

A CHEMICAL APPROACH TO INHERENT SAFETY

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Inherent safety is traditionally pursued by reducing the chemical inventory in order to minimise the quantities of toxic and flammable materials that are available for release in the event of an incident. This is often achieved by changing from batch to semi-batch or continuous operation.

An alternative approach to inherent safety is to consider the process in addition to the plant. This requires a thorough understanding of the chemistry including the thermo kinetics of the main reaction and of any possible side reactions that could occur in the event of a maloperation. Once the hazards associated with the process have been identified addition rates and operating temperatures can be set so that any accumulation/decomposition problems are eliminated or minimised.

In addition to the above there is a third and often rarely considered option to inherent safety. This involves the investigation of different processes, including their associated hazards, available to manufacture a desired product before the final process is selected and developed. A careful study of the proposed manufacturing process can sometimes identify an inherently safer route for production. This paper will describe with examples this chemical approach to inherent safety.

Keywords : Inherent Safety, Chemical Reaction Hazards

INTRODUCTION

The safe operation of our chemical processes is the most important objective of chemical manufacture. The public perception of the industry is such that its tolerance to incidents emanating from chemical plant is much lower than for other industries. Consequently the use of chemical manufacturing processes that are inherently safe is therefore very desirable.

An inherently safe process can be considered as one which by virtue of its design does not produce a hazard if a fault occurs.

The search for inherently safer processes has to date been mainly concentrated on two areas. Firstly on what can be described as the traditional approach and secondly the physical approach.

TRADITIONAL APPROACH TO INHERENT SAFETY

The traditional approach to inherent safety is centred mainly on reducing

the chemical inventory of a process (i.e. intensification) and secondly on using non-toxic and non-flammable materials wherever possible (i.e. substitution).

The use of non toxic/flammable materials has obvious benefits, however it is often, if not impossible to achieve this completely and an estimation of which material is more hazardous is often called for. An example of this compromise can be seen in the manufacture of cyclohexanol at Flixborough. Originally the manufacture was carried out via the air oxidation of cyclohexane and a leak of this material led to the Flixborough disaster (1). Following the incident, the process was changed such that the cyclohexanol was manufactured by the hydrogenation of phenol. This is a vapour phase process and is less hazardous than the original oxidation process. However *the hazards have not been eliminated as the phenol itself has to be produced and this is usually achieved by the oxidation of cumene to cumene hydroperoxide* (2) followed by its subsequent cleavage to phenol and acetone. It can be seen that this change in the manufacturing procedures may have simply transferred the hazards to another stage of the processing. In evaluating the benefits of a process change it is apparent that the hazards of the total process need to be considered.

A reduction in the chemical inventory has generally been achieved by moving from batch to semi-batch to continuous processing. Perhaps the most famous example of what can be achieved in this area is provided by the nitroglycerine process. The process involves the nitration of glycerine using a mixture of concentrated nitric and sulphuric acids and was traditionally carried out in large batch reactors containing around 1 tonne of material. Safe operation depended on the operator monitoring the batch temperature, for which purpose the famous one legged stools were invented. Failure of the control system usually resulted in the loss of the whole plant. By contrast the modern process involves the jet mixing of acid and glycerine streams, the vacuum created by the acid jet drawing in the glycerine. *Consequently a fall in the acid delivery rate results in an automatic proportional fall in the glycerine feed without the use of any external control system.* The reduced inventory means that the operator can be protected and the efficiency of the system has reduced the batch residence time from 2 hours to 2 minutes (2).

PHYSICAL APPROACH TO INHERENT SAFETY

The large variety of chemicals demanded by society cannot all be manufactured by reactions using continuous processes and non toxic/flammable materials. The majority of Fine Chemicals are produced using batch or semi-batch processes, continuous plant only being viable for large tonnage materials.

The approach to inherent safety in these cases is therefore to consider the hazards of the chemical process itself and their inter-relationship with the plant and processing conditions in order to identify conditions of operation under which hazards are minimised (i.e. attenuation). This requires a thorough understanding of the chemistry including the thermo kinetics of the main reaction and of any possible side reactions that could occur in the event of a maloperation.

The assessment includes the evaluation of the process by the use of preliminary small scale screening tests followed by larger scale Heat Flow and Adiabatic Dewar Calorimetry. Once a thorough understanding of the hazards has been achieved i.e. heats of reaction, thermal stabilities, gas

evolution rates etc then consideration can be given to designing a process that will be inherently safe or failing that, designing one that will require the minimum amount of extrinsic hardware protection i.e. trips, cut-outs etc. (3, 4, 5).

