

Chemical Reaction Hazards – Safety Precaution & Thermal Runaway Reaction Prevention

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Abstract

Thermal runaway reactions have been widely identified as a major risk in the fine chemical industry. In the previous era, the chemical industry has been the cause of numerous of major manufacturing accidents. Specific lessons have been acquired as a consequence of every accident. It is essential to develop safety technologies for controlling the reaction of thermal runaways in emergencies and mitigating the resulting hazards. Currently, there is totally inadequate research on the loss preventative measures of chemical reaction thermal runaway. Such lessons learned have been executed in the form of employee safety education and/or equipment as well as facility safety precautions, resulting in a significant reduction in corresponding disaster frequencies. This paper provides a thorough examination of the recent progress of emergency response technologies for reaction thermal runaways, as well as the major principles and potential applications of those loss prevention methods such as determining the safe operating envelope, predicting reactivity and stability and hazard assessment of chemical reactions. This article is expected to have some reference value for further understanding of thermal runaways, the design of mitigation systems, and the formulation of an emergency management strategic plan for runaway reactions.

Keywords:- Thermal Runaway, Assessment, Chemical Runaway, Hazardous chemical reaction, Prediction of reaction

1. Introduction

Chemical reactions either produce heat (exothermic) or absorb heat (endothermic). The vast majority of chemical reactions in the industry are exothermic. In some instances, an exothermic reaction can cause a thermal runaway if the rate of heat generation exceeds the rate of heat removal. The rate of reaction increases as the surplus heat raises the temperature of the reaction mass. As a result, the rate of heat production quickens.

A runaway exothermic reaction can produce various outcomes, including the heating process over the reaction mass and large increases in temperature and pressure that result in a blast. This type of violence can result in blast and missile damage. The release of flammable materials could cause a fire or secondary explosion. Hot liquids and toxic materials have the potential to contaminate the workplace or create a toxic cloud that can be scattered off-site. There is a serious risk of injury to plant operators, other personnel, and the public at large, as well as environmental damage. A runaway causes loss and disruption of production at best; at worst, it has the potential for a major accident, as demonstrated by the incidents at Seveso and Bhopal. In this paper, we will look back over the last 25 years in the study of batch and semi-batch reactor safety and runaway reaction prevention. Three lines of defense must be considered in the design and operation of a semi-batch reactor to prevent reactor incidents and runaways in general. The first line of defense is selecting the appropriate operating conditions. This refers to the degree of mixing, cooling capacity, coolant temperature selection, reactant(s) dosing rate, and so on. Numerous papers on the selection of operating conditions have been written over the years. The majority of recommendations are based on an understanding of the reaction's kinetics. Batch reactors, unfortunately, are almost exclusively used in the fine chemical sector, where time and money are usually serious constraints for the costly and time-consuming study of reaction kinetics. In the case of highly exothermic reactions, inaccurate kinetic information frequently results in an overly cautious selection of operating conditions with low reactor productivity. Over the last decade, the reaction calorimeter has gained widespread acceptance as a tool for determining operating conditions.

An early warning detection system serves as the second line of defense. A correct selection of operating conditions is insufficient for the safe operation of a reactor section in a plant. Human errors such as reactant mischarging, maintenance issues, agitator breakdowns, and so on are unavoidable. As a result, it is necessary to provide the industry with a piece of equipment or a

procedure that can provide an advanced warning to the operator that a runaway is likely to occur within such a shorter amount of time, say, 20 to 200 minutes before achieving the maximum runaway temperatures. Great strides have been made in this field in the last ten years. A suitable system to handle running away reactions is the third line of defense. Such systems are dependent on the reactants and reactions available. If vapors form, a blow-down system with catch tanks is required; alternatively, reactor contents must be discharged to refrigerated cellars loaded with ice to stop the reaction by freezing. Many different approaches can be found in practice. This aspect will not be discussed in this paper because the measures to be taken to deal with a reaction mass that is heating up toward a runaway are too specific for each case.

