

RUNAWAY REACTIONS IN BATCH REACTORS

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Case histories of 263 incidents involving runaway reactions of the type $A + B \rightarrow \text{products}$, carried out in industrial batch reactors have been analysed on the basis of unit processes involved, initiating factors and type of industry. The case histories were drawn from Health and Safety Executive files, industrial records and the open literature. Although the data has no absolute statistical value, primarily because it is difficult to place such figures in the context of all relevant aspects of industrial practice, the figures are indicative of problem areas. The initiating factors are described and the analysis is exemplified with some case histories.

INTRODUCTION

Batch reactors are ubiquitous in the chemical industry due to their convenience and flexibility. The majority of reactions carried out in them are exothermic to a degree and there is a potential for overheating to occur in circumstances where the rate at which heat is generated by the reaction exceeds the rate at which heat is removed by the system. Overheating, generally causes consequential increases in the rates of reaction and heat release and so the problem becomes compounded; in general terms the rate of heat release is exponential with respect to temperature rise whilst the ability to remove heat varies linearly with temperature difference across the heat transfer surface. This situation commonly results in an excessive rate of gas and/or vapour evolution, e.g. due to the reactor contents boiling, and clearly, matters may be exacerbated if any of the starting materials, intermediates or products are prone to thermal decomposition. Exothermic chemical reactions which overheat and follow the path outlined above are colloquially known as "runaway" reactions. The net effect usually is overpressurisation of the reactor and the common outcome is loss of containment.

STATE OF THE ART

It is perhaps self-evident that in order to avoid conditions for runaway arising it is necessary first to have a knowledge of the chemistry and associated thermochemistry of the desired reaction and potential side reactions and also of the thermal stability and physical properties of reactants, intermediates and products. Only when these parameters are understood can a proper

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specification for the process and plant design and operating conditions be established. Undertaking a structured analysis, the rigour of which would depend on the particular circumstances, facilitates the collation and appraisal of the relevant parameters. This would involve, for example, a hazard analysis investigation and techniques such as hazard and operability studies and fault-tree analysis (1). A scheme relating to the production of phenolic resins is described in reference (2). It is well established that among the factors to be taken into account are:-

(i) Thermochemistry:-

- (a) Heat of desired reaction and any side reactions
- (b) Rate of heat evolution and factors which affect it, including
 - mischarging of reactants (too much, too little, wrong order, too fast, too slow etc.);
 - accumulation of reactants and heat-effects of agitation;
 - impurities (including ingress of cooling media) with implications on materials of construction of the plant and quality control;
 - delays in process - autocatalysis;
- (c) The nature of any decomposition reactions and the temperature range in which they occur.

(ii) Heat transfer and factors which affect it, including:-

- (a) Properties of the reacting mass
 - specific heat
 - viscosity changes, formation of slurries, precipitation (caking on reactor walls);
- (b) Heat input (for initiation) and its control;
- (c) Coolant supply system;
- (d) Effect of scale-up;
- (e) Effect of agitation;
- (f) Temperature control
 - instrumentation.

(iii) Other considerations

- (a) Effect of power failure;
- (b) Reactors vapour space control
 - inerting.
- (c) Design for pressure (3)
 - to withstand maximum pressure likely to be generated, or, more commonly:-
 - pressure relief, involving, for example:-
 - a relief device
 - sizing of relief vent (4)
 - vent discharge pipeline
 - catch vessel
 - vent pipe to atmosphere
 - suitable mountings for reactor and pipeline to withstand reactive forces.
 - gas evolution data
- (d) Dumping or quenching
- (e) The organisational and procedural aspects of safe plant operation.

No system can be designed to operate on its own. There is a need for:

- personnel training
- operating instructions
- plant log sheets and records
- safety procedures
- check lists
- maintenance schedules and procedures

Information relating to the thermochemistry parameters ((i) [a c] above) which is the basic pre-requisite to provide the foundation for the engineering and control design is obtained generally by reference to the literature and/or a laboratory study using techniques discussed below. A laboratory scheme is described in reference (5).

