INCIDENTS IN THE CHEMICAL INDUSTRY DUE TO THERMAL-RUNAWAY CHEMICAL REACTIONS

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An analysis is presented of 189 industrial incidents in batch reactors involving thermal-runaway chemical reactions of the type A + B -> products reported to the Health and Safety Executive in the period 1962-1987. Although not statistically significant the results of the analysis are at least indicative of problem areas which have led to overheating and eventual runaway. The prime causes of runaway have been classified under the headings of process chemistry and plant design and operation and a number of contributing factors have been identified under each. A simple strategy is described for assessing the thermal-runaway potential of reaction mixtures based on laboratory investigative techniques.

Keywords:- Chemical reactions; batch; exothermic, runaway; incidents; industrial

INTRODUCTION

Thermal-"runaway" is characterised by progressive increases in rate of heat generation, temperature and pressure (the latter generally caused by components in the reaction mass vapourising and/or decomposing to yield gaseous products at the elevated temperatures involved).

Thermal-runaway begins when the heat generated by a reaction exceeds the heat removal capabilities of the hardware in which the reaction is being carried out. At first the accumulated heat produces a gradual temperature rise in the reaction mass which causes an increase in the reaction rate. This self-accelerating process may finally lead to an explosion. The problem is that an increase in temperature has a linear effect upon the rate of heat transfer but has an exponential effect on the rate of reaction and subsequently on the rate of heat generation.

Runaway is a major problem in unsteady-state batch reactors, since the task of specifying the design, operation and control of an apparently simple kettle reactor with stirrer, heating/cooling coils, possibly reflux facilities, and emergency relief venting can be difficult, if all the time-dependent parameters are considered. It is a task which requires a systematic approach. The problem is often compounded because batch reactors are frequently multi-purpose rather than dedicated to one process. Due to economic factors a batch reactor may be used to carry out many different chemical processes, and it is necessary to ensure that the heat of reaction does not exceed the existing cooling capacity of the vessel for each reaction.

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Barton and Nolan (1,2) have previously examined case histories of industrial incidents in batch reactors involving thermal-runaway chemical reactions of the type A + B --> products (incidents involving thermal stability problems with single components are not included) to determine any apparent trends with a view to drawing general lessons from previous mistakes, having regard in particular to lack of knowledge of the process chemistry, faulty design, e.g. scale-up procedures, and deviations from operating procedures. This present paper updates the information from that previously given and now covers the period 1962-1987.

The present analysis classifies the incidents in terms of:

(a) chemical processes;
(b) prime causes;
(c) industries involved.

<div align="center">ANALYSIS OF INCIDENTS</div>

Between 1962 and 1987, 189 incidents which occurred in industrial batch reactors were reported to HM Factory Inspectorate (Health and Safety Executive). The information available on many of the incidents was not as full as might have been wished. Even had the information on each incident been complete the data presented below would have no statistical significance because of the uncertainties of under reporting. Furthermore it is not possible to say, for instance, that a particular process has a poor record in comparison with others, because to be able to do so it would be necessary to place the figures in context taking into account such factors as numbers of reactors, production tonnages, unreported near miss data, operating standards etc.

The Chemical Processes

Eleven principal chemical processes were involved in the incidents as shown in Table 1.

It was not possible to identify the chemical processes being carried out in all of the 189 incidents, due to lack of information. However, 134 incidents could be classified.

From Table 1 it is apparent that polymerisation reactions featured in by far the most incidents, followed by nitration, sulphonation and hydrolysis reactions. Of the polymerisation reactions 20% (13) involved phenol-formaldehyde condensations. In view of the number of incidents with phenol-formaldehyde resin production the British Plastics Federation (BPF) came forward with an exemplary approach to the problem in its publication "Guidance for the safe production of phenolic resins" (3). Although the BPF document is specific to phenolic resins the general approach adopted could be used elsewhere. It is perhaps significant that no phenol-formaldehyde polymerisation incidents have been reported over the last few years.

The Prime Causes

The prime causes which led to overheating and eventual thermal-runaway for 169 of the incidents (20 were without sufficient details for the assignment of a prime cause) are classified below under the main headings:

(a)   process chemistry;
(b)   plant design and operation.