2. Hazard assessment of chemical reactions

The three major chemical reaction hazards you need to consider are:

- The thermal instability of reactants, reactant mixtures, and products (including any intermediates, potential contaminants, and by-products);
- Exothermic reactions which raise the temperature to produce decomposition reactions or violent boiling; and
- Gas evolution.

A typical safety assessment procedure will include the following

1. Defining the chemistry, the process operating conditions, and the process plant;
2. Identifying the hazards;
3. Assessing the consequences, in terms of their severity and likelihood;
4. Selecting and specifying a basis of safety;
5. Implementing and maintaining the safety measures.

For new processes and plants, beginning this assessment procedure at the earliest stages of research and development allows you to achieve the highest level of inherent safety. At this stage, you can also minimize the costs of safety precautions. For existing plants and processes, you should consider your risk assessment to ensure you have taken all necessary steps to reduce risks to as low as is reasonably practicable. Chemical reaction hazards need to be assessed by technically qualified people who have some experience in hazard evaluation and a good knowledge of process chemistry. Ideally, they should be part of an independent team to avoid conflicts of interest between production and safety. However, they do need good communication with plant staff to

minimize the chance of any misunderstandings. The depth of the hazard assessment depends on the nature and magnitude of the hazards and the scale of operation and its complexity. For example, it may be easy to show for some processes that they are unable to run away from the knowledge of the process chemistry combined with small-scale screening tests. For others, you will need to do more detailed and accurate tests. There may be little justification for accurately measuring the rate of temperature rise of a runaway reaction if the process is only being operated at the gram scale in the laboratory.

2.1. Initial assessments

Research chemists and other research and development professionals play a fundamental role in the development of a safe process. They must make an in-depth investigation into the process chemistry and into the entire process that may develop based on that chemistry. These professionals have many opportunities to incorporate inherently safer design concepts. For example, they can choose inherently safer synthesis routes.

2.2. Literature surveys

The initial assessment you can carry out at this early stage involves a desktop study of the potential reactants and routes to a given product. A literature search of the chemicals to be used and the process chemistry can be useful if it is thorough. "Bretherick's Handbook of reactive chemical hazards" and they are useful "National Fire Protection Association's Manual of hazardous chemical reactions texts". They give accounts of numerous previous incidents with many surprising and unexpected exothermic runaway reactions. However, the absence of particular information does not imply that no hazards exist. It is at this early stage that you can consider inherently safer synthesis routes. Examples of synthesis routes considered inherently safer include:

- Avoiding highly exothermic reactions or thermally unstable reactants and intermediates.
- Replacement of batch reaction processes with semi-batch or continuous processes. This reduces the quantity of reactant present and controlling the addition rate may stop the reaction in the event of a hazard arising.
- Reactions in water as opposed to those which proceed in a more hazardous organic solvent (provided water is compatible with the reaction mixture).

- The use of processes that are less sensitive to variations in operating conditions, especially those defined as critical such as temperature or pressure.
- Supercritical processing uses relatively non-hazardous materials such as water or carbon dioxide as solvents, albeit at high temperatures and pressures.

The use of catalysts that can lead to less severe operating conditions, allow the use of a less reactive reagent or the opportunity to reduce or eliminate a hazardous solvent.

3. Predicting reactivity and stability

You can obtain a preliminary estimate of the reactivity and stability of chemicals from their molecular structure. Certain molecular groupings are likely to introduce hazards into a process, and you need to identify these. Examples are n Double- and triple-bonded hydrocarbons, n Epoxides, n Hydrides and hydrogen, n Metal acetylides n Nitrogen-containing compounds, eg amides, imides, nitrides, azides, azo-, diazo-, diazeno-compounds, halogen nitrogen bonded compounds, hydrazine-derived nitrogen compounds, nitrates, nitrites, nitroso, and nitro compounds, nitrogen-metal derivatives are n Oxygenated compounds of halogens, n Peroxides. Many of these molecular groupings can be explosive or energetic materials. You may not know the specific hazards of new compounds, but you may know the hazards of analogous compounds or those with the same or similar molecular groupings. Many additional hazards result from the hazardous reactivity of combinations of chemicals.

