Systematic Approach to Process Safety

Vijay Bhujle

No chemical company can today afford a safety incident without its disastrous consequences on the company's very survival, unlike earlier.

Trends have changed from a 'reactive' approach to safety management to a proactive philosophy which starts from designing inherently safer processes. This can minimise unsafe situations significantly.

The study of process safety through relevant and correct data can help deliver efficient and the best output safely. The overview of this systematic and scientific approach to get to intrinsically safer operations during chemical manufacture is described in the article.

Introduction

The main hazard during chemical production is loss of temperature control. This can lead to catastrophic situation based on characteristic of chemicals and reactions.

Causes for loss of control can be because of disturbances/deviations in the process and system faults. Risk involved will depend upon impact of these factors. Risk is understood to be a hazard in relation to the probability of occurrence of undesirable incident. For effective risk analysis good data is a must. What data is critical and based on these generated data, a systematic evaluation can be carried out. Suitable measures would be required to be taken based on the evaluation,

Major hazard in the chemical production can be the loss of control leading to destruction and release of toxic materials. A safer operating process can be arrived by using chemical engineering principles to study potential run-away reaction situation and then can arrive at safe operating window (conditions) for a given process.

Undesired reactions or poorly controlled desired reactions may lead to thermal runaways. Processes with inherently low risks can be designed on predictions of their response to abnormal (failure) situations. Further a good process development and design can significantly reduce the risk of thermal runways and intermediate accumulations of hazardous compounds.

Vijay Bhujle has more than 35 years experience in process development, scale up and technology transfer. He has worked in pharma API manufacturing &formulation, polymer additives, soaps& detergent formulation, food and crop protection chemicals. He had a long stint from 1993 onwards with the erstwhile Ciba and later was its General Manager, Research & Technology. He had training on process safety, powder handling safety and audits at Ciba, Switzerland. He has conducted large number of EHS audits and incident investigations. Earlier he had also worked with Atul Ltd and also at Hindustan Lever Research Centre. His last stint was with Intertek, before starting his own company now, GVS Cibatech P Ltd alongwith a few of his colleagues from Ciba. His company provides consultancy services mainly in process safety, environmental services and regulatory services for pharma, food and chemical industries. He is a visiting faculty at Institute of Chemical Technology (UDCT), Mumbai.

Thermal Analysis

Hazards of thermal runaway scenarios in a chemical plant can happen when the heat generation of an ongoing reaction exceeds the heat dissipation (cooling) capacity of the process equipment. This can happen under situations like:

1. In situations having a low heat dissipation capacity, even very weakly active desired reactions can runaway over long period of time. Such situations prone to heat accumulation mostly exist in storage tanks/equipment, which are not actively controlled.
2. The main hazard of a synthetic process is loss of control of the desired reaction. High reactant accumulation can lead to runaways. Other factors which are critical to reaction rate, such as sensitivity to impurities, wrong kinetic assumptions, problems with initiation can be reasons for loss of control. Further, malfunctions like insufficient mixing, high feed rates, wrong temperatures, etc. may lead to problems. Energy balance in a batch reactor is in unstable equilibrium (**Figure 1**), where the desired reaction releases heat and this is dissipated by cooling. In case of cooling failure, this heat production continues and heat will be released adiabatically based on accumulation at this stage. Sometimes this can be hazardous by itself.
3. The runaway of the desired reaction can also lead to secondary events. It may reach boiling point or it can reach an intermediate temperature level defined as MTSR (Maximal Temperature attainable by runaway of the desired Synthetic Reaction). Starting from MTSR, further effects, particularly runaway decompositions, can be triggered.
4. Undesired decomposition reactions may occur instantaneously if reactive compounds are mixed accidentally, e.g. wrong raw material, cooling water/heating media penetrates into the reaction mass.

