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Lecture Transcripts

Why Reactions Run Away†

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Abstract:

Exothermic runaway incidents caused by poor understanding of the reaction chemistry and kinetics, under-rated control and safety backup systems, and inadequate procedures and training continue to be reported to the Health and Safety Executive (HSE). Although guidance and training to prevent such incidents is available, further work is needed to increase awareness of the problems. A recent HSE survey indicates that further information on relief system sizing is also required. A workbook on this topic is in preparation, and a leaflet, drawing attention to the hazards of exothermic runaway, is being published. Further action by the HSE to increase awareness is being considered.

Introduction

The causes of incidents leading to exothermic runaway were reviewed in 1984,[1] 1989,[2] and 1993.[3] These analyses showed the underlying causes to be (a) poor understanding of the reaction chemistry or kinetics leading to badly designed plant; (b) under-rated control and safety backup systems; and (c) inadequate procedures and training.

This paper discusses these main causes and the progress made in the UK since the initial survey in 1984. Although much has been done to provide information on the hazards and means of prevention and control, incidents attributed to the same underlying causes continue to occur. The need for more awareness of the problems is discussed in the light of a recent Health and Safety Executive (HSE) survey on standards of relief system sizing at chemical reactors.

Underlying Cause 1: Poor Understanding of the Reaction Chemistry or Kinetics

Failures to adequately assess the process chemistry or reaction kinetics accounted for a significant number of incidents in the three surveys. Specific causes included (a) underestimation of the heat evolved; (b) unanticipated side reactions, including formation of unstable by-products; (c) changes in onset temperature (for decomposition or runaway) with conditions; and (d) unpredicted autocatalysis.

Failures caused by an underestimation of the heat evolved prior to scale-up caused particular problems. Whilst the heat losses from conventional laboratory glassware are fairly high (between 3 and 6 W kg^{-1} K^{-1}),[4] those on a full-scale reactor can be much less (typically 0.5 W kg^{-1} K^{-1} for a 2.5 m^3 reactor). This is due to the reduced surface area to volume ratio of the vessel with increasing scale (see ref 5 for a fuller explanation). Often reactions that have seemed only weakly exothermic on the laboratory scale, and may even have required a heat input, can generate substantial temperature increases on the full scale. It is therefore essential that, before scale-up, accurate information on the heat of reaction and, where appropriate, the heat generation rate be obtained so that adequate cooling can be provided. Unless this is done, the large-scale vessel may have insufficient cooling capacity and an exothermic runaway reaction may occur.

Case History 1. An explosion occurred in a nitration reactor. Although the company had carried out small-scale development tests, they had not measured the heat generated by the reaction, and the cooling system was inadequate.

A particular problem associated with scale-up is the assumption that the so-called “onset temperature” for exothermic runaway or thermal decomposition will be the same in a small-scale test as in a full-scale plant. It is not always appreciated that the temperature at which such runaways/decompositions occur is dependent on a number of factors including the detection sensitivity of the test apparatus used, vessel size and heat transfer characteristics, and time.

Case History 2. An explosion occurred in a process vessel involving a thermally unstable material. The company had made the assumption that the decomposition temperature of the material was in the range 270–299 °C, the same as in small-scale tests reported in the literature. Following the incident the company carried out a fuller investigation of the thermal decomposition characteristics of the material in more accurate adiabatic tests, designed to simulate the plant environment. These tests indicated that the material could decompose at 153 °C on the plant scale, below the temperature of the heating jacket.

† This paper was originally published in the proceedings of Hazards XIII, 1997, IChemE Symposium Series No. 141, pp 361–366.

(1) Barton, J. A.; Nolan, P. F. *Runaway Reactions in Batch Reactors*; IChemE Symposium Series 85; Institution of Chemical Engineers: Rugby, UK, 1984.
(2) Barton, J. A.; Nolan, P. F. *Incidents in the Chemical Industry Due to Thermal Runaway Reactions*; IChemE Symposium Series 115; Institution of Chemical Engineers: Rugby, UK, 1989.
(3) Etchells, J. C. Prevention and Control of Exothermic Runaway; IBC Conference on the Assessment and Control of Chemical Reaction Hazards, December 1993.
(4) *Process Saf. News*, issue 3, Chilworth Technology Group.
(5) Barton, J. A., Rogers, R. L., Eds. *Chemical Reaction Hazards*, 2nd ed.; Institution of Chemical Engineers: Rugby, UK, 1997.