(a)   Process Chemistry

(i)   Reaction chemistry/thermochemistry

Thirty-four of the incidents are attributable to little or no study or research or development work being done beforehand, with the result:

-   no appreciation of the heat of reaction on which
    to base cooling requirements for the reactor
    (scale-up)   8

-   the product mixture decomposed   7

-   unstable and shock sensitive by-products
    were produced   6

-   the reaction was carried out en-masse (i.e. all
    reagents added simultaneously at start) whereas
    staged addition would have been appropriate   4

-   unintended oxidation occurred (instead of
    nitration)   3

-   the reaction was carried out with reactants at
    too high a concentration   2

-   the reaction was carried out at too low a
    temperature resulting in accumulation of reactants
    and subsequent en-masse reaction   1

-   the reaction accelerated due to:

    - catalysis by materials of construction of
      the reactor   1

    - unsuspected autocatalysis   1

-   a phase change of the product (to the vapour
    state) occurred   1
                                                                 ——
                                                                 34   (20%)
                                                                 ——

(ii) Raw material quality control

Fifteen of the incidents are attributable to the use of out of specification materials:

-   water contamination   9

-   other impurities   5

–	changed specification; a moderator should have been used on start of new supply but this change was not recorded in instructions	1
		15 (9%)

(b) Plant Design and Operation

(i) Temperature Control

–	failure to control steam pressure or time of application (includes one case of improper use of steam to unblock vessel out-let, causing decomposition of product)	6
–	probe wrongly positioned to monitor reaction temperature	6
–	failure of temperature control system (leading for example, to cooling water being automatically shut off; heating oil overheating; steam valve remaining open)	7
–	loss of cooling water (not monitored) (reactor 3; condenser 2)	5
–	error in manual reading of thermometer or chart recorder	4
–	failure to provide sufficient separation distance between reactor and adjacent hot plant	2
–	too rapid heating at reaction initiation	1
–	thermocouples coated with polymer giving slow response	1
		32 (19%)

(ii) Agitation

–	inadequate stirrer specification	4
–	mechanical failure, for example, stirrer blades sheared off due to solidification of the "heel" from previous batch; although an overload switch was fitted the motor was too powerful for the paddle securing bolts	3

− operator either failed to switch on agitator or switched it on too late, the nett result was en-masse reaction	6
− loss of power supply	2
− agitator stopped by operator to make an addition (localised high concentration caused liquor to boil and erupt)	2
	17 (10%)

(iii) Mischarging of reactants

− overcharging (includes 2 cases of overcharging a catalyst and one where the metering device was faulty. In 5 cases, the total volume of the reaction mixture was incorrect and the cooling capacity of the reactor was inadequate. In the other 6 cases the reaction mixture contained the wrong proportions of reactants)	12
− too rapid addition (including a catalyst)	8
− wrong sequence of addition	4
− wrong material	5
− undercharging	3
− improper control (use of hose-pipe)	2
− addition too slow	1
	35 (21%)

(iv) Maintenance

− equipment leaks (scrubber 1; valves 3; cooling pipes/jacket 3)	7
− blockages (vent pipes 2; transfer pipes 3; separator 1)	6
− condenser solvent locked due to valve in reflux return line being closed following shut-down for maintenance	3
− residues from previous batch	2
− water in transfer lines (including one case of water siphoning from quench tank)	3

−	in situ replacement of closures (cracked sight-glass 1; cover plate 1) during course of reaction	2
−	unauthorised modifications	1
−	loss of instrument air supply	1
		25 (15%)

(v) Human factors

−	operator failed to follow written instructions	4
−	product run off before completion	3
−	deviations caused by poor communications at times of staff changeover (change of shift, holiday, sickness)	3
−	product filtered at wrong stage of process	1
		11 (6%)

Industries Involved

Batch reactors are ubiquitous in the chemical industry due to their convenience and flexibility. The pattern of incidents, however, shows, as might be expected, a preponderance to certain specific industries (Table 2).

Recent Incidents

The analysis of Barton and Nolan (2) covered the period 1962-1984. The data covering 1985, 1986 and 1987 can be summarised:-

A total of 47 incidents were reported, 3 in 1985, 16 in 1986 and 28 in 1987. Either there was a real upsurge in incidents in 1986 and 1987, which seems unlikely, or, which seems more probable, the impact of the new reporting regulations (Reporting of Injuries, Diseases and Dangerous Occurrences Regulations 1985 [RIDDOR]) has resulted in improved reporting.

The prime causes (3 incidents in 1987 were without sufficient information for the assignment of a cause) of the incidents follow the familiar pattern:

8 (18%) (ca. average) were due to little or no study or research or development work being done before scaling up and going into production.

14 (32%) (well above the average) were due to mischarging of reactants of which 4 were due to overcharging (1 catalyst); 4 were due to addition of the wrong material, e.g. drums of wrong material were stored with drums of one of the reactants and were charged in error; 3 to too rapid addition; 1 to wrong sequence of addition; 1 to undercharging of a reactant and 1 to improper control (use of a hosepipe).

