(Paper published in The Chemical Engineer – Jan 1995)

Explosions Part 2 of 3: Minimising the Risks of Explosions and Toxic Release Due to Chemical Reaction Runaway

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Introduction

In the first article in this series Dr Paul Cartwright and Gary Pilkington of Chilworth Technology looked at the explosion of gases, aerosols and dust clouds and specifically how laboratory tests can be used to identify the hazard, and to assess and control the risk of explosion on chemical plant.

Such investigations and assessments will normally involve the examination of single component, non-reactive systems. In this article Dr Andy Starkie discusses the techniques available for the examination of chemical reactions both in terms of the hazards associated with the desired reaction and those resulting from runaway reactions.

During the manufacture of a chemical, starting materials will undergo chemical transformations resulting in the formation of the final product. These chemical changes normally involve the evolution or absorption of heat and are said to be exothermic or endothermic reactions. Of most concern in chemical processing is the exothermic process. If the heat released from such a process cannot be removed efficiently it presents a potential hazard to the operation by remaining in the reaction mass, with the consequence of raising the reaction mass temperature, and hence reaction rate, and resulting in a runaway reaction. If the vessel is incorrectly designed or specified this runaway will result in over pressurisation of the reactor and possible loss of containment and toxic release due to violent boiling and/or rapid gas generation. In addition, were such a runaway reaction to occur, the elevated temperatures achieved may well initiate secondary, competing reactions such as thermal decompositions, which will exacerbate the hazard resulting from a runaway. Clearly for safe process specification a chemical reaction hazard evaluation needs to be conducted to fully assess the hazards associated with the proposed process.

The objective of any hazard assessment is to determine the envelope of safe working conditions and to define a basis of safety for safe operation. In order to achieve this, an understanding of how the process can deviate over a period of time, resulting in a runaway reaction is needed. The most obvious deviation is insufficient cooling available on the plant. There are, however, other process deviations that can result in a runway, one of which is a lack of understanding of the kinetics of the desired process. Should the desired reaction be conducted at too low a temperature then the possibility of un-reacted reagent accumulation exists resulting in the conversion of a semi-batch process to an en-masse reaction with its inherent hazards. A summary of the different types of process deviation causing runaway reactions in batch reactors is given in figure 1.