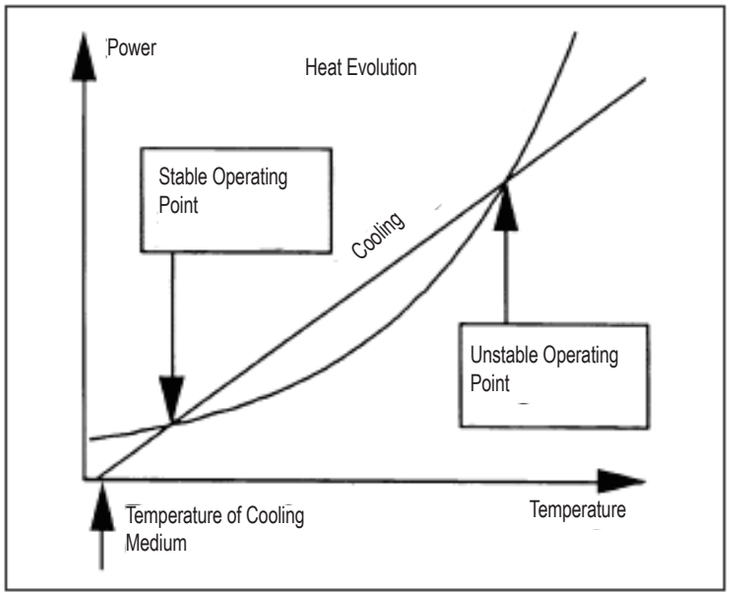

Fig 1. Heat balance diagram

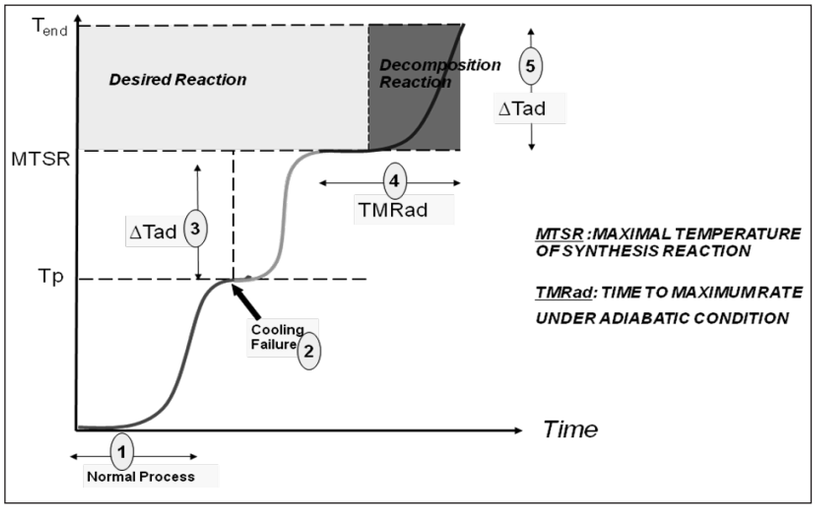

Fig 2. Runaway scenarios

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Risk Management

Knowing the hazards is a prerequisite to controlling them. In the past, a primary source of safety knowledge was learnings from the incidents themselves. Reactive approach based on incidents is no longer acceptable as a source of know-how improvement. Risk analysis and a databased predictive knowledge of the possible incidents is preferred over the old reactive approach. Based on specific chemical know-how possible paths of incidents can be identified.

In order to evaluate potential runaway scenarios and

to limit them, the data for the prediction of their course requires a thermodynamic and kinetic analysis of the system. A complete modeling of the reaction is not always feasible. The goal is to obtain an estimate on the quantities characterizing the potential runaway as shown diagrammatically in Figure 2.

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The basic questions are:

1. What is the heat evolution rate as a function of time to be coped with by the reactor/operational equipment? This will give cooling requirement on equipment.
2. What temperature can be reached when the desired process runs away, assuming adiabatic conditions for a cooling failure? This temperature MTSR is estimated by

$$MTSR\ (t) = Tp + \Delta Tad = Tp + (1\text{-}Xt)^* \Delta Hr/\ Cp$$

Where,

Tp is operating temperature; Xt is fraction of consumed reactant; ΔHr is heat of reaction; ΔT ad is adiabatic temperature rise; Cp specific heat of reaction mass

3. The most critical instant for a cooling failure is where MTSR(t) is maximum.
4. In what time, will a runaway decomposition reaction develop given the initial temperature Tp, typically set equal to MTSR(t). This time for runnaway (TMRad) can be derived based on the heat production rate and assuming zero order kinetics («Time to Maximum Rate», TMR24)
5. What is the order of magnitude of an adiabatic temperature increase caused by runaway of secondary reactions and what are the consequences?

$$\Delta Tad\ (decomp) = \Delta H\ decomp/Cp$$

Data requirements

First need is to know energy potentials. These can be obtained from micro-thermal analysis (Differential Scanning Calorimetry). Heat of reaction together with heat capacities, which are estimated or also measured by DSC analysis, the adiabatic temperature rise due to the observed reactions can be derived (points 2 and 5 above). Reaction Calorimetry is an appropriate Chemical Engineering tool for information on the desired reaction. Since chemical reactions are accompanied by heat release, the measurement of the heat flux serves as a direct indicator of the reaction rate. The measured heat output is directly linked to the risks and easily provides the basic data required above (points 1, 2, 3). The heat evolution rates measured at any given process time can be directly used in cooling capacity estimation of the operational reactor. Extent of reactant accumulation at any stage can also be derived from the calorimetric data.

