Thermal Hazards in the Chemical Industry
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Introduction

A large proportion of the incidents in the chemical industry are as a result of a lack of knowledge and understanding of the thermal properties of the system. Whether these be chemical reaction hazards or material hazards the need to fully characterise any potential energy changes within the system is critical.

Thermal hazards can be broadly divided into two categories: energy released during desired reaction and energy released during unwanted reaction. The first of these encompasses enthalpies of reaction, crystallisation, melting, and dissolution whilst the second is usually associated with heats of decomposition reaction. The majority of incidents are caused by either equipment failure (e.g. loss of cooling or agitation) or human error (e.g. mischarging and over heating) and these incidents can occur either during under standard processing conditions or by deviation from the standard conditions.

The influence of reaction kinetics cannot be ignored. Although it is the thermodynamic properties of the system, which will govern whether a reaction is dangerous, the kinetics of that process can change a dangerous situation into a controllable event or worse a mildly exothermic process into a catastrophic failure.

The pressure rise that is associated with a rise in reaction temperature is a critical factor. The rise in vapour pressure with temperature is one aspect but the generation of non-condensable gas from decomposition or side reactions is a major contributory cause in the majority of chemical plant explosions. Careful study of any possible temperature deviation is necessary to ensure that the pressure rise that can accompany this is understood and can be managed. The strategies for managing such

pressure events are many and are beyond the scope of this text. One of the main ways in which a pressure deviation event can be handled is in the use of pressure relief, the design institute for emergency relief systems (or DIERS) has published many works on how pressure events should be investigated and managed. Publications by this group can be accessed through the web[1] and the UK Health and Safety Executive have published a good workable strategy for implementation of these techniques[2].

One of the major causes of incidents is a misunderstanding of the changes in the reaction properties upon scale-up. It is important to understand that changes in the scale of a reaction can radically affect the thermal properties and that the size and shape of any chosen reactor system should be carefully considered to ensure that adequate cooling capacity is maintained. Moving an apparently "safe" process to a larger scale without fully investigating the reactor/reaction properties has caused several recent incidents[3].

History

There has been a catalogue of incidents in the chemical industry that can be directly attributed to thermal hazards. Recent works summarise some of these[45]. Examples are shown here to highlight root causes and to impress the potential damage to personnel and property caused by these incidents.

One example of the lack of understanding and incorrect approach to thermal hazards is the 1998 explosion at Morton Chemical International (Paterson, New Jersey, USA). Although, in this case, there was no loss of life nine people sustained injury two of those were serious. Conclusions from a safety board investigation highlighted that the safety investigation into the process being conducted did not anticipate the potential hazardous reaction and consequently the

vessel used for the process was not equipped with the relevant safety features. The cooling capacity for the process was therefore insufficient for the amount of heat produced and catastrophic failure resulted. The training of employees in the recognition of deviation conditions and how to react in the event of reaction runaway was also a contributory factor in this disaster.

Even in areas of chemical processing where thermal hazards are not only common but are the norm a lack of proper hazard analysis can lead to potentially catastrophic events. The distillation of solvents for recovery is a process that has a high hazard potential. The concentration of reaction by-products and impurities by removal of solvents means that the initial reaction conditions, which may be perfectly safe, can be a false indicator of the conditions at the end of solvent removal. An explosion in a solvent recovery plant in Italy demonstrated a good example of this. The concentration of unknown materials caused by the removal of solvents led to thermal decomposition of the distillation residue and caused a sudden overpressure in the boiler which ruptured giving rise to a release of potentially dangerous materials to the atmosphere[6].

Thermal explosion events are not only in the province of chemical plants. Recently an incident was reported where equipment used to assess runaway reactions was damaged by explosion[7]. The incident was caused by pushing the equipment beyond the boundaries of normal operation when trying to investigate a chemical process. The root cause of the incident was the operators of the apparatus failing to recognise the potential severity of a reaction. Although it was possible to safely investigate this process the user of the equipment did not appreciate the potential pressure release under the chosen conditions.

Techniques for Hazard Evaluation

The review above has shown that a root cause for most thermal deviations within chemical

plants is a lack of knowledge in the thermal properties of the reacting system. Obviously as there are two areas where these deviations can occur (normal process conditions and abnormal conditions) several different investigation methods must be used to accurately characterise the thermal properties of the system.

