Runaway Reaction - The Natural Behaviour

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The reaction in which, there is observed an abrupt increase in temperature leading to uncontrollable, instantaneous reaction followed by decomposition and explosion is called a Runaway reaction. In this article, one such reaction, namely nitration has been discussed.

It is suggested that before approaching to solve the problem of the runaway nature of nitration, it is necessary to understand the natural behaviour of the system, and then mathematically resolve it. The response of the nitration system to the stimulus is described below, without the relevant mathematical treatment.

Characteristics of Runaway Reactions

1. Sudden Changes
   - sudden and large increase in the rate of reaction,
   - sudden and large increase in the temperature,
   - decomposition of the material, if the decomposition point is reached, and finally explosion.
2. Unexpectedness:

   This implies the existence of certain flaws in the following:
   - detecting the runaway behaviour of the process,
   - sequence of charging the material and sometimes overcharging due to ignorance, controlling the parameters of the reaction, due to which the temperature of the process deviates from the expected path.

Nitration is an exothermic reaction, in which the heat evolved is contributed by the heat of the reaction, and the heat of dilution of the acid system. Thus, nitration is potentially hazardous in nature. When nitration begins, due to exothermicity, self-heating of the whole system occurs, that is, the temperature of the system increases, while at the same time the system begins to lose heat to the surroundings. Most of the chemical reactions are of great concern, especially where the rate increases in a strong nonlinear fashion as the temperature increases. On the other hand, the heat losses, starting from zero, will increase in a nonlinear fashion as the temperature increases, provided the physical properties of the whole system remain constant. This consistency is however seldom observed. If the reaction progress is associated with increase in viscosity, the rate of heat accumulation in the system exceeds the rate of heat dissipation. Another hindrance to the heat dissipation is the precipitation of the nitration product. If the heat accumulation is continued, the probability of the runaway increases and as soon as one of the components of the system reaches the decomposition point, decomposition being highly exothermic, all the material decomposes nearly instantaneously causing explosion. The exothermic decomposition of solids and liquids leads to a loss of part of the products, as gas or vapour and if the whole system is closed, the impact of explosion is much greater due to over pressurisation. Hence, an assessment of the process hazard involved should be sincerely determined.

Unexpectedness - Concept and Complexity

The concept of unexpectedness in nitration is much hidden within the process and it differs with the type of substrate to be nitrated. Unexpected results can be avoided if the following points are known before developing the process:

- the rate of the reaction,
- the heat evolved per unit volume,
- the instability of the nitrating system along with its degree,
- the decomposition point of each component of the system,
- the exotherm of the reaction;
- the changes in physical properties associated with the system,
- the properties of the nitrating agents, stability, limits, results of various hazard tests,
- the rate of accumulation in relation to the changes in the physical properties of the system,
- the oxidative nature of the nitrating system, and
- the overpressurisation of the reaction.

The unexpectedness in nitration may occur when the process development in relation to the thermodynamics of the process and the design of the equipments and accessories goes wrong unknowingly during the scaling up due to lack of data.

The Rate of Nitration

The rate of nitration increases with increasing temperature and with increasing temperature the rate increases further. Thus in either case, self heating of the system adds to the problem. In general terms, the rate of heat release is exponential with respect to the temperature rise, while the ability to remove the heat varies almost linearly. The heat film coefficient decreases due to the following:

- Increase in the viscosity of the system.
- Part solidification of the nitro product.
- Scaling of the inner surface of the reactor.

The process of heat accumulation is followed by excessive gas or vapour evolution, due to the reactor content boiling. The environment is made worst, if the intermediates are unstable to the conditions that prevail inside the reactor and its vicinity in the liquid phase, which could make the intermediates prone to thermal decomposition. The autocatalytic decomposition of the intermediates if not considered, makes the system vulnerable and the over pressurisation of the closed reactor is a precursor to the disaster.

Decomposition and Physical Properties of the Components

Another aspect involved is the phase separation during the process. Nitration, being carried out at low temperature, the problem of phase separation is very serious, particularly in sulphuric-nitric systems. Sulphuric acid of high concentration has high density and at near zero or sub zero temperatures it is like a viscous oil, however, nitric acid is comparatively lighter. When the latter is added slowly into the sulphuric-organic system, nitric acid may float on the higher density substance and accumulation of the lighter liquid may become significant over a period of time. This may be large eneough to start the reaction at once, and the nitration may start so vigorously that the temperature would rise steeply, without giving any warning. Due to the excess of nitrating agent polynitration can make the situation grim and the reaction can go runaway. The condition is worse if the organic phase does not dissolve, or is immiscible in concentrated sulphuric acid. Then, if the density of the organic phase is the lowest, batch nitration is very dangerous. With increasing temperature, decomposition is largely expected because nitric acid at a high temperature is more of an oxidising agent than a nitrating agent.

The case has to be thoroughly investigated during the addition of the last lots of nitric acid in a batch process. Viscosity of the system increases significantly if the product is soluble/miscible in sulphuric acid. The phase separation is more likely at such instances.

Stability

The stability of the various components of the system plays a major role.

- The nitronium ion in the presence of nitric acid.
- The exotherm of the reaction.
- Safety in material handling and storage.
- Instability and its occurrence.
- Effect of sequential charging of materials.
- The rate of reaction and the conditions to the formation of polynitro compounds.
- Decomposition point and explosive limit of all components.

Control and Safety

Essentially,there are various routes to the safe reactor and reactions.