It is also important to generate experimental data about heat evolution characteristics of secondary reactions (point 4). These data can be obtained from isothermally measured heat evolution rates using micro-thermal analysis.

Besides physical properties such as boiling points, heats of vaporization, vapor pressures, etc. and data related to process equipment are essential to assess the secondary consequences of a thermal runaway.

Evaluating the Risk

Based on these data, an assessment of the risks is now possible. Risk assessment is performed by considering two components, severity and probability.

Severities

The main factors determining severities in the chemical domain are the energies present. They can be related directly to quantities of chemicals and to the adiabatic temperature rise potentials as defined earlier. But essentially, destructive power stems from pressure increase

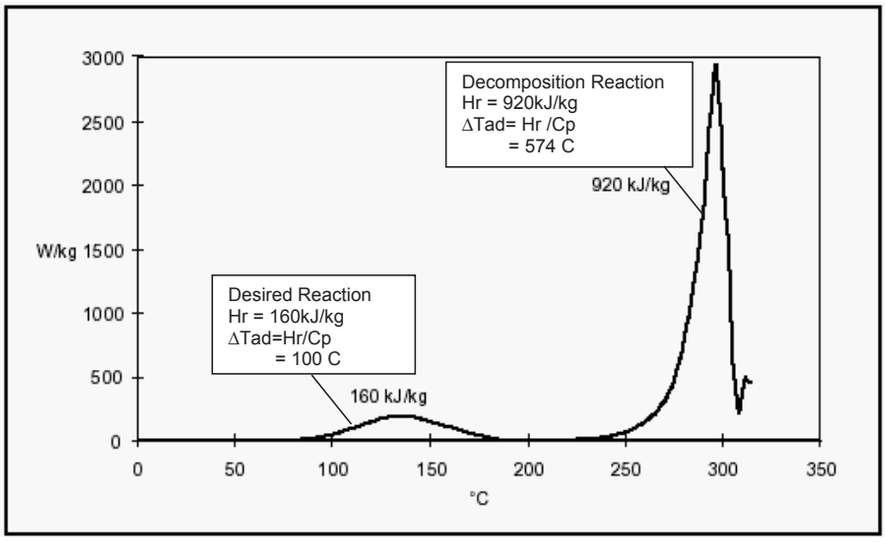

Fig 3. DSC (Microthermal analysis) of reactant mixture

due to gas evolutions and rising vapor pressures as a function of the temperature increase. Secondary effects, such as the release of explosive or toxic compounds (vapours/gases), can significantly enhance the degree of the severity.