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4 (9%) were due to temperature control failures.

5 (11%) were due to the presence of impurities, particularly water (3), in raw materials.

5 (11%) were due to problems with agitation, 2 because the agitator had not been switched on; 2 because the agitator was switched on late once the error was realised and 1 because of mechanical failure.

6 (14%) were maintenance related; 1 was due to a blocked transfer pipe; 1 to a blocked separator; 1 to unauthorised plant modification; 1 to loss of instrument air supply; 1 to a leaking cooling jacket and 1 to an improperly secured cover plate; and

in 2 (5%) the operators failed to follow written instructions; in 1 they failed to separate an aqueous phase from an organic phase before proceeding and in the other, filtration was carried out at the wrong stage of the process.

13 of the incidents occurred in the fine and intermediate organics industry; 7 in the plastics, rubber and resin industry; 13 in the heavy organics industry; 4 in the pharmaceuticals industry; 2 in the dyestuffs industry and 1 in the metal processing indusry.

Of the chemical processes involved polymerisations accounted for 17 incidents. The polymerisations involved vinyl acetate; vinyl chloride (9); polyester resins (2); butadiene/acrylonitrile; hydroxyethyl methacrylate; and urea-formaldehyde (due to contamination of the urea with ammonium nitrate).

Other chemical processes involved were sulphonation (4); amination (3); nitration (2); halogenation (2); diazotisation (2); alkylation (1); esterification (1) and hydrolysis (1).

9 persons were injured (8 operators and 1 fireman). In one incident (runaway nitration) 20 people off-site were affected by acid-spray.

Injuries and Damage

The result of the runaway incidents ranged from a simple foam-over of the reaction mass to a substantial increase in temperature and pressure leading to violent loss of containment, with in some instances the release of large quantities (up to several tonnes) of flammable and/or toxic materials into the environment. In a few cases where flammable materials were released a fire and/or a secondary explosion followed. As a result 4 fatalities and 82 injuries (as defined in relevant health and safety legislation (4)) occurred in the period 1962-1987.

The injuries to operators were due, for example, to splashing by hot liquors or the effects of blast, missiles or toxic fumes. They generally occurred when the operators were attempting to regain control of a reaction. Eleven injuries, one of which was fatal, occurred when manual additions of ingredients were being made to the reactor and the reaction mixture then erupted over the operator.

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 small

number of cases, surrounding areas both on- and off-site were put at risk. In one incident 20 people off-site were affected by acid spray.

GENERAL LESSONS

The analysis indicates that incidents occur due to:-

(i)   a basic lack of proper understanding of the process chemistry and thermochemistry;

(ii)   inadequate engineering design for heat transfer;

(iii) inadequate control systems and safety back-up systems (including venting);

and

(iv)   inadequate operational procedures, including training.

In order to deal with hazards it is first necessary to identify them, then decide how likely they are to occur, and how serious the consequences would be. A formal system should be used to study the plant, and identify and record process hazards (see Appendix 1). This area is further developed by other speakers at the symposium. It is apparent from the analysis of incidents that this is still not common practice for batch reactors.

It is axiomatic that in order to avoid conditions for runaway arising it is necessary to have 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.

Some of this necessary information can be obtained from the literature or from computer-based modelling of reactions. The thermal behaviour characteristics of reactants, products and occasionally reaction intermediates/mixtures can be found using laboratory techniques. A variety of laboratory techniques are available for use to acquire this knowledge. The Association of the British Pharmaceutical Industry developed a laboratory scheme (5) for screening new products and processes. More sophisticated techniques include use of accelerating rate calorimetry (6) or other adiabatic calorimetry systems. The study of reaction mixtures is ideally carried out by using a heat flow calorimeter (7). These techniques will be described in more detail by other speakers at the Symposium. A thermal hazards assessment strategy is discussed below.

It is also possible to obtain information relating to changes in heat transfer coefficients and control parameters, due to changes in properties such as viscosity and specific heat as the reaction proceeds, using heat flow calorimetry (8).

The laboratory studies can provide data on the onset temperature of and magnitude of exotherms. The detected onset of an exotherm is scale dependent i.e. the larger the reaction mass, the lower the onset temperature. From such information and a thorough examination of previous plant operating experience, it is possible to set safety margins and hence select the operating temperature for the given reactor charge size.

The ensured quality of the raw materials is vital to safe operation. The analysis shows that the presence of impurities, water in particular, appears to present a problem. The presence of water can cause additional heat evolution, raising the total heat output above the reactor cooling capacity, leading to temperature rise and increased rate of reaction causing subsequent further increases in heat generation.

