

**The Protection of
Exothermic Reactors
and Pressurised
Storage Vessels**

EFCE E

The Protection of Exothermic Reactors and Pressurised Storage Vessels

Organised by the Institution of Chemical Engineers, North Western Branch, in association with the Institution of Mechanical Engineers, and held at the Gateway Theatre, Chester, 25-27 April 1984.

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Preface

The protection of exothermic reactors and pressurised storage vessels is an area of particular concern for safety, and it is especially important that new methods and experience are recognised in the design of safe systems at acceptable cost. This symposium aims to assemble the most up-to-date information on the design of protection against runaway reactions and accidental discharges from vaporising liquid storage systems. Expert reviews of current art are supplemented by reports of recent advances.

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* These papers were received late and appear out of sequence.

THE CONTROL OF EXOTHERMIC REACTORS

W. Regenass*

The possibilities of protecting operating personnel and process equipment from thermal explosions are discussed. It is shown that technical measures may not be totally sufficient, and the search for inherently safe processes is advocated.

1. INTRODUCTION

There are essentially 3 routes to safe reactors:

- containment
- on-line detection of process deviations associated with systems for corrective actions.
- inherently safe processes

These categories include pressure relief systems (devices which combine detection and corrective action) and organisational measures such as hazard identification, rigorous instruction and strict enforcement of appropriate operating rules, which - if well done - come near to inherent safety.

The above mentioned categories have a clear hierarchy

- reduce damage
- stop excursions before they become explosions
- eliminate the causes of explosions

Clearly the elimination of hazards is the most effective safety measure, and often the least costly. However, it requires a thorough understanding of the potential hazards and it is not easy to exclude mistakes in the hazard assessment. Therefore, the manager charged with responsibility is tempted to opt for containment measures, for they give evidence of concern in the case of an event, whereas a wrong judgement in the hazard-elimination study can easily be interpreted as negligence or even as profit-oriented endangerment of humans and environment.

The engineer, on the other hand, is tempted to devise sophisticated safety systems, particularly as microprocessors have become inexpensive.

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In this contribution, cases are discussed where generally accepted safety devices did not work. After a review of conventional safety measures, the search for intrinsic safety, as recommended by Prof. Kletz [1], is advocated.

2. THREE INCIDENTS WITH NITRO COMPOUNDS

2.1. Water Getting into a Batch Sulfonation

A batch sulfonation was worked out to proceed safely under adiabatic conditions (high dilution with H_2SO_4). The process was considered inherently safe, since any error in the ratio of the reactants (SO_3 , nitro compound) would result in a lower than standard adiabatic temperature rise (Fig. 1b). It was considered impossible that a temperature range could be reached, where rapid decomposition takes place, particularly because there was no cooling required and consequently no water in the jacket which might break through into the batch.

The reactor (Fig. 1a) was equipped with a rupture disk and a vertical relief pipe. On preventive maintenance, the disk was removed and, by mistake, not replaced. The reactor was still closed by sublimate which had accumulated in the relief pipe and completely blocked this pipe below the position of the disk. One day, water from heavy rain accumulated above this sublimate plug. Also the operator forgot to open the venting valve of the reactor when starting the batch. Compression of the gas in the reactor by the added reactants, combined with heating up, built up a small pressure which was sufficient to blow the sublimate plug in the relief pipe. Consequently, the water above poured into the reactor. By the heat of dilution, a temperature was attained where decomposition proceeded fast. A moderate explosion occurred, strong enough to tear off the lid of the reactor.

Note: The relief system did not protect the reactor but - by a highly unlikely sequence of events - became the cause of an accident.

2.2. Deflagration at the Start-up of a Continuous Sulfonation

The start-up procedure for the first stage of a cascade of stirred tanks (Fig. 2) is as follows:

Fill the reactor with converted material up to a specified level. Heat this mixture to T_0 (with steam of $150^\circ C$), then start the feed of the reactants. The temperature sensor was positioned near the bottom of the reactor to ensure immersion in the reaction mixture. This temperature sensor was connected to a temperature controller which initiated heating below T_0 and cooling above T_0 (the specified reaction temperature).

The paddles of the stirrer were in the middle of the reactor, well below the specified start-up level.

At the start-up which led to the incident, much too little reaction mixture was loaded into the reactor, caused by a faulty level indicator, with the consequence that the stirrer was not immersed.

Due to lack of agitation, stratification occurred during the heat-up phase.

By the time the mass at the bottom of the vessel, where the temperature sensor was installed, reached the specified starting temperature T_0 , the upper layers of the mixture were heated to approximately the temperature of the heating medium (i.e. $50^\circ C$ above T_0).