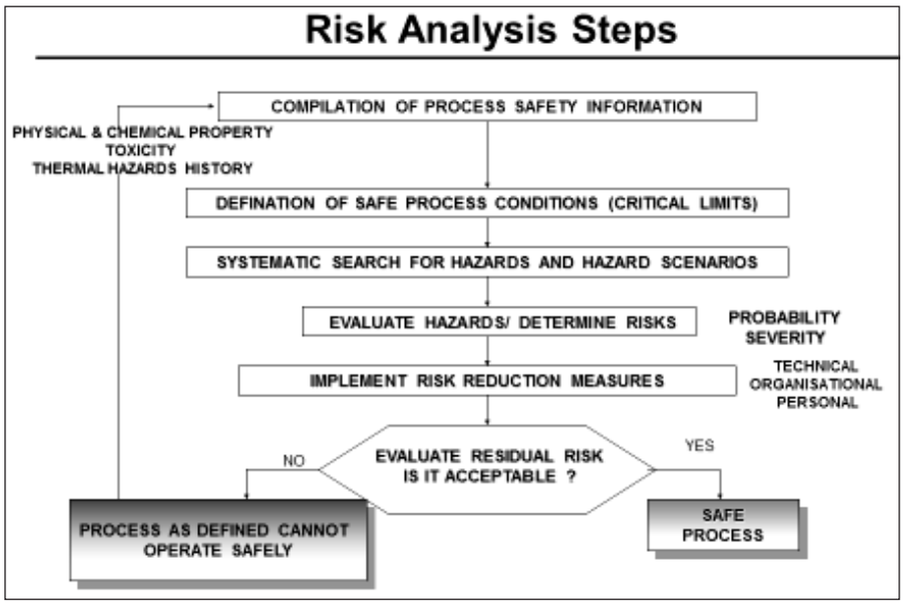

Fig 4. Risk Management Approach

Probabilities

Probabilities of runaway reactions are more difficult to evaluate. They depend on varied triggering factors. A failure that triggers a severe runaway within a few minutes or hours is dangerous. Runaway times on the order of hours or days can be tolerated in the plants as corrective action can be effectively taken before runaway occurs. For reactions generally TMR (time for maximal rate or simplistically time for runaway) of 24 hour is taken as safe. For the assessment of storage or transport, however, one must assure heat dissipation effects dominate and time scales are long. One has to carefully evaluate the situation as runaways are possible even with long time scales.

The thermal characteristics of the process by micro thermal analysis (DSC run), with a mixture of starting materials to be investigated (Figure 3). By looking at the thermogram, it can be concluded that the adiabatic temperature increases corresponding to the total conversion of the desired reaction is 100°C. Further, a highly exothermic decomposition takes place after main reaction. A first hint about its kinetic behavior can be obtained from the relative position of the signal, the micro-thermo gram shows 'on set' above 230°C (Figure 3). On set temperature depends upon sensitivity of thermal analysis instrument. As a rule of thumb, one can assume, that in the neighborhood of the «onset-temperatures» (using the experimental conditions referred to in Figure 3) the decomposition is running as fast as production scale reaction. More data is required of the decomposition in order to estimate runaway times as a function of initial temperatures.

A good safety approach is to implement what has been learned at the risk assessment stage back into process design. Creating safety at the source by better designs (proactive approach) has a number of advantages over providing passive protection measures:

1. Including safety aspects in the process development stage creates a greater opportunity to eliminate the hazards and thus reduce the severities of potential incidents. Incidents, which occur even after application of risk analysis procedures, are often due to highly unlikely coincidences. This represents a serious remaining risk if its severities are high.
2. A remaining risk with a high severity and a very low probability is less accepted than another risk involving only moderate severities. Reducing severities by improving designs is preferred option.
3. Integrating safety in process development rather than applying safety audits just before implementing process would take care of safety requirements as well as productivity (cost effective). Dealing with risk reduction is an iterative process (figure 4)At the evaluation stage if remaining risks are not acceptable you have modify the process conditions till you arrive at acceptable then risk levels.

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Designing Safer Processes

The guidelines for improving process safety:

1. Know your chemistry. Are there dangerous side reactions? Can initiation be a problem?

2. Keep energy densities low by either avoiding unnecessary accumulation of exothermically reacting compounds or by dilution.

3. Keep inventories of toxic compounds and unstable products low.
4. Maximize heat transfer capacities per unit of reactor volume.
5. Avoid external sources that trigger runaways, i.e. utility which do not overheat, and utility fluids, which do not dangerously react with reaction mass.

Process safety way forward

1. For good risk assessment and control, both a scientific exploration of hazard scenarios and managerial commitment are required. Knowledge of chemical engineering principles and safety technologies allows the risks to be minimized effectively and economically. It must become part of management system and a corporate culture.
2. Knowing the critical conditions is a prerequisite for assessing the safety of operations and hence needs a careful consideration.
3. Questions on process safety are necessarily different on different levels. The presented approach of prediction of runaway scenarios using basic chemical engineering reasoning, can serve as an interface between the chemical engineer and the plant manager
4. If the safety analysis functions only as an audit, which considers the finalized process, it can merely identify unacceptable risks and suggest investments for passive protection (end of pipe solutions) against them. The search for better solutions, which reduce severities and thus create safety at the source, is a worthwhile effort. The message to the plant manager, is to invest into chemical reaction engineering and motivate development people to integrate safety into their processes.

One can arrive at inherently safer processes by following the methodology mentioned above.

Reference: *Mainly based on earlier Ciba guidelines and notes, updated to current situation.*