With reference to the prime causes relating to plant design and operation, it is obvious that heat removal rate is an important criterion for batch reactor design, to which adequate agitation, eg stirrer speed, is related, particularly with regard to scale-up from laboratory data. Numerous correlations exist for heat transfer in agitated, jacketed vessels (9,10) and it is possible to scale-up data on inside film heat transfer coefficients from heat flow reaction calorimeters to industrial size batch reactor plant (8). It is imperative that the cooling capacity of the designed plant can cope with the heat generation from all the chemical processes envisaged.

It is unusual for batch reactor plant to be designed to resist any calculated pressure rise resulting from a runaway reaction. Ideally, of course, the objective should be for process control to eliminate any runaway potential. However, pressure relieving of the reactor or dumping the contents or quenching the reaction should be considered in case of emergency. If pressure relief venting is considered, attention must be paid to the nature of the material likely to be released, e.g. its toxicity and/or flammability, and it may be necessary to install catchpots or other means of containment or entrainment to capture the released material (11). The vent sizing of reactors has been advanced recently by the work of the AIChE's Design Institute for Emergency Relief Systems (DIERS) (12). This work has included the development of two-phase flow equations and the 'Safire' computer code for vent sizing of realistic releases. For reactions not previously investigated or adequately covered in the literature, the DIERS programme also produced a laboratory-scale apparatus to provide the necessary information for input into the developed models. Vent sizing for reactors is covered by other speakers at the Symposium.

Many of the incidents resulted from the mischarging of reactants, inadequate temperature control and poorly defined operating procedures and operator training. The safe operation of plant can be aided by the use of computer or other automatic control techniques; however, two of the incidents in this analysis occurred due to the operator over-riding the alarm signals.

ASSESSMENT STRATEGY

Runaway inside a batch reactor is characterised by the loss of thermal control.

The purpose of a thermal hazards assessment strategy is to:

(a) identify materials and unit processes which are potentially hazardous;

(b) quantify the hazards which arise from these with a minimum of testing.

It involves a sequential approach, which covers thermochemical evaluation, reaction calorimetry and the effects caused by scale, accumulation and cooling/agitator failure.

A typical strategy is shown in Figure 1 (13,14). This is discussed more fully in the references given.

The thermochemical evaluation consists of data on the thermal stability, heat of reaction and total heat capacity of reactants of the desired reaction, the expected adiabatic temperature rise and any general process hazards, e.g. flammability and toxicity of reactants.

Reaction calorimetry, either in the form of heat flow or adiabatic Dewar-based calorimeters allows the measurement of many process variables (agitation, heating, and cooling requirements) and reaction characteristics (kinetics, reaction enthalpy, heat release rates and reactants' heat capacity) under known environmental heat loss conditions. The reaction calorimetry stage of the assessment also allows for the determination of adiabatic temperature rise and gas generation potential. The heat release per unit mass or unit volume of reactants can be used with the previously established plant cooling capacity to ascertain safety margins for safe operation. It is also usually necessary to consider the potential results following the failure of agitator and cooling systems, along with the results from heat accumulation storage tests.

CONCLUSIONS

Despite the apparent knowledge which exists, the techniques which are available and the commercial instruments on the market for the assessment of potential runaway reactions, to aid process and plant design, control and operation, incidents continue to occur due, in the main, to common errors.

The hope is that more chemical manufacturers will introduce systematic assessment procedures. A systematic approach should reduce the types of common errors exemplified in the analysis. It is essential to have a thorough understanding of the process chemistry and thermochemistry and then to ensure adequate engineering design for heat transfer, adequate control systems and safety back-up systems and adequate operational procedures, including training.

An assessment strategy for chemical reaction hazards, has been outlined.

A need is perceived for coherent and concise guidance to be produced, particularly for small and medium-sized companies, covering the areas of thermal hazards assessment, venting, and a formalised approach to process control. HSE has now initiated, and in part, sponsored, the production of a User Guide on safety in exothermic reactions by I Chem E. Other sponsors have come from industry. The publication is being written by an Industrial Fellow reporting to a Steering Committee. It will seek to bring together information produced in the last few years on all aspects of the subject, including thermal hazards assessment, process design, heat transfer problems, process control, vent sizing and operator training. It will not be a full text-book but should alert smaller to medium sized companies to the problems in these areas and point out where to go for further help and advice.

