarted; the reactants are intermixed at concentrations and rates not simulated in Figure 2. The rates of increase in pressure, temperature and gas evolution can be an order of magnitude greater than that predicted by a technique that merely initiates runaway by continuously increasing the temperature of the reaction. The experimentation used to characterise a process must take account of the basis for safe operation that can be applied to the process and the plant.

3. CHARACTERISATION OF PROCESS FOR CHEMICAL REACTION HAZARDS

A typical investigative sequence is shown in Figure 3.

An essential first stage is to exclude from manufacture any materials/reaction masses/residues that could have detonation or deflagration explosive properties.

Once this has been done the procedure

- (a) examines the normal process situation
- (b) determines the initial exotherm temperature and
- (c) quantifies the characteristics of the runaway situation.

3.1. Explosibility Screening

The following procedure has been used to exclude detonating and deflagrating explosive materials.

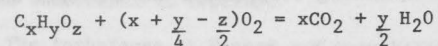
3.1.1. Consideration of Chemical Constitution

Groups such as nitrate ester, aromatic nitro and nitramine are closely linked with explosibility; azo, azide, nitroso, peroxide and acetylene groups can form part of explosive structures. No all embracing guide can be provided but materials containing these or similar groups should be tested for detonation and deflagration properties.

3.1.2. Calculation of Oxygen Balance

For oxidation reactions the Oxygen Balance enables a material to be compared to those of known explosive potential.

The basic equation is



$$\text{Oxygen Balance} = - \frac{1600 (2x + \frac{y}{2} - z)}{\text{Molecular Weight}}$$

Typical values for materials of recognised instability are nitrobenzene (-163), glycerol trinitrate (+3.5), dinitrotoluene (-114). It is recommended that materials with an oxygen balance more positive than minus 200 should be tested for explosibility.

3.1.3. Explosibility Tests

A number of tests, developed by the explosives industry, to identify materials with detonating and deflagrating explosive properties are available. The most appropriate for the explosibility screening of chemicals are Pressure-Time Test, Trauzel Lead Block Test and Koenen Tube Test. These have been reviewed by Cutler (2).

Materials giving a positive result in these tests normally require specialised manufacturing facilities.

Certain materials not classified as explosives can decompose very violently when subjected to localised heating. Gibson and Harper (3) have shown for example that, under confinement, the propagating decomposition of o-anisidine nitrate can generate pressures up to 500 bar at a rate of 5-6 k.bar s⁻¹.

Wright and Butterworth (4) have developed a small scale (3 g) test that enables pressure effects to be determined for reaction masses and powders.

A Carius Tube (Figure 4) containing the sample, is heated by placing it inside a circular oven. The temperature of the sample can be measured by the bottom entry thermocouple and the pressure by a transducer mounted on top of tube but outside the oven. Predecomposition gases and volatiles can be released via a side arm.

The test can detect compounds that undergo high rate decomposition and quantify the conditions necessary to support high rate decomposition.

It can measure

- (1) the onset temperature for exothermicity (no allowance for scale factors).
- (2) the onset pressure - provided predecomposition gases and volatiles are vented prior to onset.
- (3) rate of decomposition as indicated by rate of pressure rise. The measured pressures depend on test cell volume and geometry. Dangerous pressures are avoided by allowing the tube to burst safely inside the oven enclosure.

Temperature and pressure traces for dinitrotoluene, a material not classified as an explosive but capable of high rate decomposition are shown in Figure 5.

On the 3 g scale with a 2°C/min ramp rate self heating is evident at ca. 250°C but the high reaction rates associated with propagative decomposition do not occur until the sample temperature is well above the atmospheric boiling point of 300°C.

Using normal rates of data capture the high rate event starting at 350°/120 psi is not recorded in Fig. 5a. The system is also provided with a transient recorder triggering at 300 psi to capture the high rate event. For a 0.1 sec event time the system is arranged to record 0.09 sec. before 300 psi and 0.01 sec. after 300 psi as shown in Fig. 5b. Rise time between 200-400 psi is 6 milliseconds.

Applying a heat source to dinitrotoluene without confinement will not produce propagation/deflagration - the material will vaporise. Propagation would be expected (and has occurred) in heated pipelines which can confine the material.