3.1. Thermochemistry

You can get a useful indication of thermochemistry by considering the heat of the reaction. Published references exist quoting many heats of reaction. However, it is possible to calculate the heat of the reaction from the heat of the formation of the reactants and products. The calculation assumes 100% conversion to the chosen products. The accuracy of the calculation depends on the accuracy of the heat of formation, but you must also take account of any changes of state that may occur such as heat of solution, vaporization, etc. Once you have estimated the heat of the reaction you can use it to predict the maximum temperature rise expected in the reaction mass under conditions of no heat loss. This assumes all the energy from the heat of the reaction increases the temperature of the reaction mass. It is a maximum temperature rise depending only on the specific heat capacity of the reaction mass and assumes no heat losses at all.

$\Delta T_{ad} = -\Delta H/C_p$ where:

ΔT_{ad} = adiabatic temperature rise (K)

ΔH = heat of reaction (kJ kg⁻¹)

C_p = specific heat of reaction mixture (kJ kg⁻¹ K⁻¹)

Therefore, the maximum temperature that the reaction process can reach is the sum of the adiabatic temperature rise and the maximum expected processing temperature. This sum is an important value because if this maximum temperature is below the temperature at which:

- Additional chemistry (decomposition);
- Physical transition (boiling or gas generation)
- Overpressurization from increased vaporization can occur.

Then there is a little hazard due to the heat release of the desired reaction, although there may be dramatic effects on product quality or yield.

3.2. Interpreting the information obtained

- These simple but effective desktop screening methods are likely to have given you valuable information. They will have indicated the exothermicity of the desired reaction. They will have indicated if any of the reactants or products are thermally unstable, and they will have estimated the maximum reaction temperature of the desired reaction (sometimes referred to as the maximum temperature of the synthesis reaction or MTSR). These screening steps may not be necessary where generic chemistry and full testing are routine. Actual test results are always preferable to theoretical calculations.
- Your initial screening may have given you sufficient information to narrow down the choices for a synthesis route, and to determine a safe operating strategy for the reaction, particularly at the laboratory stage.
- However, you need to take care that you have adequately assessed the process. In particular, the temperature at which decomposition or a runaway can occur varies with the conditions under which the materials are held. The adiabatic temperature rise may also be underestimated, particularly if you have not taken into account any changes of state or side reactions.
- What these screenings have not done is give you any information on:

- The kinetics of the desired reaction;
- The rate at which heat can be produced;
- Any unwanted and potentially unsafe side reactions including decompositions;
- The effect of contaminants in the reaction mixture;
- The effect of any foreseeable variation in feed quality
- Gas evolution.
- You may need more accurate information on the heat of the reaction and the rate of reaction to determine whether an exothermic runaway can occur.
- To determine this additional information you need to carry out further screening involving physical testing.

3.3. Further screening

There are several small-scale test methods (0.01-10g sample size) available that you can use to indicate:

1. The rates and quantities of heat and gas evolution;
2. Whether a runaway reaction may occur; and
3. What the consequences are of a runaway in terms of the heat and gas evolution rates?

These include differential scanning calorimetry (DSC) and various forms of differential thermal analysis (DTA): the insulated exotherm test (IET); decomposition pressure test (DPT); and the more complicated explosibility tests that need expert advice and specialized facilities. If your calculations or testing demonstrates potentially explosive properties then you should not use the material further until you have done a detailed evaluation of its properties. It is recommended that, where practicable, detonable materials are not handled in reaction.

4. Determining the safe operating envelope

Armed now with the results of the simulation tests, you understand a great deal about the reaction hazards of the process. You have defined your safe operating envelope. You understand, for example, what happens if the agitator stops during the reaction; if cooling stops; or if reactants are charged in the incorrect order, or too fast or too slow; or at lower or higher temperatures than desired.