Underlying Cause 2: Under-Rated Control and Safety Backup Systems

Runaway can also be caused by system failures, such as operator error or instrument failures. These may upset the heat balance, result in secondary reactions or the formation of thermally unstable materials. In addition to the normal operations being assessed, the effects of foreseeable process deviations should be assessed at an early stage in process development so that, where necessary, they can be prevented or controlled.

The main options for prevention and control of exothermic runaways are either preventive measures or protective measures.

Preventive measures are designed to prevent the conditions that can lead to exothermic runaway. Such measures include inherently safer design, safe systems of work, control systems, and trips.

Protective measures are designed to mitigate the effects of an exothermic runaway, such as emergency relief vents, reaction inhibition, quenching, and drown-out. These are rarely used on their own, as some preventive measures are normally required to reduce the demand on them.

Information on the selection and specification of preventive measures is given in ref 5. Particular problems include (a) insufficient information (e.g., from the initial hazard assessment) to properly specify the safety measures; (b) poor installation; and (c) the provision of a combination of measures that was not sufficiently reliable to ensure safe operation.

Case History 3. An explosion occurred in a resin reactor. It was found that the thermocouple used to measure and control the vessel temperature was above the liquid level. Although the level of reactants in the vessel was variable, insufficient account had been taken of this in the vessel design.

Emergency relief vents are probably the most common protective measure used in the UK for the protection of reactors against exothermic runaway. The design of emergency relief vents in Great Britain was the subject of a recent survey by the HSE. Data on 94 vessels used for exothermic reactions at 82 different factories was collected by HSE specialist inspectors and collated onto a central data base. The main findings were as follows:

(a) Emergency relief venting was provided in 73 vessels (the others relied on alternative combinations, including inherently safe design, as the basis of safety).

(b) A significant percentage of companies did not have ready access to the design standards to which their reactors were constructed.

(c) Less than half of the companies had clearly carried out any form of reaction hazard assessment, either to determine that overpressurisation was possible or to identify the "worst case" reaction for vent design purposes. It is possible that in some companies this work had been done at some stage, but it had not been recorded.

(d) Although many papers have been published on reactor relief system design, particularly by the Design Institute for Emergency Relief Systems (DIERS), and there is a DIERS Project Manual,[6] only a few of the companies appear to have used the available technology. Many companies either did not know how the emergency relief systems had been designed (and the information was unobtainable) or had used invalid techniques, such as (i) API 520 for fire venting of flammable solvents (in two cases the solvent was known to be thermally unstable, but this had not been taken into account); (ii) "professional judgement" (without any calculations or reaction runaway data to back it); (iii) largest existing vessel opening.

(e) Most of the relief systems were specified by professional engineers, either employed by the companies themselves or by relief system suppliers.

(f) No correlation between following the correct relief system sizing procedures and company size or vessel age could be found. This may be due to the limited size of the sample studied.

(g) Companies that were part of large multinational groups were more likely to have followed the recommended methodology.

(h) Although some multinational companies had sufficient expertise in-house, this expertise had not always been called upon.

(i) Just over half of the vessels were multipurpose, the remainder being used for one reaction only.

It should be emphasised that the prime purpose of this survey was to identify what methods had been used to design emergency relief venting of chemical reactors. Of particular interest was the extent to which design techniques developed by DIERS had been adopted. Consideration of other safety measures provided for the vessel, in addition to the emergency relief vents, was not a core part of the survey.

Case History 4. A reactor failed during an exothermic runaway despite being fitted with a bursting disc, which ruptured. It was found that the company had progressively increased the rating of the bursting disc at the reactor vessel, so that it was much higher than originally designed.

Case History 5. An exothermic runaway occurred, leading to the destruction of a reactor vessel. The reactor had been provided with a 50 mm diameter relief vent. The subsequent investigation showed that a 200 mm vent would have been required to protect the reactor.

Underlying Cause 3: Inadequate Procedures and Training

Inadequate procedures and training were identified as the third underlying cause of exothermic runaway. Particular problems include (a) inadequate training, instruction, and supervision of operators; (b) unauthorised changes to instructions; (c) poor maintenance procedures; (d) operators not able to properly respond to abnormal situations; and (e) failures to test emergency procedures.