Experience has shown that compounds that propagate decomposition (detonation/deflagration) are characterised in this test by a rise time of less than 50 m.s. between 200-400 p.s.i.

The test identifies materials that have detonating or deflagrating properties akin to explosive materials, identifies materials capable of high rate decomposition and indicates semi quantitatively the consequences of decomposition. Materials with uncontrollable decomposition characteristics can be excluded from manufacture or kept in the more stable damped form.

3.2. Characterisation of the Normal Process

Process development requires a knowledge of:

- (a) the kinetics (particularly the equation linking reaction rate with concentration) of the desired reactions.
- (b) the optimum reaction conditions to maximise yield/quality.
- (c) heats of reaction and rate of heat generation.

- (d) plant cooling characteristics (e.g. heat loss from plant, evaporation, reflux, etc.).
- (e) gas evolution rates and scrubber capacity.

Definition of the normal process is however insufficient to ensure safe manufacture. Account must also be taken of the effect of manufacturing change (e.g. variation in reactant concentrations, addition times, temperature profiles, hold times, etc.) on heat generation and gas evolution. The margin of safety between the "normal process" conditions and those that initiate a runaway situation must be established. The effect of potential mal-operations identified in Hazard and Operability Studies on reaction safety has to be established.

Isothermal Reaction calorimetry (5) has been developed to simulate in the laboratory the behaviour of full scale isothermal semi-batch chemical processes under normal and maloperation conditions. Adiabatic calorimetry can be used to simulate "all in" batch processes with self heating (6).

The Reaction Calorimeter has to satisfy a number of complex requirements:

- (1) the heat generation data must be obtained whilst simulating the full scale reactant addition rates, batch temperature and time and the desired process conditions (e.g. stirring, distillation, boiling under reflux, etc.).
- (2) other sources of heat flow must be included in the heat equation e.g. energy input from the stirrer, energy loss in a condenser.
- (3) the effect of changes in physical properties during the reaction (e.g. viscosity, specific heat, precipitation).
- (4) the effect of change in cooling through the reactor wall due to changes in the wetted area and inner wall fouling.
- (5) the heat flux has to have a detection limit of the order of ± 0.1 Watts.

Reaction Calorimeters and their use to prescribe safe manufacturing conditions have been described by Regenass (5), Riesen (7), Hub & Kupr (8), Stockton et Alia (9) and Wright and Butterworth (10).

All the techniques provide similar information but the methods used to obtain it differ in detail.

In the design originating in Ciba-Geigy and now marketed by Mettler Instrumente AG a stirred tank reactor is surrounded by a jacket in which a heat transfer fluid is circulated at a very high rate. A cascaded controller adjusts the temperature of the circulation loop so that the heat transfer through the reactor wall equilibrates the heat evolution in the reactor. Injection of thermostatted hot or cold fluid is used to adjust the temperature in the loop.

The rate of heat transfer (which equals the rate of heat evolution) is related to the observed temperature difference T between the jacket fluid and the reaction mixture by the equation

$$q = U \cdot A \cdot T - F_c \cdot T$$

where the calibration factor F_c is the product of U , the overall heat transfer coefficient, and A , the active (= wetted) heat transfer area. Because both A and U depend on the reactor contents and on the stirring conditions, specific calibration is required. This is done by producing a known heat input rate to the reaction mixture by means of an electric heater. The need of frequent calibration is of some inconvenience as compared with heat balance calorimeters. On the other hand, the method chosen permits the use of an uninsulated glass reactor and thus allows visual observation of phase changes, colour changes and mixing conditions. This is a distinct advantage for process development work.

In the design described recently by Stockton et Alia (9) all except the base of the reactor is surrounded by an "adiabatic shield"; this maintains the temperature of the air space surrounding the reactor at the same temperature as the reactants in the inside of the vessel. Heat flux only occurs through the flat base of the reactor - this minimises problems associated with changes in wetted area.