You can use this knowledge now about the design of your process. For example, you can:

1. Use a heating medium whose maximum temperature will ensure safety in the event of loss of direct control.
2. Install a restricting orifice in a feed pipeline to restrict the flow rate if a control valve or meter should fail.
3. Size the reactor charge vessels so that the quantity of reactant that can be added at any one time is limited to a safe amount.

What you now need to do is design the process and plant, and operate the process and plant Selecting and specify a basis of safety.

Take the opportunity at this stage to review the process chemistry and plant required. You need to try and reduce the number, complexity, and cost of 'add-on' safety features and increase the integrity of any features you do use. Answers to the following questions will be helpful in this regard.

- Is it possible to eliminate hazardous raw materials, process intermediates, or by-products by using alternative chemistry?
- Is it possible to substitute less hazardous raw materials?
- Have all in-process inventories of hazardous materials in storage tanks been minimized?
- Has all processing equipment handled hazardous materials been designed to minimize inventory?
- Is process equipment located to minimize the length of hazardous material piping?
- Is it possible to generate hazardous reactants in situ from less hazardous raw materials, rather than to have to store them on-site?
- For equipment containing materials that become unstable at elevated temperatures or freeze at low temperatures, is it possible to use heating and cooling fluids that limit the maximum and minimum temperatures attainable?
- Can reaction conditions be made less severe by using a catalyst?
- Can the equipment be designed to contain the maximum pressure generated?

- Can equipment be designed so that it is difficult or impossible to create a potentially hazardous situation due to operating error?
- Can process units be located to reduce or eliminate adverse impacts from other adjacent hazardous installations?
- Can semi-batch processes be modified to reduce the accumulation of reactants?
- Has the heating effect of the surroundings been considered under failure conditions when working below ambient temperatures or using reactor heating?

This list is not exhaustive, but it should give you a flavor of the thinking you can adopt in trying to produce an inherently safer process. In many situations, it will be necessary to provide additional safety measures. These can be of two types

- Preventive, i.e. They reduce the likelihood of a hazardous situation occurring; and
- Protective, i.e. they reduce the preventive measures

4.1. Preventive measures

Preventive measures relate to your defined safe operating envelope. These are the means by which you control the desired chemical reaction. They include measures to control:

- Temperature: The safety margin between the temperature at which an undesired exothermic reaction starts and the operating temperature.
- Reactant addition: To prevent addition of the wrong reactant; or the correct reactant(s) too early, too late, too quickly, too slowly, in too much or too little quantities, or in the wrong order.
- Agitation: What happens when the agitator or circulation pump fails, is started too late, is stopped or not turned on, or is operating at the wrong speed?
- Other variables: Used to control reactions including varying pH, conductivity, concentration and pressure, etc.

Other measures include aspects of the design of the process and plant already discussed, particularly the inherently safer options. But they also include the

engineering and procedural controls; the safety interlocks and emergency shutdown systems.

4.1.1. Controlling rates of reaction

You can affect the heat balance by how you control the rate of reaction. If all the reactants are present in the reactor at the start of the process, and you then start the reaction (eg by heating), then this is a batch reaction. The main disadvantage of batch reactions is that because all the reactants are present, if something goes wrong (eg failure of cooling) then nothing can be done to control the reaction. You must then rely on protective measures to mitigate the consequences. If you add one or more reactants gradually during the reaction then the process is a semi-batch reaction. The rate of reaction is controllable by several factors, in particular addition rate and temperature. In most cases, stopping the addition will not completely stop the reaction. Some temperature rise can be developed in the reaction mass because some reaction of accumulated reactants continues. The effect of this accumulation and its extent depends on the balance between reaction kinetics and addition rate. It may be possible to control addition rates and temperatures so that there is only a small accumulation of unreacted material in the reactor. In this case, the reaction mixture cannot reach an unsafe temperature. Isothermal calorimetry can be useful in determining the optimum conditions for this. If there is a process malfunction, for example, loss of agitation that may result in a runaway, it should be possible to detect this. Stopping the addition prevents an increase in the accumulation of unreacted material and the possibility of an exothermic runaway. In some cases, although complete control may not be possible, a reduced accumulation can reduce the level of protection required. For example, the cross-sectional area of emergency pressure relief needed may be smaller. You will have been able to determine if accumulation occurs, and when in the process it occurs, from your testing.