EXISTING LABORATORY TECHNIQUES

Several laboratory-based tests and simulation using computer programs have been and are being developed to aid the hazard assessment of potential runaway reactions. These techniques relate substantially to the investigation of single substances rather than reaction mixtures. The study of process reaction mixtures is in its infancy compared to the study of the thermal stability of single substances.

Many of the tests are based on the concept of differential thermal analysis and due initially to economic constraints many non-commercial methods have been devised in order to use larger, representative samples. Results indicate that these cheap methods can be just as sensitive in detecting exotherms as the considerably more expensive commercial apparatus including differential scanning calorimetry, accelerating rate calorimetry (6), Sikarex (7) and Sedex (8).

The simplest experimental techniques have been devised to detect exotherms. The level of accuracy in detecting the onset of an exotherm is dependent on the sensitivity of the instrumentation. If positive, the simple exotherm test can be followed by a range of tests based on isothermal and/or adiabatic storage. These latter tests can employ the use of Dewar vessels. Many of the simple tests can incorporate process variables and deviations from process conditions. For instance, it is possible to add samples of the industrial reactor's materials of construction and determine any catalytic or side reactions.

Experience of the use of calorimeters is limited, at present. Some of these instruments can approximate to near adiabatic conditions, which mimic the case of an uncooled industrial reactor in which the agitator fails. They provide a range of data but have some limitations regarding the continuous assessment of reaction type, $A + B \rightarrow \text{products}$. For instance, in some apparatus it is not possible to stir the reaction mixture and relatively small amounts of sample are investigated.

Possibly, the best method of studying chemical reaction mixtures on a continuous basis is the heat flow calorimeter. A number of versions of a basic design (7,9,10) incorporating a stirrer, reflux facilities and heating/cooling jacket are available. At present the models have certain physical restrictions.

REVIEW OF CASE HISTORIES

The study briefly reported here is of an analysis of 263 case histories of

incidents involving batch reactors in which runaway exothermic reactions of varying severity occurred. The study was undertaken primarily to gain a better appreciation of the most common factors which have, in industrial practice, led to runaway and with a view to highlighting particular areas for attention by those, particularly chemists, chemical engineers and managers, who research, devise, design or operate existing, new or modified products, processes, plant or procedures.

The data presented here were obtained from industrial records and the literature (not exclusively U.K. experience) and from the files of the Health and Safety Executive (HSE). The latter data comprises 123 incidents reported to HSE (HMFI) in the period 1962-1982 which caused a total of four fatalities and 66 injuries (i.e. injuries which caused the injured person to be off work for the qualifying statutory period of time).

The information available on many of the incidents was not as full as might have been wished and so it was not possible unequivocally to classify them. Even had the information on each incident been complete the figures would have no statistical significance because of the uncertainties of under reporting and incomplete retrieval. Furthermore it is not possible to say, for instance, that a particular process has a poor record in comparison to others, because to be able to do so it would be necessary to place the figures in context taking into account such factors as production tonnages, near miss data, operating standards etc. Notwithstanding these qualifications, it is believed that the information is of value as being at least indicative of general trends.

The incidents have been classified according to

- (1) unit processes.
- (2) initiating factors
- and (3) industries involved.

THE UNIT PROCESSES

The unit processes for 134 cases of the 263 have been identified and details are given in Table 1.

Table 1

Number of incidents per specified unit process

<u>Unit process</u>	<u>Number</u>	<u>Unit process</u>	<u>Number</u>
Alcoholysis	3	Isomerisation	2
Amination	3	Methylation	2
Cyclisation	3	Nitration	33
Diazotisation	2	Oxidation	4
Electrolysis	1	Polymerisation	
Esterification	2	Phenolic resins	12
Halogenation		Other resins	16
Chlorination	6	Condensations	4
Bromination	3	Other polymerisations	13
Hydrogenation	7	Sulphonations	12
Hydrolysis	6		

The following case histories have been selected as illustrative examples

Case history 1 (Nitration):-

In the manufacture of meta-nitro-benzonitrile, an intermediate and mixed acid were charged to a vessel and cooled to 283K. Benzonitrile was then added slowly and the temperature maintained between 283-293K. About one third of the normal charge of benzonitrile had been added over a six hour period and the addition was stopped because the temperature rose to 294K. The vessel eventually exploded, removing the roof of the building and one employee was injured. This was the first time this reaction had been carried out on this scale. Scaling up was not done with due regard to ways of controlling the reaction. The probe to monitor the temperature of the reaction mass was not immersed in the liquid but was in a through draught.