A second problem can arise with the design of a sufficiently fast response cooling system. Wright and Butterworth (10) have overcome this by maintaining a constant temperature difference between the calorimeter contents and the cooling jacket. Essentially the reactant mass is heated by an electrical heater. As the reaction generates chemical power the electrical power is correspondingly reduced. Measurement of the electrical power reduction provides quantitative data on chemical power generation rates.

A fourth variation on design has been described by Hub and Kupr (8) and defined as the Heat Balance Method. The test cell incorporates a condenser and reactions under reflux can be studied.

No one technique is intrinsically superior to all the others. Each has its advantages and disadvantages. However all can be used to provide the data on the normal process that is required to evaluate potentially hazardous process conditions.

A classical experiment to demonstrate the use of isothermal heat flow calorimetry is the nitration of toluene. In the example shown in Fig.6 nitrating acid containing 1.14 mol nitric acid is added uniformly to toluene 0.9 and at 60°C. The calorimeter indicates instantaneous power output during the addition and work off, for comparison with plant cooling capacity. By measurement of the area under the power/time curve the total heat of reaction is calculated to be 35 Kcal/ml. toluene. Power output profile in this particular case is square indicating rapid reaction and freedom from significant accumulation problems provided the system is agitated.

3.3. Identification of Minimum Temperature for Runaway Reaction

Safety can be achieved by ensuring that a reaction mass does not attain the temperature at which an uncontrolled reaction is initiated.

The minimum temperature for runaway reaction depends not only upon the kinetics of the reaction but also on the rate of loss of heat that will occur from the full scale reactor. Heat loss from batch reactors depends on the size of the reactor, agitation, condition of the vessel jacket. Typical values for stirred vessel with filled jackets are $0.04-0.08 \text{ W.kg}^{-1}\text{.}^{\circ}\text{C}^{-1}$ for a 5000 gallon vessel.

Experimental techniques to achieve test sensitivities appropriate to these values require accurate, stable temperature control and high levels of detector sensitivity.

Laboratory testing has developed on two levels:

- (1) screening tests that enable a large number of reactions to be investigated quickly with respect to the possibility of exothermic activity and the approximate value of the minimum temperature.
- (2) adiabatic tests that simulate plant scale heat loss conditions and provide data on self-heating rates directly relevant to full scale manufacture.

3.3.1. Screening Methods

Ideally the screening test should satisfy the following criteria:

- (1) be capable of monitoring starting materials, samples of the reaction mass as the reaction progresses, final reaction mass, isolated final product and distillation residues.
- (2) provide data from measurements on the small samples (grammes) available during product development.
- (3) clearly identify exothermic activity.
- (4) provide some guidance as to the size of the exotherm - ideally a closed test cell to avoid effect of evaporation.
- (5) provide some guidance on rate of heat generation.
- (6) detect production of gas/volatiles.
- (7) detect high rate of events.
- (8) detect induction period phenomena leading to time dependent onset.

3.3.1.1. DSC/DTA

DSC/DTA are well known thermo-analytical techniques. When used for the study of exothermic decomposition the following lead to certain limitations:

- (1) test condition is essentially isothermal whereas under plant conditions, decomposition occurs in a situation corresponding more to the adiabatic limiting case.
- (2) sensitivity of the test used in the traditional manner is relatively low ($1-5 \text{ W.kg}^{-1}$).
- (3) measured onset temperature is a function of the sample heating rate. The temperature determined for p-nitroaniline increased from 210°C to 300°C when the heating rate moved from 0.1 K min^{-1} to 5 K min^{-1} (11). Duch et alia (12) have confirmed this effect.
- (4) non-sealed cells can produce errors due to evaporation losses.
- (5) small sample size can lead to it being unrepresentative of plant material.
- (6) violent decompositions can cause damage to the equipment.

The limitations and advantages of DSC/DTA are discussed in detail by Hentze (11), Schulz, Pilz and Schacke (13) and Duch et alia (12). Certain of the above limitations can be overcome by the use of sealed pressure cells and by control of the sample heating mode (low rates, isothermal "stepping" of the sample, etc.) but there still remains the high rate of heat loss from the sample, relatively low measurement sensitivity and absence of gas evolution data. Nonetheless these techniques do provide a display of exothermic activity and provide some indication of heat generation characteristics under isothermal conditions.