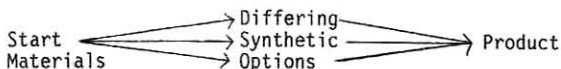
For example in an exothermic process involving the addition of a reactive ingredient, an addition time can be stipulated that would ensure that if cooling were lost either during or at the end of the addition then the amount of residual reaction remaining would be insufficient to raise the batch temperature to a level at which exothermic decomposition or vigorous boiling could occur. Similarly the use of an external heating medium should have a maximum temperature insufficient to initiate any exothermic decomposition in the reactor contents. Probably the most well known incident where inherent safety should have been applied was the Seveso incident where steam at 300 deg C was used to heat a process whose maximum operating temperature was 160 deg C. It is believed that while unattended the steam heated the reactor walls above the reaction mass to 300 deg C and then a combination of conduction and radiation lead to the temperature of the top layer of the mass being raised to a level sufficient for thermal runaway to start, believed to be around 185 deg C. Obviously the use of steam at a temperature of around 160 - 180 deg C would have prevented the incident (6).

Another area where an increase in inherent safety has been sought has been the sequence of addition. If, for example we were dealing with a reaction of the type A+B+C --> D+E there are obviously various permutations possible for the initial charging. The process as written calls for the initial addition of A and B followed by the controlled addition of C. However experimental examination of the process revealed that A and B reacted together at elevated temperatures where as B and C did not. Consequently if cooling were lost whilst the initial process was being operated the side reaction involving A and B would take place. A simple change in the order of addition i.e. initially charging B and C and then controlling the addition of A would prevent this possible maloperation from occurring and would thereby make the process inherently safer.

CHEMICAL APPROACH TO INHERENT SAFETY

In addition to the previously described options there is an additional and often rarely considered approach to inherent safety. This involves the investigation of the different chemical processes and their associated hazards that are available to manufacture a desired product before the final process is selected and developed. A careful study of the proposed manufacturing processes can sometimes identify an inherently safer route.

Highly exothermic reactions are often the cause of incidents in chemical manufacture however in any process where a chemical reaction occurs to convert a starting material/materials to the desired product, the total change in heat is fixed by the laws of thermodynamics irrespective of the route chosen. Thus the heat of "reaction" is the difference between the initial enthalpy and the final enthalpy of the system.



$$\Delta H_r = \Delta H_{\text{Product}} - \Delta H_{\text{Start materials}}$$

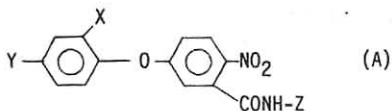
Although it is not possible to change the heat output of a system inherently safer processes can be achieved by considering the following:-

intermediates produced
 reagents used
 material compatibility
 catalysts used
 solvents chosen

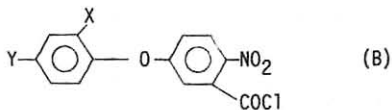
Some of the benefits that can result from this initial screening of the available processes are described below with examples.

Stability of Intermediates

A synthetic route for the manufacture of the substituted nitrocarbonamide (A) was required.



One of the suggested routes involved the preparation and isolation of the nitrobenzoyl chloride intermediate (B)



Previous experience suggested that this material was likely to be thermally unstable. A survey of the literature revealed that 2-nitrobenzoylchloride itself had been the cause of "many previous explosions" (7) and that "aromatic acyl halides containing a nitro group adjacent to the halide function show a tendency towards violent thermal decomposition". This instability in the actual compound was later confirmed experimentally. It was apparent that a synthetic route involving the preparation of the nitrobenzoylchloride intermediate would involve considerable hazards. Further experimental study identified a viable synthetic route that involved the nitration of the molecule at a later stage, after the acid chloride group had been reacted further, thereby resulting in an inherently safer manufacturing process.

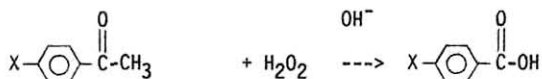
Choice of Reagent

The choice of the most suitable reagent can have a great benefit in achieving a robust process with a greater degree of inherent safety.

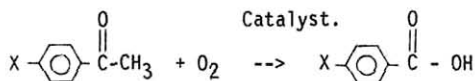
It is well known that oxidation reactions are very exothermic and that there are numerous reagents available to carry out these reactions. Hydrogen peroxide is a commonly used oxidising agent that decomposes with the evolution of oxygen. This decomposition is known to be sensitive to various impurities and this sensitivity obviously presents a potential problem in cross contamination from materials used in other processes.

One of the of the major problems of using hydrogen peroxide or other oxidising agents that are added in a controlled manner is that loss of agitation during the addition can lead to a build-up of unreacted material which on restart of the agitator will result in a very large exotherm and possible ejection of the batch. Processes often require the presence of a catalyst and problems can occur with the initiation of certain reactions. Continued addition of the peroxide in the absence of reaction initiation gives rise to a similar hazardous situation as that generated from addition in the absence of agitation.