When the feed of the reactants was started, another segregation phenomenon took place: the nitro compound which is a hot melt and less dense than the starting mixture, accumulated on top of this mixture, whereas the cold oleum sank to the bottom of the reactor and kept the temperature sensor cool, thus preventing the initiation of cooling. Near the surface, a small portion of the reactants reacted, nearly adiabatically, starting from much too high

initial temperatures and reaching a temperature domain where exothermic decomposition proceeds fast. As the agitator became immersed (by the rising level), the hot nests were spread across the surface and the decomposition propagated from the top down. The deflagration blew the lid from the reactor (despite the fact that a rupture disk was present) but did not damage the body of the reactor. (The thermal explosion of a well-mixed reactor would have caused significantly more damage).

Note: The temperature sensor indicated the correct temperature of its environment. An on-line warning device, attached to this sensor, would not have responded.

2.3. Explosion of a Batch Reactor which was Partially Charged and Left Unattended

A nitro compound is caused to react with a second reactant in aqueous dimethyl-sulfoxide (DMSO).

According to the procedure, the nitro compound is dissolved in DMSO and then the second reactant is added gradually. To remove the heat of reaction, refrigeration is required, as the specified reaction temperature is too near the temperature of the cooling water.

At the incident batch, refrigeration failed after the nitro compound was charged to the DMSO. Consequently, work on the batch was stopped and repair was organized. The reactor was left unattended with the stirrer on. The steam valve was closed and cooling was not available due to the failure of refrigeration. The repair took longer than expected. After 5 days fumes coming out of the vent were noticed, and a check of the reactor unit showed that the reactor contents (which had been left at ambient temperature) had reached a temperature of 160°C. At this time, the manhole was opened for inspection. Some time later, froth came out of the manhole. Attempts to bring the temperature under control failed and when the temperature exceeded 170°C, the plant was abandoned. Shortly afterwards, the reactor exploded with the manhole fully open.

The investigation of the incident gave the following results:

- The reactor was heated up by an unknown external heat source (probably a leaking steam valve) to >120°C, where the water was slowly evaporated from the mixture.
- DMSO is unstable at temperatures >100°C in the presence of strong acids (some sulfuric acid was present in the batch). The DMSO decomposed or reacted with the nitro compound exothermally, thus increasing the temperature progressively to >170°C, where the highly exothermic decomposition of the nitro compound proceeds rapidly.
- As the water was removed and most of the DMSO had disappeared by reaction, there was no temperature stabilization by evaporation in the critical temperature range of 150 to 200°C.

Note:

- The open manhole (diameter: 0.5 m) did not relieve the reactor.
- A simple temperature alarm, however, would have given a warning in time.
- The warning was required at a period, when the reactor was on hold, i.e. considered absolutely passive.

3. TECHNICAL SAFETY MEASURES

3.1. Containment

In its broadest sense, containment is a good principle for the design and operation of chemical reactors, i.e.

- keep toxic chemicals away from humans and from the environment
- avoid chain incidents (spreading fires, splashing of combustible liquids which cause vapour-cloud explosions or set whole process plants on fire).

As a means of protection against runaway and reactor explosions, the choice is often a concrete or steel barricade.

In this respect, the author has a strong opinion: the use of barricades should be restricted to the handling of explosives (i.e. substances which can detonate) and to experimental set-ups where one is intentionally moving towards the limits of safe operation, i.e. accepts the occurrence of explosions to gain experience not otherwise available.

As a protection for the operation of pressure equipment (handling non-explosives), concrete barricades do more harm than good for safety, particularly in experimental facilities. For two reasons:

- Remote control is rarely so elaborated that all necessary operations are covered. Consequently one compromises and works within the barricades "for short moments" and so experiences, in case of an incident, a degree of exposure not possible in an open facility.
- Working through barricades is so awkward that the acquisition of process understanding is seriously hindered. With the same amount of time and money, significantly fewer experiments and generally less sophisticated experiments are possible behind barricades in comparison to the work in an open facility.

This is not advice to take unnecessary risks, but a recommendation to make use of the methods of safety investigation developed recently. It is possible to investigate materials and reactions sufficiently on a microscale to allow safe bench operation in standard laboratories. Of course, in pressure work there remains the problem of mechanical leaks. In this sense containment has to be provided. However, runaway and thermal explosion (of not-so-well-known reactions) are no issue in laboratory work, when development is done according to the state of the art.

Unfortunately, in many countries, barricades are required by law for experimental pressure facilities. Consequently, when visiting different countries, one finds a wide range of safety measures for the same type of hazard, from much too little to more than useful.