3.3.1.2. Linearly Ramped Closed Vessel Tests - CV Test

These tests are variants on the ASTM 76-79 test. The sample, in a container fitted with an internal thermocouple and transducer, can be heated with a linear ramp up to 500°C . Fenlan (14) comparing this test with the ARC found that the onset temperature for the CV Test lay in the range 59°C above to 8°C below the comparable ARC result with a mean value of 21°C above the ARC results.

3.3.1.3. I.C.I. Sealed Tube Test

The I.C.I. test uses a glass Carius tube (fitted with re-entrant thermocouple and pressure transducer (Figure 4)). In the screening test 10-20 g sample are sealed in the tube which is then heated at $2^{\circ}\text{C min}^{-1}$ up to 400°C or up to a set pressure cut off. Temperature and pressure are monitored continuously. The onset temperature can be read directly from the trace - Figure 7. The test sensitivity is $3-10 \text{ W kg}^{-1}$.

The test is primarily used as a screening test - it provides an indication of exothermic activity, the minimum temperature under the test conditions, vapour pressure-temperature data.

3.3.1.4. Commercial Calorimeters in Programmed Mode

Commercial adiabatic calorimeters (e.g. ARC, Sikarex) can carry out screening tests.

The Heat-Wait-Search operational logic of the ARC (15) is shown in Figure (8). The sample is heated to a desired starting temperature and held for a time to establish thermal equilibrium. A rate search is performed to detect exothermic activity. If none is detected at a selected threshold level (normally $0.02^{\circ}\text{C min}^{-1}$) the temperature is increased and the sequence repeated. The temperature at which exothermic activity is eventually detected is a measure of the onset temperature.

The screening procedure for the Sikarex Calorimeter employs a linearly ramped temperature scan.

3.3.2. Adiabatic Test Methods

The limitations of the screening tests with respect to simulation of the plant conditions can be overcome by the use of adiabatic test methods.

In the simple tests the temperature monitor may underestimate the heat generation due to

- (1) heat loss from the sample to its surroundings - this can be minimised or eliminated by reducing the temperature difference between the sample and its environment.
- (2) heat loss from the sample to the test cell. A parameter phi is used to characterise this effect.

$$\phi = \frac{\text{Thermal Capacity of Sample} + \text{Thermal Capacity of Test Cell}}$$

Thermal Capacity of Sample

This can be minimised by reducing the mass of the container or by using a relatively large sample to reduce the ratio of the thermal capacity of the test cell to sample.

Two techniques are used to obtain data under adiabatic or near adiabatic conditions.

3.3.2.1. Adiabatic Calorimeters

The adiabatic condition is achieved by using the sample temperature as the "set point" in the instrumentation. Once exothermic activity has been detected the temperature of the oven is increased to match the temperature of the sample. This minimises heat loss from the sample/container to the environment but account still has to be taken of the phi factor. An analysis of the importance of phi has been given by Townsend (15) and recently discussed in the ARC Newsletter (16). For direct simulation of plant situations phi values of 1.0-1.5 are required. In practice phi values up to 3 are used and the experimental results adjusted mathematically to correspond to a phi = 1 situation. Changes in reaction mechanisms are usually small at the levels of activity present

when the exothermicity is first detected so the correction is usually reasonable. It can be invalid however if complex chemical or mass transfer mechanisms are involved (17).

3.3.2.2. Dewar Techniques

The use of Dewar vessels to simulate low heat loss situations are well established (18).

The construction of the Dewar vessel leads to low heat loss and phi factors. Rogers and Wright (6) have developed a simple adiabatic Dewar system that further reduces heat loss and reduces the need for accurate temperature control. The phi factors are in the range 1.05-1.5 depending on the thermal capacity of the reaction mass. The inherent low heat loss enables temperature drifts as low as 0.1 K hr^{-1} (2 K per day) to be obtained from a control system that maintains a sample/oven temperature differential within 1 K. To achieve corresponding stability in small scale adiabatic calorimeters a drift free temperature differential within 0.01 - 0.1 K has to be achieved.

3.3.3. Comparison of Onset Temperatures obtained from Different Tests

Typical sensitivity data for commercial equipment has been given by Schulz et alia (13).