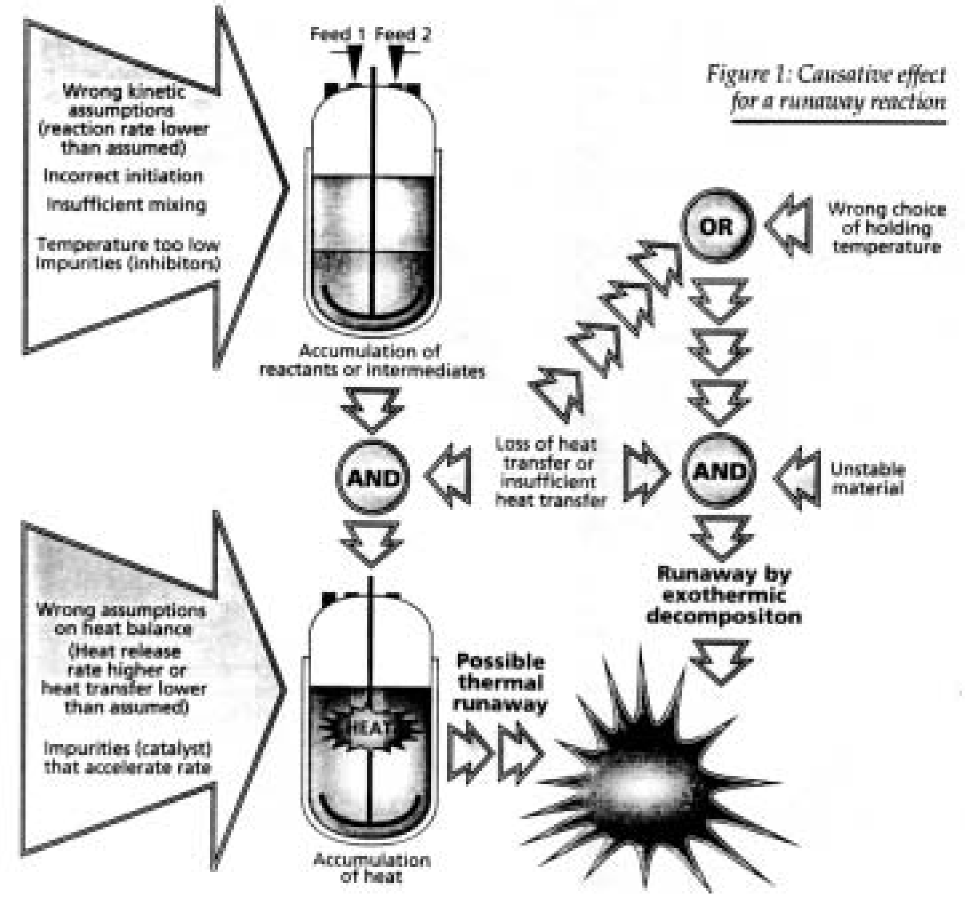

Figure 1: Causative effect for a runaway reaction

Assessment Procedure

The assessment procedure has one principle objective, to define a basis of safety for safe operation. That is an operating protocol that ensures that:-

"The process is sufficiently understood that conditions that will permit a runaway reaction are never achieved"

however, even though this is the most desirable option it is not always possible and the approach that is most common is :-

"The possibility of a runaway reaction is minimised but should it take place then certain protection and prevention methods will have been designed and incorporated to ensure that the runway will proceed with the minimum hazard."

Such an approach will normally involve the provision of process control to minimise the probability of the runaway and the incorporation of a secondary safety measure, such as crash cooling or reactor venting to reduce the consequences.

Clearly if this is to be the case then an extensive testing programme is required to provide the data upon which such design and operation decisions can be made.

Initial Laboratory Assessment

During the laboratory stage of the development of a process the prime objective is to ensure that development can be conducted on the small scale without risk to personnel. Initial screening should be conducted to assess the risk resulting from possible detonation or deflagration. Desk based techniques, such as calculating the oxygen balance, should the molecule contain an oxidising group, or use of computational programmes such as CHETAH, a computer based programme based on Benson's method of reactive #group contributions, will enable the initial prediction of such properties. If such investigations suggest the possibility of detonating or deflagrating properties being present then formal explosives testing will be required. Such an approach is the subject of a future article by experts at Chilworth Technology.

However, during laboratory scale development it can be appropriate to conduct a more detailed study of the reactive hazards associated with the desired process. This can be termed Reaction Characterisation and will provide data relating not only to thermal instability hazards but also heat of reaction and heat release rate data. The earlier such testing is conducted the better, as it may indicate that a certain chemical stage is so hazardous that it may be unwise to scale up the process any further, thus requiring a re-design of the proposed synthetic route. Far better to conduct this while the process is in the laboratory than when a full plant design has been completed.

Initially testing will be on the small scale providing a rapid thermal screening of the starting materials, reaction intermediates, final products and waste streams to identify any potential for thermal instability and for gas generation. The type of test data employed will be dependant on the process stream being investigated, however, within safety constraints, the larger the scale of operation the better. Such tests will include differential scanning calorimetry (DSC), differential thermal analysis (DTA) or the 10g Carius tube test. The type of data and the type of sample tested is summarised in Figure 2.

Figure 2 :- The use of screening tests in Chemical Reaction Hazard evaluation.

Sample Type	Data Generated
Starting materials	A preliminary indication of:-
Reaction intermediates, ie, samples taken from different stages in the synthetic route	Possibility of thermal decomposition
Final products	The quantity and rate of heat release
Waste streams	Gas evolution
Distillation residues	The effect of prolonged storage at elevated temperatures, ie, the possibility of auto catalysis
Synthetic samples simulated possible process deviations such as mischarge of reagents.	Possibility of deflagration

However these screening tests, because of the environment in which they are conducted, may not be sufficiently sensitive to scale the data to the manufacturing operation, and hence will only give a preliminary indication of any hazard. As the process is scaled up the full definition of a basis of safety will require in depth studies employing test methods that directly reproduce the manufacturing environment.