3.2. On-line Detection of a Starting Runaway

The devices proposed in the literature have an extremely wide range of sophistication: from fixed alarm limits on the value of a single process variable to process simulation for pattern recognition.

Temperature is the process variable most widely monitored for alarm purposes, as it has the most important influence on reaction rate and is very easy to measure. For continuous processes and simple batch processes a fixed alarm-temperature will suffice. For batch reactions with temperature programs, temperature gradient monitoring is a good choice.

A method which is independent of process specific settings, because it detects progressive heat evolution, has been proposed and implemented by Hub [2]. A runaway situation is likely given, when the second derivative of the reaction temperature T_R and the first derivative of the temperature difference between reaction temperature and heat transfer fluid (T_H) are simultaneously positive, i.e.

$$\frac{d^2 T_R}{dt^2} > 0 \text{ and } \frac{d(T_R - T_H)}{dT} > 0$$

An on-line warning device based on this reasoning is commercially available [3] and performs according to its specifications.

The most sophisticated method is advocated by Gilles [4]: on-line comparison of the time behaviour of measured process variables with values calculated from process models. No industrial application of this approach is known to the author.

There are two obstacles to a general introduction of this method:

- the high parametric sensitivity of process systems which tend to runaway, and consequently the high accuracy of process data required for the application of the method.
- the difficult (almost esoteric) nature of the theory, which is not easily understood by the man in practice who has to assume responsibility for the safety of the processes he operates.

An interesting discussion of pros and cons of different on-line detection methods has recently been given by Hub [5].

In the opinion of the author, the simplest method available for a specific task should be chosen, i.e.

- fixed alarm settings for continuous reactors and most dedicated batch reactors
- gradient monitoring for specific batch processes where fixed alarms are not possible or not safe
- second derivative methods for multipurpose reactors, when there is danger of wrong alarm settings on change of product.

The main argument for this reasoning is the sensitivity of the alarming: it decreases with increasing order of derivation. A fixed alarm, properly set, can give the earliest warning of a process deviation and hence provides a maximum of time for corrective actions.

3.3. Stopping the Runaway

On-line warning makes sense only, when appropriate corrective actions are possible.

The type of action required is highly dependent not only on the nature of the reaction which must be kept under control, but also on the cause which created the potentially dangerous situation:

- When, due to a failure in the control system, a too high temperature has been attained, but the rate of heat release is still within the heat removal capacity of the reactor, then switching to full cooling will suffice. Interlocking systems of this type are implemented on most reactors for potentially dangerous reactions.
- When the heat release exceeds the capacity of the reactor and the reaction rate is not feed controlled (i.e. cannot be reduced by stopping the addition of a reactant), then only quenching will help.

There are several ways to effect quenching:

- a) Add an inhibitor. This requires intimate knowledge of how the reaction rate can be influenced.
- b) Add a considerable amount of cold liquid which reduces reaction rate by cooling the mixture and also by dilution. This requires that a number of previous considerations and preparations be made
 - choice of an appropriate liquid which does not react too exothermally with the reaction mixture
 - sufficient free volume in the reactor
 - technical installations which provide the addition of the liquid in due time
- c) Dump the reactor contents into a vessel which contains cold diluent. This again requires knowledge and technical installations and particular care that the dumping line is not blocked or does not become blocked during the dumping procedure. Dumping, as a rule, requires more time and is less reliable than dilution.

The author is familiar with very few quench systems, all of which are of the types a) and b)

- When the runaway situation has been caused by a sudden event, e.g.
 - a breakthrough of reactive heat transfer fluid
 - the addition of false ingredients
 - the intrusion of unexpected extraneous materials (as the rain water mentioned above)
- then very often there is no way to stop the runaway.

3.4. Pressure Relief

This most widely used safety measure is effective for high vapour pressure systems [6,7]. Its application to polymerisation reactions (ethene, vinylchloride, styrene) is well understood and well documented.

Pressure relief has two major problems

- the containment of the ejected material
- its ineffectiveness for low vapour pressure systems.

The high desirability of containing the material escaping through relief pipes is generally accepted, at least since the Seveso incident. The difficulty of designing a containment system which fits the needs of a multiproduct batch plant is known to everybody who ever tried it, and the problem of retrofitting existing plants with containment systems is even worse.