Case History 6. An incident occurred during a catalyst activation process. The operating team had decided to increase the inlet gas temperature by 30 °C to improve process performance. However, they did not recognize this as a significant process change, so the effect of the increased

(6) Fisher, H.; et al. *Emergency Relief System Design Using DIERS Technology*; DIERS Project Manual; American Institute of Chemical Engineers: New York, 1992; ISBN 0-8169-0568-1.

temperature on the reaction rate was not evaluated. Shortly into the operation, the temperature detectors on the reactor went off range. The operators concluded that the detectors were malfunctioning and discounted them. The vessel eventually ruptured due to the excessively high temperatures reached in the reactor.

Case History 7. Five people, including two fire-fighters, were injured when a reactor ejected its contents into a work room. It was found that, at an earlier stage in the process, a separator in a reflux line had overflowed, leading to the loss of one of the reactants. Although a number of high-level alarms on the separator had sounded, these had been accepted by the operator and no action taken. Exothermic runaway occurred in the next stage reactor when the product, which contained an excess of sulphate as a result of the overflow, was transferred into sodium hydroxide.

Progress Made

The need for more information on the assessment and control of exothermic reactions led the HSE and others to develop a textbook on the subject.[5] This has recently been revised and now includes a number of case histories. A video has also been produced by the HSE,[7] and this was followed by an Institution of Chemical Engineers training package,[8] which includes the video, the book, and incident case histories. There have also been a number of meetings and conferences on the subject (for examples, see ref 1, 3, and 9). The Institution of Chemical Engineers runs a number of training courses, and many companies have their own in-house training. However, such training courses are not attended by all process development chemists and engineers, and training is not generally included in university syllabuses. Until this apparent lack of awareness is addressed, the problems are likely to persist.

In response to the need for more awareness, the HSE is currently preparing a free leaflet on the hazards of chemical reactions. This is particularly aimed at small to medium-sized companies without their own "in-house" experts. This should give companies a clear picture of the hazards and where further information is available. An HSE guidance note is also underway, and further action to increase awareness is being considered.

In the area of relief system sizing, an HSE workbook, entitled *Emergency Relief System Sizing for Chemical Reactors*, is at an advanced stage. This is particularly aimed at professional engineers in medium-sized and small companies, the main professional institutions, manufacturers, and suppliers. An HSE research contract report on disposal system design[10] has recently been published, and it is also worth mentioning that the Center for Chemical Process Safety in the US is preparing guidance on the subject.

More generally, an EC project on methods of inherent SHE[9] (safety health and environmental design) is currently being sponsored by a number of organisations, including the HSE. The main objectives are to assess the current status of inherent SHE, to raise awareness, and to develop an inherent SHE tool kit. In the UK, the HSE is preparing guidance to raise awareness of this topic.

Conclusions

1. Exothermic runaway incidents, resulting from a poor understanding of the reaction chemistry/thermochemistry, under-rated control and safety back-up systems, and inadequate procedures and training, continue to occur.

2. Although guidance and training on chemical reaction hazard assessment and control are available, further work and information are still needed to increase awareness of the problems. A free HSE leaflet drawing attention to the hazards and where guidance can be obtained is in preparation. Further action by the HSE is being taken.

3. A recent survey by the HSE on standards of relief system sizing for exothermic runaway indicates that further information on this topic is also required. A workbook by the HSE on this topic is at an advanced stage. This is particularly aimed at chemical engineers in medium-sized and small companies, manufacturers, and suppliers.

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1997.

(7) *Control of Exothermic Chemical Reactions,* HSE video, available from CFL Vision, PO Box 35, Wetherby, Yorks LS23 7EX, UK.
(8) *Control of Exothermic Chemical Reactions*; IChemE Training Package; Institution of Chemical Engineers: Rugby, UK, 1993.
(9) Rogers, R. L. Scale Up to an Inherent SHE Process. Conference on The Scale Up of Chemical Processes; Scientific Update, 1994.
(10) Singh, J. Safe Disposal of Vented Reacting Fluids. HSE Research Contract Report No. 100/1996; HSE Books: Suffolk, UK.