Standard DTA	: 5 W/kg
DTA - Isotherm Stepping	: 0.5 W/kg
DTA - Low Heat Rate	: 0.1 W/kg
ARC	: 0.5 W/kg
Reaction Calorimetry	: 0.5 W/kg

The corresponding data for I.C.I. tests are

10 g Tube Test	: 3-10 W/kg
250 ml Glass Dewar - Adiabatic	: <0.07 W/kg
500 ml Glass Dewar - Adiabatic	: <0.03 W/kg
1000 ml Metal Pressure Dewar - Adiabatic	: <0.10 W/kg

Onset temperatures obtained from the different test methods are available in the literature.

Typical results are:

(1) H-Acid Nitration Mass (19).

ICI 10 g Tube Test	: 98°C
Sikarex Programmed	: 95-98°C
ARC Heat-Watch-Search	: 95-100°C

(2) 3-5 dinitro-ortho-toluamide powder (19).

ICI 10 g Tube Test	: 115-120°C
DTA (Fast Scan)	: 274-284°C
ARC	: 120-125°C

(3) O-Nitroaniline (12).

DSC (5°C/min.)	: 293°C
ARC	: 271°C

(4) O-Nitroaniline Reaction Product Mixture (12).

DSC (5°C/min.)	: 263°C
ARC	: 230°C

Comparisons of the above type show that, provided a slow temperature scan rate is used, the screening tests satisfactorily indicate the possibility of exothermic activity and provide guidance on the onset temperature. It must be emphasised that due to the limitations of the screening tests a minimum safety factor of 60-100°C be required. If the temperature differential between operating and test result is less than this then the onset temperature must be confirmed using an adiabatic method.

3.4. Characterisation of the Runaway Reaction

Characterisation of the runaway reaction requires data on the rate and magnitude of temperature, pressure and gas evolution changes that could occur in the plant situation. The pattern of a runaway reaction will tend to take one of three forms:

- an accelerating reaction that is linked by a continuous function to the normal process reaction rates as displayed in Figure 2, e.g. caused by inadequate cooling.
- a step change in which the reaction increases markedly over a short period of time e.g. caused by restoration of agitation in a two phase system.
- a combination of (a) and (b).

The progression of the reaction will be determined by the fault condition that causes it.

The experimental techniques must not only be able to simulate the normal process and plant operations but also be sufficiently flexible to allow maloperations (e.g. loss of cooling, loss of agitation, incorrect reactant additions, etc.) to be simulated at any stage of the process.

Adiabatic calorimetric techniques must be used.

3.4.1. Commercial Calorimeters : ARC

Commercial calorimeters as typified by the ARC can be operated under adiabatic conditions. Data can be generated on adiabatic reaction pressure and temperature parameters, kinetic data, reaction rate constants and time to maximum reaction rate (15). Gas evolution cannot be directly measured but can often be inferred from pressure data. Wilberforce (20) and Coates (21) have described the application of the ARC in thermal hazards evaluation.

It can successfully provide adequate data on the parameters listed above. A practical limitation however is the small size of test cell (10 g maximum) that precludes the addition of reactants as the reaction proceeds.

3.4.2. Adiabatic Dewar Techniques

Stainless steel Dewars of the type described by Rogers and Wright (6) can be used to measure directly pressure, temperature and gas evolution changes under heat loss conditions that simulate the plant situation.

The larger sample and test cell access make it possible to manipulate the process conditions as the reaction continues. The data are directly applicable to batch reactions up to 5000 gallons. The basic pressure/temperature data are exemplified by that for Methanol/Acetic Anhydride shown in Figure 9. The temperature-time curves can be rapidly analysed to yield thermodynamic and kinetic data for simulation purposes (6).

3.4.3. V.S.P. Apparatus

A recent addition to commercially available equipment is the V.S.P. Apparatus (22). This, produced as part of the D.I.E.R.S. project (23), is intended to produce the data required to design reactor relief systems.