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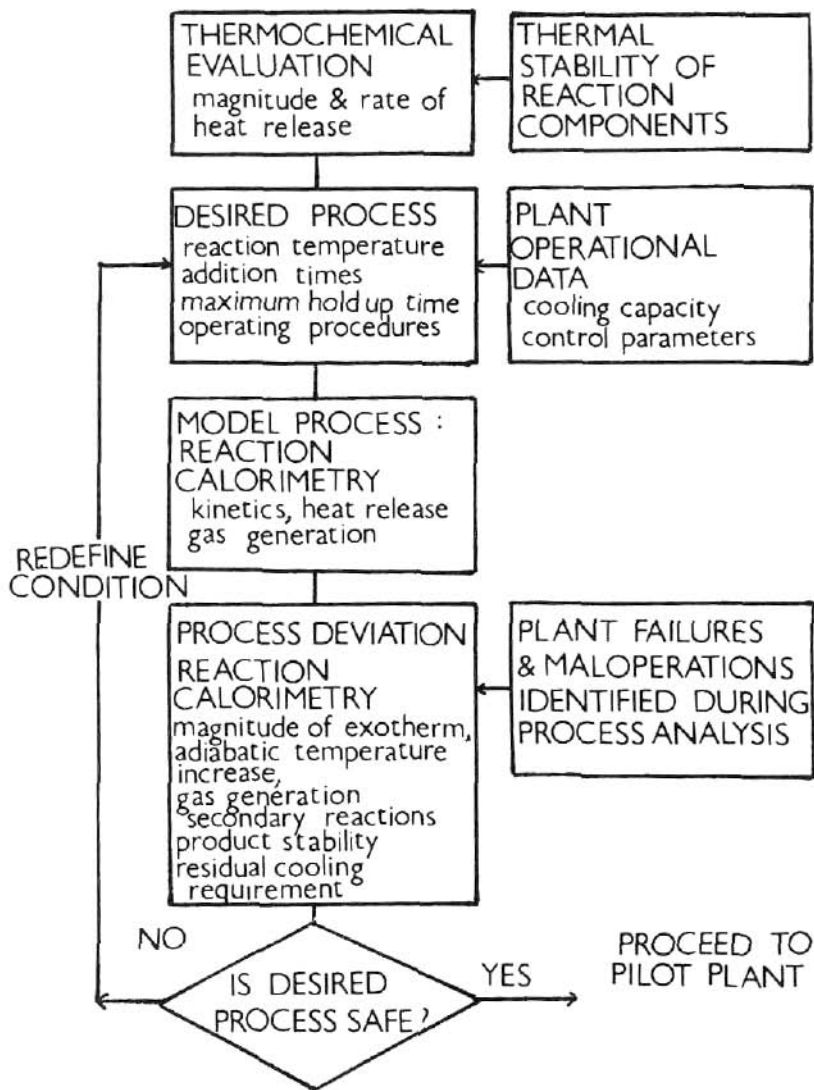
FIGURE I ASSESSMENT STRATEGY
CHEMICAL REACTION HAZARDS

Table 1

Number of incidents per specified chemical process

Chemical Process	Number of Incidents
Polymerisation (including condensations)	64
Nitration	15
Sulphonation	13
Hydrolysis	10
Salt formation	8
Halogenation (Chlorination and Bromination)	8
Alkylation using Friedel and Crafts Synthesis	5
Amination	4
Diazotisation	4
Oxidation	2
Esterification	1
	134

Table 2

Specific manufacturing industries, in which reported batch reactor
runaway incidents have occurred during the period 1962-1987

Manufacturing Industry	Number of incidents
Fine and intermediate organics	51
Plastics, rubbers and resins	41
Heavy organics	20
Metallurgy and metal processing	13
Dyestuffs	13
Pharmaceuticals - including animal health products	13
Agricultural chemicals	5
Food and flavourings	5
Paint and varnish	5
Miscellaneous	23
	189

APPENDIX 1

IDENTIFYING HAZARDS

Among the better known formal systems are 'Hazard and Operability Study' (HAZOP), used to identify hazards, and Hazard Analysis (HAZAN), used to quantify hazards (15,16).

Having identified a hazard it is still necessary to decide what to do about it. Ways must be found to reduce the probability of a runaway occurring.

Where consequences are judged to be severe, or where the causes giving rise to the hazard are many or interrelated, it is recommended that a 'fault-tree' (17) is constructed, showing the way in which various events or faults can give rise to a hazard. When constructed the tree can be used to see where the most likely causes of an incident lie, and where additional precautions can be introduced to minimise the risks.

For the most rigorous examination it is necessary to allocate probabilities to each event in the fault tree, allowing the total probability of the final event to be calculated (HAZAN).

Where companies are not able to carry out such examinations of their batch processes alone, they can call on the services of consultant practitioners to assist them.

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