The fact that reactors burst despite the presence of rupture disks or even with an open manhole was mentioned above (cases 1-3). These ruptures were caused by runaway reaction which remained in the thermal explosion domain, not by detonations. The problem of relieving low vapour pressure systems has obtained little attention in the literature. It was mentioned by the author some years ago [8] and shall be discussed here in some detail. Fig. 3 shows the heat generation of a reaction mixture which heats up adiabatically after a loss of cooling, starting at the "normal" operating temperature of 147°C where the specific heat release rate is a low 10 W/kg. The reaction is assumed to be first order with an activation energy of 100 kJ/mole and an adiabatic temperature rise of 500°C. The same figure also shows vapour pressure curves for a high volatility reaction mixture (styrene as an example) and for a low volatility reaction mixture (sulphuric acid as an example).

For high vapour pressure mixtures, the main effect of pressure relief is temperature stabilisation, caused by vigorous evaporation. A slight temperature increase with a moderate pressure increase will cause the relief system to respond. This mechanism does not work with low vapour pressure mixtures. Here, very high heat release rates which exceed by far the evaporation capacity of the system can be attained before appreciable pressure is built up. Even the static pressure of the liquid may keep thermal decomposition going until it is much too late.

The relief capacity indicated in Fig.3 (with an upper limit for one phase vapour flow and a lower limit for two phase flow) was obtained by a short-cut estimation. The following assumptions were made

- heat of evaporation: 40 kJ/mole; molecular weight of vapour: 100
- unrestricted expansion from 2 atm to 1 atm (abs.) through an orifice of 0.2 m diameter
- reactor contents: 2000 kg

Rigorous calculations [6] show that real systems have, due to friction losses, considerably lower relief capacities.

4. INHERENT SAFETY

4.1. The Concept

A process is inherently safe in a rigorous sense, when no disturbance, whatsoever, can cause an incident. In practice, such "absolute" inherent safety is rarely attainable.

The recommendation by Kletz [1] to search for synthetic routes which avoid hazardous reactants, intermediates and reaction mixtures, is an impetus to be seriously considered by process designers. Nevertheless, we will have to cope with potentially hazardous materials and reaction mixtures in future process design work. For ecological reasons, in order to reduce the load of waste water and spent acids, future processes will have more concentrated process streams which have a higher specific content of latent energy than the existing ones and are hence less stable. So much the more, we should try to improve the inherent safety of future processes by

- keeping inventories of hazardous materials low
- keeping the process conditions sufficiently far away from stability limits
- avoiding the presence of materials which can react in a dangerous way with the process streams (or reactor contents).

Inherent safety should be an objective in process design, and the fact whether a design alternative makes a process inherently safer or less safe should be an essential decision criterion.

4.2. Design for Inherent Safety: an Example

Sulfonation of nitroaromatics with $\text{SO}_3/\text{H}_2\text{SO}_4$ and the resulting reaction mixtures cause particular hazards due to a combination of properties:

- The reaction mixtures are thermally unstable and can decompose highly exothermally (ΔT_{ad} up to 1000 K).
- The heat of the desired reaction is considerable (ΔT_{ad} : 50 to 250 K) while the reaction is not very fast: accumulation of reactants and subsequent runaway of the desired reaction is easily possible.
- The melting temperature of the reaction mixture is often high, leaving a narrow band for operation with freezing at the lower end and decomposition at the upper end.

- The vapour pressure of the reaction mixtures is very low at operating temperature. Consequently high temperatures causing very high reaction rates are reached before a relief system responds.

For a sulfonation which produced much waste acid, the amount of H_2SO_4 in the reaction mixture had to be considerably reduced. This caused a sharp increase of the potential adiabatic temperature rise (by sulfonation as well as by decomposition).

Investigations at the materials testing laboratory led to the facts and recommendations given in the following table:

Type of Investigation	Result	Routine Recommendations
Decomposition	$\Delta T_{ad} = 1000 \text{ K}$	1) exercise utmost care
Sulfonation	$\Delta T_{ad} = 150 \text{ K}$	2) avoid accumulation
Decomposition	Catalysed by iron	3) use glass-lined reactor
Kinetics	Auto-catalytic	empty the reactor 4) immediately after a stop of operation

While the recommendations 1) and 2) were accepted by the design team readily, the proposals 3) and 4) would have caused more safety problems than they would have solved. 3) would have seriously limited the freedom of reactor design; 4) would have caused a difficult and safety-critical start-up after each weekend interruption.

A further investigation revealed that the heat release caused by the decomposition is very low at operating temperature, even when iron-catalysis and auto-catalysis are taken into account (Fig. 4: the righthand ordinate shows the isothermal "time to maximum rate" of this auto-catalytic reaction, not the adiabatic TMR according to Townsend [9]).