It consists essentially of a 120 ml metal test cell that is heated by the oven enclosure and an electric heater wound on its outer surface. The latter reacts to the temperature of the sample and minimises heat loss. The phi factor of the cell is approximately 1.5. A novel feature is the pressure control system that produces a pressure outside the cell equal to that produced by the reaction inside the cell. This enables pressure reactions to be studied in a relatively weak test cell (low thermal capacity).

When used with a closed cell, the equipment is essentially an adiabatic calorimeter that can provide information on the reaction rate under runaway conditions, the maximum pressure and temperature, the overall heats of reaction and the vapour pressure/temperature relationship. An open cell can be used to provide information specific to the design of relief systems - flow behaviour of the discharging reaction mass, identification of tempered and non-tempered reactions.

A number of organisations are testing this equipment but few results are available in the open literature. In this symposium Gibson, Maddison and Rogers (24) report comparative testing that indicates that thermal data from the V.S.P. apparatus is in reasonable agreement with that from Dewar Calorimetry.

The character of a runaway reaction depends on a number of interacting factors (e.g. "kinetics" of the runaway reaction, autocatalytic effects, influence of volatiles, heat loss from reactor, effect of pressure, etc.). In assessing a process the "worse case" conditions must be identified and simulated in the laboratory tests. No one system gives unequivocal data that can be used without interpretation but provided this is correctly done then data can be obtained that enables protective systems to be designed.

4. SELECTION OF SAFETY MEASURES

Safe operation can be based on

- (A) Process control that prevents conditions being attained under which uncontrolled exothermic reaction will be initiated.
- or (B) Process control to minimise the probability of a runaway reaction combined with protective measures should such a reaction occur.

Options are:

- (1) Process control + containment.
- (2) Process control + reactor venting.
- (3) Process control + crash cooling/drown out.
- (4) Process control + reaction inhibition.

The most appropriate safety measure depends on process detail - including toxicity of products, magnitude and rate of the runaway parameters and the practicality of implementing and maintaining the safety measures.

Critical technical considerations for each are:

4.1. Process Control

- definition of minimum temperature at which uncontrolled exotherm will start under plant conditions.

- safety margin between operating temperatures and exotherm temperature.
- monitoring and control systems to maintain temperature in the safe region.
- maintenance of temperature should agitation or cooling fail - e.g. stop feed of reactant, use solvent that boils at safe temperature.
- control sources of risk external to process - e.g. addition of wrong materials.
- specification of lower temperature limit to prevent accumulation.
- reaction of two phase systems to agitation failure.

4.2. Process Control and Reactor Venting

- definition of worst case - i.e. conditions leading to maximum rate of exothermic activity.
- establishment of "kinetics" of the runaway reaction.
- nature of discharge material - gas, liquids, solids.
- methods for calculating reactor vent area and discharge system for the vented materials.
- safe discharge area - flammable and toxic hazards - dump tanks.

4.3. Process Control and Crash Cooling/Drown Out

- rate of temperature rise/heat generation after runaway detected.
- time to hazardous pressure.
- availability of compatible cooling medium.
- relative thermal capacities of reaction mass and cooling medium.
- plant design/operation to intermix reaction mass and cooling medium and stop temperature rise before maximum permissible pressure is attained.

4.4. Process Control and Reaction Inhibition

- availability of compatible reaction inhibitor.
- time to hazardous pressure.

- inhibitor efficiency.
- plant design and operation to intermix reaction mass and inhibitor and stop temperature rise before maximum permissible pressure is attained.

In addition to the technical considerations, the selection of the most appropriate basis for safe operation must take account of:

- (a) acceptability to the engineering and manufacturing functions with respect to their compatibility with the design, construction, operation, maintenance and economic requirements of the process.
- (b) the essential features of the safety measures must be understood by the manufacturing personnel.
- (c) the safety measures must be fully implemented and maintained.
- (d) the boundaries of the safety evaluation and the effect of changes in plant construction or process operation.

5. THE INTEGRATED APPROACH - CONCLUSION

The evaluation of chemical reaction hazards and the specification of realistic and practical measures that ensure manufacturing safety can best be achieved by an approach that integrates process and plant definition, process characterisation for the normal and runaway situation, the selection, design, implementation and maintenance of safety measures.