Reaction Calorimetry

Reaction calorimetry has been traditionally employed for characterising the heat evolved during a chemical process. Reaction calorimetry is usually a heat-flow technique allowing the reacting mixture to remain at the processing temperature whilst measuring the heat evolved. The additional advantage of these instruments is that a degree of time dependency can be attributed to the data allowing operators to determine basic kinetic parameters from the data and assess possible reactant build-up.

Most of these devices are similar to standard lab reactors with the philosophy of mimicking standard operating conditions of the process and the aim of them being operated by people conducting the lab scale testing. In practice these calorimeters are usually complex to operate and the data analysis and interpretation require experienced operators with a good understanding of the thermal processes occurring.

Historically the first systems operated under strict heat-flow conditions; here heat generated, or consumed by the reaction is transmitted through the vessel wall and is removed by coolant liquid. These instruments depend on the thermal properties of the liquid mixture, the heat transfer properties of the vessel and the heat transfer area. These dependencies mean that accurate measurements require careful calibration whenever the contents of the vessel change in either volume or composition.

More recently power compensation calorimetry has become more popular. In this technique the temperature of the coolant liquid is maintained slightly below the reaction temperature a separate heater within the vessel is then used to supply the correct amount of heat to obtain the correct

temperature. The power consumed by this heater is then altered during the reaction to maintain isothermal conditions and the changes in power reflect the power output of the reaction. The advantage of this technology is that the thermal transfer area critical to measurement is that of the power compensation heater not the vessel wall and therefore fewer calibrations are needed.

One of the major problems with reaction calorimetry is the measurement of processes under reflux conditions. Under reflux conditions the main area of heat loss is within the condenser. Heat-flow calorimeters usually maintain a constant temperature difference between the jacket and contents and then measure the heat-flow of the reaction by monitoring the temperature difference between the inlet and outlet of the reflux condenser. This method is usually inaccurate because of heat losses from the reactor head (a heated reactor head is usually used to reduce this) and from the reflux condenser (although vacuum jacketing and lagging can reduce this effect).

The study of deviations from standard conditions is an area where reaction calorimetry is also employed. This unfortunately requires a large amount of time, material and effort for what is in effect waste. Nether the less this is essential for evaluating possible process deviations.

A new area of reaction calorimetry has recently been established by the use of peltier elements as thermal detection systems. Small scale "Reaction Calorimeters" have many advantages over more traditional large volume systems (low cost, low chemical requirement, speed of use, flexibility and sensitivity) however are unable to operate at reflux and in the main have limited pressure ability.

Small scale instruments are still generally unproven for process hazards assessment but show great potential especially when used in conjunction with more traditional systems as validation. One area where the speed and low

volumes would be ideal is with process deviations where several weeks of large-scale calorimetry could be reduced to a couple of days.

Scanning Calorimetry

Scanning calorimetries (differential scanning calorimetry (DSC) and differential thermal analysis (DTA)) are normally employed to study temperature (or time) initiated processes and as such are frequently used to investigate thermal decomposition processes. In these techniques a sample of material is subjected to a constant temperature ramp and the heat evolved from the material is measured. These techniques are called differential calorimetry as they use a "representative reference sample" as a comparison. The use of a temperature ramp limits the detection limits of the devices and these systems can in no way be considered adiabatic. The heat losses from the sample will be dependent on the ramp rate of the experiment and therefore care needs to be taken to ensure that several different ramp rates are used to remove experimental artefacts from the data.

Scanning calorimetries have advantages over more adiabatic techniques as the test duration is shorter and given ideal conditions and careful data manipulation good results can be achieved. One criticism usually levelled at DSC is an unrepresentative sample size (usually in the mg range) DTA samples can be much larger (1-10g) and as such are more representative however thermal gradients within the sample have to be considered especially at higher scanning rates. The larger samples also allow for good pressure data to be measured in fact several of these systems utilise pressure deviation as a way of detecting exothermic runaway.

Adiabatic Calorimetry

An adiabatic situation is defined as one where heat is not lost from the sample. Adiabatic calorimetry is therefore testing where all the heat generated by a reaction is kept within the sample; as such most reactions are self-accelerating. In general adiabatic calorimetry can be considered a worst-case simulation of the runaway reaction.

There are several adiabatic calorimeters available.

Historically Dow Chemical developed the first adiabatic device, the Accelerating Rate Calorimeter (ARC), in the 1970's. The original ARC utilised a spherical sample contained mounted within an oven. By using a combination of thermocouples and heaters the temperature within the oven is kept the same as the temperature of the sample and therefore the only loss of heat from the sample is that used to increase the temperature of the sample holder. This "thermal dilution" is referred to as the ϕ factor and in ARC testing is the main deviation from true adiabatic behaviour.