4.1.2. The integrity of process control

Your preventive measures could rely upon operator intervention. This allows the operator to apply judgement and the measures taken can be very flexible. However, a number of factors can affect the reliability of this type of approach. These include:

- The complexity of the tasks;
- The system design;
- The time available for a response;
- Operator availability
- Operator training.

Automatic safety control systems have the advantage that high levels of safety integrity are achievable. You need, however, to take great care in designing the system. You need to consider what are the critical sequences of failures that can cause a hazard. This needs to be done in a systematic way. There are many techniques available for this type of analysis, eg hazard and operability study (HAZOP), fault tree analysis, etc.

Where loss of control could lead to significant injury to people, or damage to plant or the environment, then the integrity of the control system must be to a high standard. The integrity of the control systems can be increased, or the system can be made inherently safer, by a number of means.

Consider a semi-batch chemical process to produce a given desired product. There is a well-defined safe operating envelope concerning the reactor contents temperature. It is known that there is little or no accumulation even if the temperature is allowed to drop. Provided the temperature remains within the safe operating envelope not only are product yield and quality as required but also excursion into a region that could result in an exothermic decomposition of a by-product is avoided. Reactor contents temperature is therefore a safety-critical parameter.

4.2. Designing Protective measures

Protective measures mitigate the consequences of a hazard. They are rarely used on their own. Some preventive measures are usually present to reduce the demand on the protective system. Protective measures include:

- Containment within the reactor system;
- Emergency pressure relief or venting, and dumping;
- Crash cooling;
- Reaction inhibition;
- Drown-out and quenching; and
- Secondary containment.

All the protective measures, with the exception of containment and venting, normally rely on a control system to operate them. Therefore, the safety integrity of the protective measure and the integrity of the control system are both important in its selection.

As with all other aspects of safe chemical processes, it is important that the design of any protective measure is adequate. For this to happen you must understand the runaway reaction process in detail. An undersized vent on a reactor will not totally protect the reactor against damage. As the protective measure is the last line of

defence, it needs designing to protect against the worst-case scenario.

5. Assessing the worst-case scenario

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5.1. Containment within the reactor

In this particular instance, the reactor system should be designed to withstand the maximum pressure generated by the runaway reaction. Remember that all reactor-accessible equipment, such as reflux condensers, charge vessels, instrument connections, piping, and sample points, must be able to withstand this extreme load. You should also think about the possibility of maximum reactor pressure causing reverse flow, such as through reactant feed lines.

5.2. Emergency pressure relief or venting, or dumping

For chemical reactor systems, a common method has been to continue providing precautionary measures such as control systems and safety trips, which are backed up by an emergency pressure-relief system. The emergency relief or vent is simply a means of limiting vapor or gas pressure buildup throughout a runaway. Although an emergency relief protects the reactor system, the

disposal from the relief must be handled securely. The majority of the time, the relieving fluids will still be reacting. It is highly improbable than you will be able to release directly into the atmosphere if the reactor contents are hazardous or damaging to the environment. The relief discharge in such instances can be to a disposal system. Knock-out drums, quench tanks, flare stacks, and scrubbers are a few examples. Any disposal system needs to be adequately sized and designed to protect against the worst-case scenario. For systems that evolve non-condensable gases, relief from the bottom of the reactor (dumping) may be a more efficient way to reduce the pressure in the reactor. However, if a top relief system or process vent is also required, the efficiency of bottom relief may be impaired.

- Overpressure relief may additionally be installed on a reactor system to cope with
- Compressed air, nitrogen, steam, or other service fluids that enter the system unexpectedly;
- Venting of vapors produced during an external fire;
- Pumping liquids into the vessel, or
- Heating the vessel with the vent closed.