Case history 2 (Polymerisation):-

In the manufacture of polyvinyl acetate a small quantity of monomer and catalyst were added to a stainless steel reactor, which was heated to initiate the reaction. The monomer was then progressively fed into the vessel, which was kept at 348K and the pressure of the reaction was about 0.14 bar (g).

On the day of the incident, the progressive monomer additions were nearing completion and the temperature rose to 373K accompanied by a rise in pressure. A bursting disc rated at 1.4 bar (g) ruptured and 6m³ of reactant mass was discharged through the vent.

The investigation revealed that the transmitter attached to the thermocouple had failed and caused the coolant water supply to stop.

Case history 3 (Sulphonation):-

Monoethanolamine was added slowly with stirring to 98% sulphuric acid which was maintained at 383K in a glass-lined reactor. The monoethanol amine and sulphuric acid were immiscible. When the reaction was complete the mix was cooled and iso-propyl alcohol was added to precipitate the product.

On the day of the incident, the reactor was charged with sulphuric acid, there was then a shift change and the oncoming shift not realising that the stirrer had not been switched on proceeded to add the mono-ethanol amine. Later it was seen that the temperature was not rising and investigation showed the stirrer was not switched on. This was done and the two liquids were mixed causing an instantaneous chemical reaction and explosion.

INITIATING FACTORS

The current analysis of 263 incidents allowed the initiating factors to be classified into the categories shown in Table 2.

The following case histories have been selected as illustrative examples.

Case history 4 (Mischarging):-

During the manufacture of sodium lactate solution, solid caustic soda was added through an open manhole over 15 hours to aqueous lactic acid in a steel reactor. The mix erupted when 13 of the 30 bags had been added in 1.7 hours. The caustic soda had been added at too fast a rate and this was coupled with inadequate cooling capacity of the reactor to give rise to localised boiling of the mix.

Table 2

Number of incidents per initiating factor

Initiating Factor	I	UNIT PROCESSES		
		P	N	S
1. Basic lack of knowledge of process chemistry /thermo-chemistry	34	1	1	2
2. Mischarging				
- omission of reactant	2			
- undercharging of reactant	7			
- overcharging of reactant	14			
- charging reactants too rapidly	7			
- charging at wrong temperature	3			
- other e.g. not following precise operating procedure	5			
TOTAL	38	8	6	
3. Accumulation of reactants	7		1	
4. Presence of impurities				
- raw material changes	9	3		
- water	10			
- other	14	2		
TOTAL	33	5	4	3
5. Delays in processing	9	1		
6. Inadequate cooling				
- due to incorrect scale-up	9	5	2	
- due to methods of operation, instrumentation, supply	12	7	5	
TOTAL	21	12	7	
7. Agitator failure/stoppage				
- inadequate agitation	4			
- breakdown	6			
- failure to start agitator	10			
- intentional stoppage of agitator	4			
TOTAL	24		2	5
8. Inadequate temperature control				
- due to method of operation	14	4	2	
- due to instrumentation	8	5	2	
TOTAL	22	9	4	
9. Problems with valves leaks and blockages	31	4	3	2
10. Opening of wrong manhole or reactor	2	1		
11. Failure of auxiliary equipment	10	4		
12. Case histories with insufficient detail	32		5	
GRAND TOTAL	263	45	33	12

NOTE: I = No. of incidents

P = Polymerisations

N = Nitrations

S = Sulphonations

Case history 5 (Presence of impurities):-

An initiating mix of ether, butyl chloride, cyclohexane and butyl bromide for the preparation of a Grignard reagent was added to a reactor containing the magnesium. Cyclohexane was added and immediately vapours emerged from the condenser vent and the bursting disc ruptured. The investigation revealed that the cyclohexane transfer line was wet and the Grignard reagent had reacted with the water to produce hydrogen and ethane.

