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SOME LESSONS FROM THERMAL-RUNAWAY INCIDENTS

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Summary

An analysis is presented of 142 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) occurring in the UK during the period 1962—1984 and brought to the attention of the Health and Safety Executive. The purpose was to seek for any apparent trends with a view to drawing general lessons from previous mistakes. The underlying problems which led to overheating and eventual runaway have been classified under the headings process chemistry and plant design and operation; a number of contributing factors have been identified under each. Injuries are briefly discussed.

Introduction

The majority of industrial processes for the manufacture of chemicals are exothermic and hence there exists the potential for thermal-"runaway", which is characterised by progressive increases in rate of heat generation, temperature and pressure (generally caused by components in the reaction mass vaporising and/or decomposing to yield gaseous products at the elevated temperatures involved).

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. Expressed simply the problem is that an increase in temperature has only a linear effect upon the rate of heat transfer but exercises an exponential increase on the rate of reaction and hence upon the rate with which heat is generated by reaction.

Thermal runaway is much more of a problem in non-steady state batch processes than it is in steady state continuous processes. The latter generally involve a smaller inventory at any one time, are easier to model and moreover since the plant is dedicated to the process it often justifies more technically sophisticated means of operation and control. Batch reactors on the other hand are often multipurpose, due to economic forces, and less sophisticated in their means of operation and control because of changing requirements and there is scope for errors. 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 complicated if all likely eventualities of the time dependent processes are given due consideration. It is a task which requires a systematic approach. (It is unusual on grounds of cost for a reactor to be specified which is sufficiently strong to resist any calculated pressure rise resulting from a runaway reaction.)

With a view to highlighting matters requiring particular attention Barton and Nolan [1] in an earlier analysis of many incidents taken from the open literature, industrial sources and the files of the Health and Safety Executive (HM Factory Inspectorate), presented general classifications of the incidents in terms of unit processes, initiating factors and industries involved.

This paper takes a closer look at the incidents from the files of the Health and Safety Executive from which, in general, more detailed information is available than from the other sources.

The incidents

Between 1962 and 1984, 142 incidents which occurred in industrial batch reactors were reported to HMFI. Polymerisation reactions featured most with 42 incidents, including 13 phenol—formaldehyde condensations followed by nitration (11), sulphonation (8), Grignard reagent preparation (3), and alkylation using Friedel and Crafts synthesis (2).

Ten principal unit processes were involved: alkylation, amination, diazotisation, halogenation (chlorination and bromination), hydrolysis, nitration, oxidation, polymerisation (including condensations), salt formation, sulphonation.

Analysis

The prime causes of 126 of the incidents (16 were without sufficient information) are classified below.

Process chemistry

(1) Reaction chemistry/thermochemistry

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

— the product mixture decomposed	7
— no appreciation of the heat of reaction on which to base cooling requirements for the reactor (scale-up)	6
— unstable and shock sensitive by-products were produced	5
— the reaction was carried out en-masse (i.e. all reagents added simultaneously at start) whereas staged addition would have been appropriate	3
— unintended oxidation occurred (instead of nitration)	3
— 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
	27 (21%)

(2) Raw material quality control

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

— absorbed moisture	6
— other impurities	3
— changed specification; a moderator should have been used on start of new supply but this change was not recorded in instructions	1
	10 (8%)

Plant design and operation

(1) Temperature control

— failure to control steam pressure or time of application (includes one case of improper use of steam to unblock vessel outlet, causing decomposition of product)	6
— probe wrongly positioned to monitor reaction temperature	
— failure of temperature recording system (leading for example, to cooling water being automatically shut off; heating oil overheating)	5
— 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
	28 (22%)

(2) 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	2
— loss of power supply	2
— agitator stopped by operator to make an addition (localised high concentration caused liquor to boil and erupt)	2
— operator failed to switch on agitator, the nett result was en-masse reaction	2
	12 (10%)