Reaction Characterisation

For an exothermic chemical process the rate of heat evolution increases exponentially with regard to reaction mass temperature, as dictated by Arrhenius kinetics, however the cooling capacity of a chemical plant only increases linearly with regard to temperature. In order to fully define the basis of safety an understanding of the desired process, with relation to the proposed plant, has to be achieved. Clearly such a characterisation requires the generation of data relating to a number of different areas of the process and is primarily concerned with the heat of reaction and heat release rate. Such data will normally be provided by an isothermal heat flow calorimeter such as the Mettler RC1. Figure 3 provides a list of the type of data required and its use in safe process design.

Figure 3 :-Thermal data required for process characterisation.

Process Characteristic
The heat of reaction
The rate of heat production
The heat capacity of the reaction mass at varying points during the process
The rate of gas generation
The heat transfer properties of the reaction mass
The kinetics of the reaction
Factors that effect optimum operating conditions, eg pH, catalyst concentration, reaction temperature etc
The effect of basic process deviations such as mischarging

Based on the data generated from such an experimental programme the operating protocol for the safe operation of the desired process can be defined. Factors that will be considered will enable the minimisation of inventories of hazardous chemicals, specification of heating media that will ensure that hazardous temperatures cannot be achieved, specification of flow rates for the addition of chemicals involved in highly exothermic stages and specification of low boiling reaction solvents to minimise the chance of elevated temperatures being achieved.

Runaway Characterisation

The characterisation described above only provides information that minimises the possibility of an explosion and consequent loss of containment. As part of the assessment strategy a characterisation of the un-desired process or thermal runaway is also required. This will necessarily be conducted employing experimental techniques that simulate the thermal inertia and heat loss characteristics encountered on the manufacturing scale. This part of the experimental assessment can only be conducted using adiabatic calorimeters such as the adiabatic dewar calorimeter or Accelerating Rate calorimeter and must be able to simulate not only the thermal characteristics of the proposed process plant but also the process deviation that may initiate the runaway, ie the worst case scenario.

Identification of the worst case scenario will normally be conducted as part of the process safety assessment. Such events may be loss of cooling due to power failure at a critical step or loss of control of addition rate due to valve failure. These will all contribute to the causative factors outlined in Figure 1.

Having identified the process deviation, in order to conduct such runaway characterisations information is required on a number of parameters that indicate the sensitivity of the process to thermal runaway and subsequent explosion and it consequences.

Figure 4 :- Characterising the runaway reaction

Process variable	**Use**
The measurable onset temperature for the specific plant and scale of operation being studied	To define the safe operating temperature to prevent runaways occurring
The rate of heat production or the "kinetics" of the runaway The rate of gas or vapour generation during the runaway The maximum pressure developed during the runaway.	To define the basis of safety to cope with the runaway reaction. EG specification of reactor vent or design of vessel for total containment

The course of a runaway reaction will involve both the loss of control of the desired reaction and the consequences resulting from any secondary decomposition reactions that may only be initiated at the elevated temperatures achieved under plant operation conditions. Direct simulation of such events, using adiabatic calorimetric techniques, simulating the kinetics of the worst case scenario is prerequisite in characterising the runaway reaction and hence providing a means for the correct definition of the basis of safety for safe chemical manufacture.

Conclusions

The implementation of an assessment procedure to correctly specify a basis of safety for the safe and profitable operation of a chemical process is a complex task involving the interaction of a number of differing variables that may be process specific or relate to plant operations. In order to achieve this successfully the specification of a basis for safe operation has to be based on experimental evidence. Implementation of the experimental programme, particularly with regard to the correct experimental technique, has to be conducted at the correct time during the development programme.

Provided that the right tests are conducted at the right time it will be possible to achieve the most desirable outcome for a research and development programme, that is, inherently safe chemical manufacture.

In the next article Dr Paul Cartwright and Gary Pilkington discuss thermal instability of powder and the associated risks of fire, gas evolution and detonating or deflagrating explosion.

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