Therefore, the limitation of the reaction temperature to values below a critical value (i.e.: normal operating temperature + 10°C) is a sufficient condition for safety. This requires avoiding all actions and reaction which could cause a fast and/or considerable temperature rise of the reaction mixture, e.g.

- exothermic reaction with the heat transfer medium
- high temperatures of the heat transfer medium
- heating by mechanical friction
- heat accumulation due to too efficient thermal insulation of the reactor
- accumulation of reactants.

Furthermore the following design recommendations were made

- use a plug flow type of reactor for completing the reaction, in order to keep the reactor volume as small as possible
- use excessive heat transfer capacity in order to maintain sufficient heat transfer even when circulation fails
- make the heat capacity of the reactor high, thus compensating for the low ratio of heat capacity to latent heat in the reaction mixture.

5. PROCESS ANALYSIS FOR SAFETY

Inherent safety must be achieved in the progress of process development. There is no easy or simple way to this goal. One of the keys is understanding how a runaway can proceed in a specific situation. Using this approach, it is often possible to arrive at conditions which will ensure safety and which can be easily met.

5.1. The Causes of Runaway

In a runaway situation - by definition - a reacting mixture heats up progressively to temperatures where the reaction rate becomes very high. If the pressure generated by product gases or by volatility bursts the reaction vessel, we call the incident a thermal explosion.

A runaway will occur, when two conditions are met, namely

- when the latent energy of the reaction mixture is high, and
- when the heat generation by the reaction exceeds the heat removal from the system.

Source of the latent heat may be the desired reaction or the thermodynamic properties of the materials involved (tendency to exothermic decomposition).

The heat of the desired reaction may be eliminated as a hazard by appropriate reaction conditions (continuous or fed-batch reaction). Dangerous situations arise, when unintended accumulation of reactants takes place. The hazardous properties of the material involved have to be coped with, i.e. too high temperature ranges where heat generation by exothermic decomposition exceeds the heat removal capacity of the system must be avoided.

The simple scheme shown in Fig.5 relates the above mentioned most frequent causes of reactor incidents. Many authors [10-12] have presented more elaborate schemes. Fig. 6 is another attempt of this kind, mainly devoted to the causes of reactant accumulation and unexpected temperature increases.

5.2. A Systematic Approach to Inherent Safety

The following basic questions may provide helpful guidelines for process design [13]:

- 1 Are the materials involved stable or is there a highly exothermic decomposition to be feared

Data answering this question are easily obtained by means of micro-thermo-analytic instrumentation [14,15].

If exothermic decomposition is found, all care must be taken for keeping the decomposable material within the allowable temperature range, as explained in the design example given above (Sect. 4.2.).

- 2 Can the heat of the desired reaction bring the reaction mixture into a temperature domain where
 - high pressure is generated by volatility or by product gases, or
 - an exothermal decomposition is triggered

The heat of reaction data required are best obtained by heat flow calorimetry [16,17,18].

If the heat of reaction is dangerously high, then the concentration of at least one of the reactants has to be kept low in the reactor, i.e. accumulation has to be avoided.

- 3 To what extent is an accumulation of reactants in the reactor to be expected and how is accumulation affected by the process conditions.

There are many ways to acquire the necessary kinetic data, the most efficient method in the experience of the author is heat flow calorimetry. Kinetic information is helpful for process optimisation. It also provides guidelines as to which deviations from the specified process conditions are tolerable and which are not.

- 4 At what rate will temperature rise as a result of a disturbance

For temperature rise by exothermic decomposition this question is best answered by sophisticated "safety calorimeters" [19,20] which have become available recently. Temperature rise rates caused by intrusion of heat transfer fluid may be investigated by heat flow calorimetry. For heating by heat transfer from the outside or by mechanical friction, one has to make use of engineering estimates or do specific experimental work. Knowledge of worst case temperature rise rates is required for the choice of appropriate corrective measures.

6. CONCLUSIONS

- Reactor safety should be based on inherently safe design rather than on technical devices.
- On-line detection systems combined with automatic actions to stop a runaway will, in most cases, prevent thermal explosions or at least reduce the extent of an incident, but there are exceptions where these means are ineffective.
- As inherent safety should be achieved in the progress of process development - rarely can it be added to an established process by simple measures - the chemist or engineer responsible for process development should be familiar with safety concepts. This includes the understanding of the nature of potential hazards, as well as the knowledge of the means available for investigating specific situations and for eliminating the hazards encountered.
- Achieving inherently safe processes which are at the same time simpler and less costly than "conventional" ones requires an approach which combines the pragmatic analytical thinking established among chemical engineers with experience of incidents and measures to prevent them.

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