The Accelerating Rate Calorimeter uses a "Heat-Wait-Seek" methodology where the sample is heated to a set temperature before a wait period where constant temperature is maintained to allow thermal equilibration. The system then enters a "seek" mode where self-heating of the sample above a threshold value causes the instrument to enter an adiabatic-exotherm mode where temperature evolution is tracked to completion. If the threshold value is not reached the system will then re-start the heat-wait-seek sequence first increasing the temperature by a set heat step.

One of the key features of Accelerating Rate Calorimeters is the excellent ability to generate pressure data. Care should be employed to ensure that corrections are applied for both vapour pressure and gas-pad if critical values are derived from the pressure data.

Traditionally the Accelerating Rate Calorimeter has suffered criticism for a high phi factor (a minimum of 1.2 is attainable however values in the range of 1.5 are more usual) and low tracking rates (the standard ARC can only track exotherms up to 20°C/min in magnitude). More recently Thermal Hazard Technology in England has updated the Accelerating Rate Calorimeter[8].

Improvements include the ability to use larger volume test cells (to reduce ϕ), faster tracking rates (up to 150°C/min), sub-ambient testing (starting from –35°C), stirring and sample addition.

Other adiabatic techniques use dewar technology to minimise heat loss from the vessel under runaway conditions and although the larger sample volumes used in these instruments give realistic conditions and low ϕ values care should be taken in reactions where pressure generation is suspected.

Vent-Sizing Calorimeters

The requirements of the DIERS technology to assess the possible release of material from a reactor has led to the development of several technologies to measure the physical properties of material released from the reactor under certain conditions. It is critical, when determining the correct size of a reactor vent, to characterise the type of material ejected from the reactor, the pressure at which this occurs, the temperature rate at this time and the properties of that material.

Vent-sizing calorimeters utilise the "Heat-Wait-Seek" methodology described above. There are two systems based on designs from the DIERS programme. The VSP and Phi-Tec both operate using a pressure equalisation technique where the pressure inside the test cell is matched to the pressure outside of the cell using a high-pressure gas. This allows very thin test cells to be used; this gives higher potential heating rates and low ϕ values. The high sample volumes used in these systems means that the data is highly representative of the simulated reaction, although care must be taken to ensure that this in itself does not lead to complications[7].

The ability to conduct experiments, which can determine flow regimes, material properties and other vent sizing related parameters, has also been added to both the Accelerating Rate Calorimeter and Adiabatic Dewar Calorimeter.

Strategies for Hazard Evaluation

The successful employment of hazard evaluation depends critically on the way in which it is utilised. Obviously if every process is extensively characterised by both reaction and adiabatic techniques then there is little chance that a lack of knowledge could result in a "thermal event". The main problem with this strategy is the large time requirement that this requires. Usually companies tend to employ screening techniques using scanning calorimetry to isolate potential problems before more time consuming instruments are used.

The evaluation of process deviations is another area where company strategies determine the level of investigation needed. It is always possible to think of another deviation that could lead to a hazardous situation. It is therefore important to consider what is a credible deviation. There is no point in trying to establish what could happen if a chemical came into contact with silicone oil if the system was using a water jacket and there was no silicone oil in the building!

Several companies have published approaches to this kind of investigation where the results from one test are assessed and the level of hazard determines where further testing is appropriate. These schemes are generally are based on a flow-chart system and show the progression from one stage to the next depending on the evaluated hazard.

[1] www.iomosiac.com/diers
[2] Handbook for emergency relief, UK Health and safety executive.
[3] Chemical Reaction Hazards Forum http://www.crhf.org.uk/
[4] Balasubramanian, S. G., and Louvar, J. F., "Study of Major Accidents and Lessons Learned" Process Safety Progress, Vol. 21, No. 3 (2002), 237-244
[5] *Barton, J.A., and Nolan, P.F., 1990.* Incidents in the Chemical Industry due to Thermal Runaway Chemical Reactions. Paper presented at the 1990 conference and Exhibition on Techniques for the Assessment of Chemical Reaction Hazards, Amsterdam, December 1990.
[6] Lunghi.A, Cattaneo.M, Cardillo.P, *J.Loss Prev.*, **11** (1998), p249.
[7] Chi-Min Shu *, Chun-Jen Wang, *J. Loss Prev.* **In Press**
[8] www.thermalhazardtechnology.com