(3) Mischarging of reactants

— overcharging* (includes one case of overcharging a catalyst and one where the metering device was faulty)	8
— too rapid addition (including one catalyst)	5
— wrong sequence of addition	3
— undercharging	2
— addition too slow	1
— wrong material	1
— improper control (use of hose-pipe)	1
	21 (17%)

(4) Maintenance

— equipment leaks (scrubber 1; valves 3; cooling pipes 2)	6
— blocked pipes (vent 2; transfer 2)	4

*Note: In three cases the total volume of the reaction mixture was incorrect and the cooling capacity of the reactor was inadequate. In the other five cases the reaction mixture contained the wrong proportions of reactants.

— 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 cracked sight-glass during course of reaction	1
	19 (15%)

(5) Other factors

— product run off before completion	3
— operator failed to follow written instructions	3
— deviations caused by poor communication at times of staff changeover (change of shift, holiday, sickness)	3
	9 (7%)

Damage and injuries

The results of these 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 cases the release of flammable and/or toxic materials in the form of vapour, liquid or aerosol.

As a result four fatalities and 73 injuries (as defined in relevant health and safety legislation) occurred [2].

The injuries to operators generally occurred when they were attempting to regain control of a reaction. Eight injuries, one of which was fatal, occurred as a result of adding solid material to reaction mixes, which then erupted over the operator.

Discussion

The analysis shows that many incidents occur due to lack of knowledge of reaction chemistry. It is axiomatic 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. It is possible to acquire this knowledge by reference to standard works [3, 4] and/or use of such models as a simple oxygen balance and the computer program, CHETAH [5]. Such initial screening techniques may then be supported by laboratory studies. These studies may include the use of heat flow calorimetry [6], accelerating rate calorimetry [7] and/or simpler onset of exotherm tests [8]. The case of an uncooled industrial reactor in which the agitator fails can be simulated using adiabatic conditions. This can be achieved by the use of Dewar flask tests [8, 9] and in the recently designed laboratory apparatus for the direct scaling of vent requirements [10].

Essentially these studies should give some idea of the temperature at which exotherms begin and indicate their magnitude. It must be remembered, however, that it is usual for the detectable onset of an exotherm to occur at a lower temperature in a larger mass when considering scale-up of laboratory data to the design and operation of industrial plant, i.e. safety margins are required.

As part of the study of process chemistry, it is important to bear in mind the importance of the quality of raw materials. The analysis reveals that the presence of impurities, water in particular, appears to present a problem. The presence of water caused additional heat evolution, raising the total heat output above the reactor cooling capacity, hence leading to excessive temperature and reaction rate.

The analysis further shows that inadequate cooling area for heat removal was a cause of incidents. Heat removal rate is an essential criterion as well as stirrer speed for batch reactor design, particularly with regard to scale-up from laboratory data. The engineer must ensure that the cooling capacity of the designed plant can cope with the heat generation from all unit processes envisaged. Numerous correlations exist for heat transfer in agitated, jacketed vessels [11, 12].

In 93 of the 146 incidents (64%), the venting provision on closed reactors was either non-existent or inadequate. The methods [13, 14] for sizing a vent to relieve a runaway reaction have recently been advanced by the work of the AIChE's Design Institute for Emergency Relief Systems (DIERS) [10].

Many of the incidents resulted from mischarging, inadequate temperature control and poorly defined operating procedures and operator training. The techniques of, for example, hazard analysis and hazard and operability studies [15] provide a systematic approach designed to determine critical features of the control system (including operability aspects) and assess whether the reliability of such features are satisfactory. Safe operation of plant can be aided by the use of computer or other automatic control techniques, however two of the incidents occurred due to the operator over-riding alarm signals.

Conclusion

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, incidents continue to occur due to the classic problems 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.

It is emphasised that use of a systematic approach utilising, for example, HAZAN and HAZOP is essential and such techniques are being increasingly used with the expectation that they should help to reduce the types of common errors exemplified in this analysis.

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