The procedural details will depend on the infrastructure of the organisation but the essential details for initiation, evaluation, implementation and monitoring are shown in Figure 10. Fully implemented it will ensure manufacturing safety.

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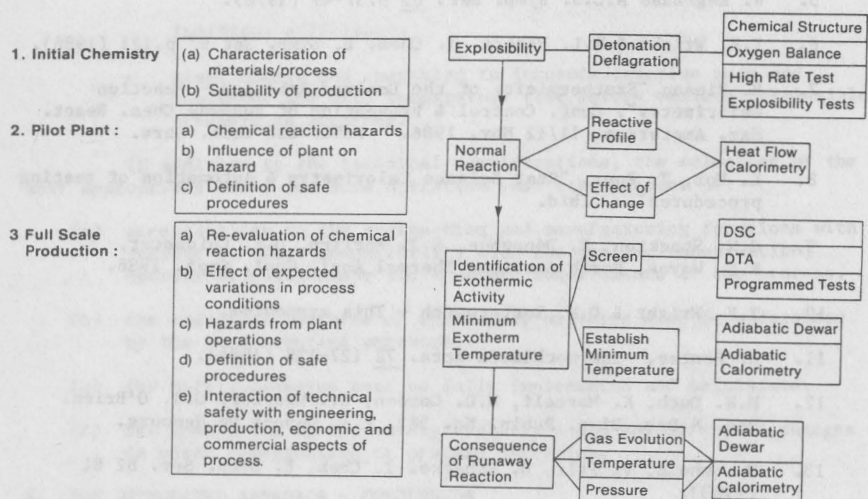