Case history 6 (Agitator failure/stoppage):-

During the purification of an acid, it was necessary to add a number of chemicals. The mix had been cooled down and analysis indicated that more caustic soda was required. The operator opened the manhole lid and thinking that it would overflow turned off the agitator before adding more caustic. The mix immediately erupted because the lack of stirring gave rise to localised high concentrations, which when reacted caused the liquor to boil.

Case history 7 (Problems with valves, leaks, blockages):-

During the day of an incident, there had been problems with leakages necessitating the shut-down of a mononitrochlorobenzene plant. Repairs to the plant were followed by the high temperature alarm sounding in second, third and fourth reactors consecutively after the previous reactor had been cooled down. The fourth reactor could not be cooled due to a blockage in the monochlorobenzene return line to the first reactor. This blockage was cleared using live steam, shortly afterwards an explosion occurred.

The plant shut-downs and particularly the blockage in the monochlorobenzene return line led to an excess of nitric acid instead of the normal excess of the monochlorobenzene. This resulted in the oxidation of monochlorobenzene instead of nitration, the oxidation proceeding as an uncontrolled exothermic reaction.

Case history 8 (Lack of knowledge regarding process chemistry):-

In the manufacture of tetrachloroethane excess chlorine was reacted with acetylene at 373K in the presence of a ferric chloride catalyst. The temperature of the mix dropped and an explosion ruptured the bursting disc and also cracked the reactor. It was suggested that monochloroacetylene had decomposed initiating the explosion.

COMMENT ON THE REVIEW

The majority of the incidents resulted in some degree of loss of containment ranging from controlled venting via a purpose-provided emergency relief system, through mild ejection of part of the reactor contents into the working area, to explosive rupture of the reactor which in some cases was followed by a fire and/or a secondary explosion when flammable materials were consequentially released. Personnel were injured due, for example, to splashing by hot liquors or the effects of blast, missiles or toxic fumes. Plant usually suffered down-time at least and/or it was more or less seriously damaged as also in some cases was the building housing the plant. In a few cases surrounding areas both on - and off - site were put at risk.

It is apparent that despite the knowledge which exists and the techniques which are available for the assessment of potential runaway reactions, to aid process and plant design, control and operation, that incidents continue to occur due

to the classic problems (11) of a basic lack of proper understanding of the process chemistry and thermochemistry inadequate engineering design for heat transfer, inadequate control systems and safety back-up systems, and inadequate operational procedures, including training. This brings into doubt the degree to which the available information and techniques are employed before a process is brought into production and also raises questions as to the relevance, suitability and accessibility of existing techniques, in particular the laboratory tests for assessing the fundamental thermochemical hazards and particularly for the smaller operator.

FUTURE WORK

The Health and Safety Executive has sponsored a three year Ph.D. studentship and contract with the Polytechnic of the South Bank to design an experimental apparatus, which will allow a complete safety assessment for liquid phase reactions in batch reactors at atmospheric pressure, and also provide suitable data for scale-up to allow the design of batch reactors for a range of unit processes. The objectives are:-

- (i) To examine the existing techniques used for the determination of thermal stability and exothermicity of reaction systems.
- (ii) To evaluate the techniques and parameters measured, in terms of a safety assessment for initial reactants, intermediate and final products.
- (iii) To draw-up a technical specification for an apparatus to allow a full safety assessment for a range of unit processes.
- (iv) To design the apparatus in accordance with the specification and then to subject the design to scale-up criteria.
- (v) To build the apparatus on an economic basis, so that small companies without expensive support laboratories could afford the unit to allow safety assessment and scale-up.
- (vi) To obtain experimental data and compare it with existing knowledge from pilot and industrial plant.
- (vii) To devise the strategy and experimental regimes for the small companies to test reactants, intermediates and final products, and to predict the effects of loss of control or deviations in the prescribed process operation.

CONCLUSIONS

1. A review of 263 case histories of runaway exothermic reactions in batch reactors has shown that incidents continue to occur for the classic reasons despite techniques being available for the structured assessment of hazards and their remedy.
2. Laboratory-scale tests for investigating reactions under simulated batch reactor process conditions which permit scale-up are in their infancy.
3. Research sponsored by the Health and Safety Executive is being undertaken at the Polytechnic of the South Bank with the objective of devising a test apparatus to allow thermochemical data to be determined under simulated process, as a basis for full-scale design and operation.

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