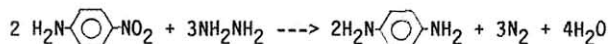
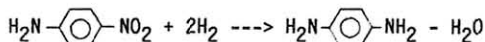
The hazards associated with peroxide oxidations are such that alternatives should be evaluated. For example the use of air as the oxidising agent would be desirable as not only is the reagent itself cheap but it also has no stability problems. The use of aerial oxidation also makes the reaction more controllable, there is no danger of accumulation, unreacted air just bubbling through the batch, and turning off the air supply completely stops the reaction. This change to aerial oxidation has been achieved in a process involving the oxidation of a substituted acetophenone to a carboxylic acid. Thus instead of using a reaction with hydrogen peroxide:-



the process now uses air and a catalyst.



Another example in this area of reagent choice involved the use of either hydrazine or gaseous hydrogen to effect the reduction of 4-nitroaniline to 1,4-diaminobenzene:-



The use of hydrogen could result in major hazard problems and could in simplistic terms be considered less inherently safe than a process that did not use it. However the process using hydrogen as the reducing agent had no initiation and relatively little accumulation problems i.e. only the vapour space in the reaction. In contrast the process involving the use of hydrazine had a serious defect in that temporary failure of the nickel catalyst could occur. Subsequent accumulation of the unreacted hydrazine could have then resulted in a chemical runaway problem not encountered in the process using gaseous hydrogen.

Compatibility of Materials

Careful study of the materials involved in a process, including all the work-up procedures, as well as the main reaction can lead to a significant reduction in the hazards of a process and an increase in its inherent safety.

A proposed process for the manufacture of a heterocyclic intermediate involved the use of sodium hydrogen sulphide as one of the reactants and methanol as a co-solvent. The reaction was found to proceed smoothly with good yield but a detoxification process was required in order to destroy the small quantities of sulphur compounds still present at the end of the reaction.

Most detoxification procedures involve the removal of sulphurous impurities by treatment with sodium hypochlorite. What had not been recognised during the initial drafting of the process was that methanol can react with sodium hypochlorite to produce methyl hypochlorite. Methyl hypochlorite is an extremely dangerous impact sensitive explosive. The literature (7) revealed that in aqueous solution the solubility of methyl hypochlorite is approximately 6% and that at concentrations greater than 2% the material presents a serious hazard. The methanol comprised approximately 21% of the filtrates in this process. Methyl hypochlorite is also low boiling (11-12 deg C) and could therefore evaporate and perhaps condense in pipework during winter. The process was changed to operate in the total absence of methanol, thus removing the problem of formation of explosive methyl hypochlorite.

It is not only the compatibility of materials involved in a single process that needs to be examined. Interaction of chemicals involved in adjacent reactors can lead to serious problems. This cross contamination proved to be the cause of several anthraquinone charging incidents. These all involved the manual charging of anthraquinone or a substituted anthraquinone powder to sulphuric acid where upon burning of the anthraquinone powder on top of the acid was seen or a flash fire occurred in the dust cloud. The ignition source for these incidents proved very difficult to track down until it was observed that sodium chlorate, a very powerful oxidising agent was being used in the same area of the plant. Extensive testing confirmed that the reaction between sodium chlorate and sulphuric acid could cause ignition of the anthraquinone powder.

Catalysts

The use of a specific catalyst can make a potentially very hazardous process much safer, particularly where the catalyst becomes de-activated under fault conditions. This concept is exemplified by the following example, described above, that involves the aerial oxidation of a substituted acetophenone to the carboxylic acid.

The process essentially involves the passage of air through a solution of the substituted acetophenone at 80-85 deg C in the presence of a catalyst. In common with other oxidation processes it is very exothermic having a heat of reaction of -220 Kcals/mole of substituted acetophenone. Consequently loss of cooling and uncontrolled reaction could lead to rapid vaporisation of the solvent and subsequent exothermic decomposition of the residues. However it has been found that the catalyst chosen for this process stops working if the temperature exceeds 100 deg C and the reaction stops.

Choice of Solvent

The choice of a suitable solvent for a process can involve various factors. These include the toxicity of the solvent itself and its compatibility with the other materials present in the process.

Another feature to be considered is the solvents boiling point. The synthesis of an intermediate was first proposed using acetone as the solvent. The heat of reaction was such that an uncontrolled addition of one of the reagents or loss of cooling during addition would have resulted in the vigorous boiling of the batch with the possibility of loss of material and/or over-pressurisation of the reactor if the condenser logged.

The simple change to using toluene as the solvent produced a reaction mixture with a boiling point sufficiently high as to be inaccessible from the heat generated by the reaction.

Conclusion

It can be seen that a careful examination of the potential hazards at an early stage in process development can lead to the choice of an inherently safer synthesis. Consideration of the intermediates produced, the reagents used, compability of materials, choice of catalysts and the solvents used can result in safer processes.

The future will hopefully provide the development of new improved reagents and catalysts that will enable more selective and hence inherently safer reactions to be carried out. The development of biological processes working on the principle of the bacteria dying, if the temperature gets too hot, could again be an area where significant improvements in inherent safety could be made. However this paper has shown that significant benefits in *inherent safety can be gained now by the careful study of the manufacturing processes prior to manufacture.*

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