Fig 1 STAGES IN ASSESSMENT PROCEDURE

Fig 3 TYPICAL TESTING PROCEDURE

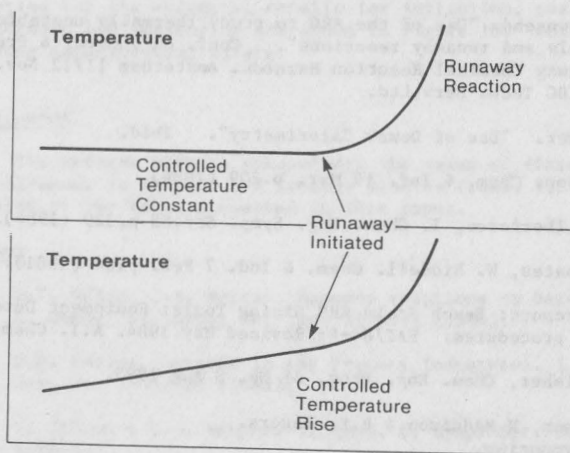


Fig 2 REACTION STAGES

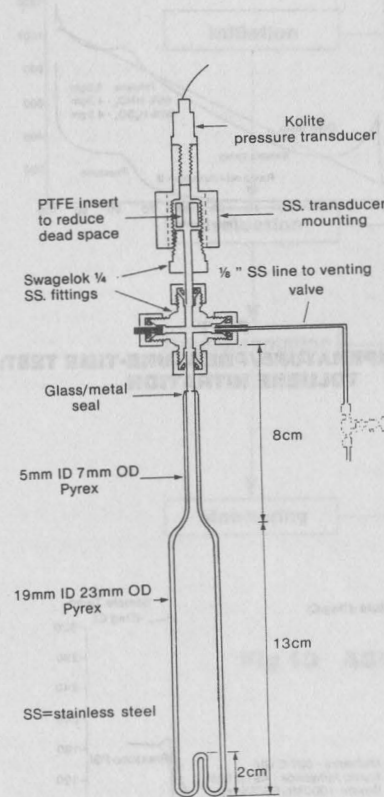


Fig 4 CARIUS TUBE CELL: PRESSURE-TIME TEST

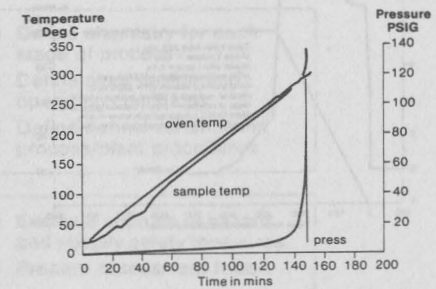


Fig 5(a) HIGH RATE DECOMPOSITION OF 2,6 DINITROTOLUENE

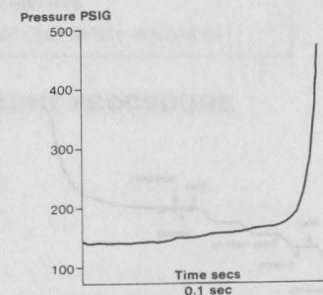


Fig 5(b) EXPANSION OF PRESSURE TRACE

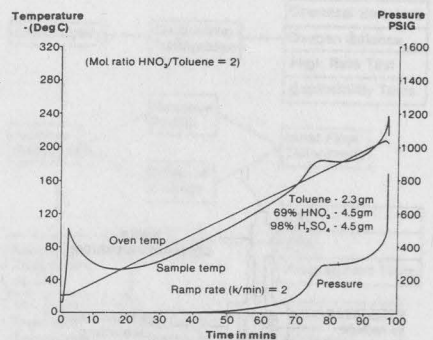
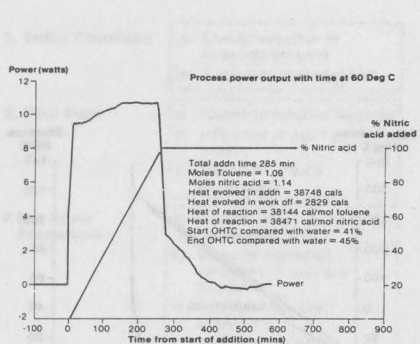


Fig 6
ISOTHERMAL REACTION CALORIMETER:
NITRATION OF TOLUENE

Fig 7
TEMPERATURE/PRESSURE-TIME TEST:
TOLUENE NITRATION

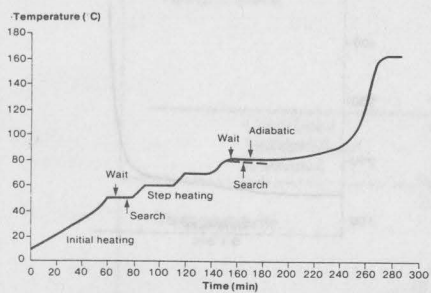


Fig 8
HEAT-WAIT-SEARCH OPERATION - ARC

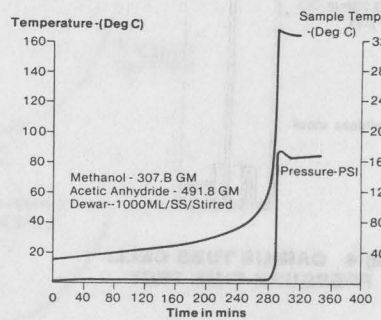


Fig 9
ADIABATIC CALORIMETER...
METHANOL/ACETIC ANHYDRIDE
REACTION

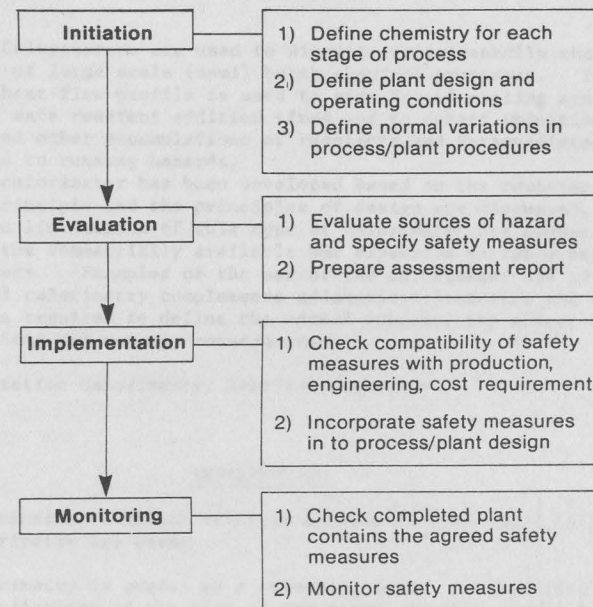


Fig 10 ASSESSMENT PROCEDURE