Relief systems designed to deal with these risks are unlikely to be sufficient to protect the reactor from the effects of a chemical reaction runaway or decomposition. Whenever there is a risk of fire engulfing the reactor, the thermal stability of the reaction mass must be considered when tailoring the relief system. It is critical that your management systems explicitly indicate that in these instances, relief is not part of the basis of safety in terms of chemical reaction hazards. There have been instances where operators ignored process alarms and other warnings even though they assumed that if everything else ceased, the system would've been safe since a Designed relief vent was installed.

5.3. Crash cooling

In some cases, utilizing additional cooling could be able to bring a runaway reaction under control, especially in its early stages. Typically, this is accomplished by:

- Bringing a reflux condenser online;
- Using a refrigerant in the reactor cooling coils or jacket; or
- Pumping the reactor contents through an external heat exchanger.

In all of these instances, individuals must evaluate the program's dependability and integrity.

5.4. Reaction inhibition

A few reactions can be suppressed by injecting a chemical inhibitor, like a free-radical scavenger, or poisoning a catalyst, into the reaction mechanism. Such systems must be carefully designed. In the worst-case scenario, can you add the inhibitor and distribute it quickly enough? Is it thoroughly mixed into the reaction mass? The worst-case scenario is that the agitator fails. In this case, the injection of an inhibitor is unlikely to be successful. Inhibition is highly unlikely to just be advantageous if the reaction mass becomes more viscous during a runaway, which is common in many polymerizations.

5.5. Drown-out, quenching or dumping

These might be categorized as crash-cooling exceptions. The goal is to slow down the reaction by mixing in a huge amount of cold liquid. It either creates a sufficient heat sink to remove the heat of the reaction or slows the reaction down by reducing the temperature or diluting the reactant concentrations. Unless it were to react to the reaction mass, the liquid used is usually water. If this occurs, it may be simple to add enough water to cool the exothermic reaction with the water. If there is adequate space within the reactor, you could probably introduce the quench fluid straight from such a backup water reservoir. This will need to be kept under pressure. Put another way, the components of the reactor can be discharged directly into a separate containment vessel containing the quench fluid. Throughout all instances, the measure must be implemented quickly to avoid overpressurizing the reactor.

5.6. Secondary containment

Secondary containment may be presumed in certain circumstances, especially when dealing with extremely energetic substances. Whenever a reactor's leakage is insufficient, this may be required. Blast walls or mounds can direct the blast to a safe location. This, however, is a costly option. This also necessitates remote operation of the plant, which is located in an unoccupied area. As a result, this technique of protection is rarely used in the chemical industry.

Conclusion

Good knowledge of the factors influencing the thermal stability of chemical compounds is essential in preventing accidents. The identification of dangerous process situations based on general considerations of hazard factors such as those described in this paper helps to decide on making process hazard reviews and investigating thermal stability and runaway reaction hazards on a detailed experimental basis. Chemical

reaction hazards need to be assessed by technically qualified people who have some experience in hazard evaluation and a good knowledge of process chemistry. Ideally, they should be part of an independent team to avoid conflicts of interest between production and safety. The depth of the hazard assessment depends on the nature and magnitude of the hazards, the scale of operation, and their complexity. A review of accidents in the literature may help in understanding which type of process is dangerous, and where a high frequency of accidents is observed. In the field of runaway reaction prevention and mitigation, the design of safe processes must be considered first. You need to try and reduce the number, complexity, and cost of 'add-on' safety features and increase the integrity of any features you do use. It is often considered that the decomposition of chemicals is so violent that protection by venting is not possible. This may not be true for contaminated chemicals whose decomposition is less rapid. If the basis of safety is to be containment then the worst case scenario is that which results in the highest final pressure and temperature. Contaminated chemical decompositions are often gassy reactions producing foaming viscous heavies which can be vented. The problem is again to guess where decomposition will occur.

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