- Containment.
- On-line detection of process deviation associated with the system and corrective actions.
- Safer design of the process and equipments.
- Automation.
- Regular, rigorous checking and maintenance of the devices, equipments and accessories.
- Rigorous instruction and strict enforcement of operation rules.
- Inherently safer processes.

Containment: It is generally opted by the management while process developers go for the controlling of the runaway. In broader sense, containment is the safe design of more of the reactor and its vicinity where the hazardous reaction is carried out, rather than the introduction of high level sophistication into the system. It involves:

- Safer handling and storage of the materials.
- Avoiding chain incidents (splashing out of the materials, spreading of fire,etc.),
- placing the reactor inside the barricades (steel or concrete)
- Installation of better fire control system.
- Techniques leading to less exposure of chemicals to the workers.
- Routine and rigorous checking of valves, pumps, motors, stirrers, safety devices, etc.

On-Line Detection:

It is the temperature which contributes almost entirely to the runaway. Thus, in most cases, the on-line detection devices are the temperature measuring devices. Having more than one such detection device is safer; but, control can be best attained by Programmed temperature control.

Programmed temperature control:

The temperature variation in standardised lab scale, bench scale and pilot scale can be accurately noted with respect to the rate of addition of the reagents, the time of the reaction, and the data can be programmed in a computer and the plant scale process can be run through this standardised temperature path. Any deviation in the temperature is detected by the highly sensitive device and compensated by chilled brine cooling or external heating when the motorised valve opens automatically to bring the temperature to the set path. This automatic system ensures safety, but monitoring should not be avoided as automation may fail.

Heating in case of fall in temperature may not be advised by many, but, if nitric acid is added at a lower temperature, it may lead to its accumulation. For example, if the actual nitration occurs at 80-90°C, it is necessary to avoid charging of nitric acid at room temperature, because the optimum rate of nitration occurs at 80-90°C and the addition of the nitrating agent accumulates it in the process. Considering that the phase separation at the lower temperature does not occur, even the hazards involved are not eliminated simply because, increased concentration of nitronium ions may destabilise the system.

Another question that may arise is the unexpected fall in temperature in the mid of the process. What should be the cause and the remedy of this? In this case the following checkings are suggested.

- The rate of brine flow through the jacket.
- The rate of agitation to disperse the local heating.
- The accumulation of nitric acid.

Checking the Accumulation

Physical method : While standardising the process in various scales, one can standardise the variation of specific gravity of the homogeneous system and prepare the table as shown in Table 1.

Table 1

Amount of nitric acid added	Time taken for consumption of fixed percent of nitric acid	Specific gravity of homogeneous system

If any variations in temperature are observed in the system, the specific gravity must be checked. When such a deviation is observed, that is, the temperature goes down the set path the accumulation can be ceased by -

- keeping the temperature below that of the optimum rate of nitration,
- keeping the agitation at a faster rate to dissolve nitric acid in sulphuric acid,
- frequently checking the specific gravity of the mixture.

Chemical method : A measured sample from the reactor can be taken out and diluted to known volume with water. To this accurately measured volume of diphenylamine in sulphuric acid is added when the solution turns bluish violet. The optical density (OD) of the system then can be determined and compared with the prior standardized result. Thus, the above table can be extended as shown in table 2.

Specific gravity and OD in a standardised process: The process is carried out in the chosen standard parameters of safety and control. At the fixed interval of time, exact amount of the sample is taken out, diluted with fixed amount of cold water to suppress the reaction, filtered and at a fixed temperature specific gravity and OD of the mixture are determined.

By studying the kinetics of the reaction, the time taken for consumption of exact amount of nitric acid can be determined. After the same span of time has, the above test can be carried out by adding the lot(s) slowly in the stream. Thus, the above table can be constructed using the data.

The OD and specific gravity in the standardised process may not tally with the plant result, if there is any variation in the concentration of sulphuric acid or nitric acid. Thus, accuracy in concentration is a better practice.

Plots

1. Specific gravity against amount of nitric acid added.
2. O.D. against amount of nitric acid added.

Stopping the Runaway

On-line detection systems may give the warning signals of the runaway, but stopping the reaction that is running away is a difficult task. The corrective and preventive techniques must be efficient enough to control the runaway.

When the system runs away, but the rate of heat dissipation is still within the

Table 2

Amount of nitric acid added nitric acid	Time taken for consumption of fixed percent	Specific gravity of homogeneous system	OD

removal capacity of the design of the complete system then switching to full cooling may bring the reaction under control.

The quenching technique is the only choice of most engineers. It can be done by the following methods :-

1. Addition of inhibitors has been proposed. However, the choice of it, its capacity of removal of heat, and its stability require thorough investigation. Types of inhibitors and intimate knowledge of their reaction is at present very limited.
2. Adding chilled liquid to the reaction mixture. Again, the choice of such an efficient liquid is not enough and the presently known such liquid demand the large free volume of the reactor, and other suitable installations.
3. Dumping is another choice, but the time taken is long. Also keeping the drowning tank filled with chilled material everytime is not practicable. Thus, dumping is less reliable.

In the above quenching technique [(1) and (2)] the heat of dilution is not seriously considered, moreover, there is a probability of losing the complete batch or workup for recovery may be tedious and uneconomical.

For example, if we consider a nitration reaction with mixed acid where conc. sulphuric acid is 98-100%, the amount of heat liberated due to dilution can be calculated.

The following suggestions are made to bring the reaction going runaway immediately under control and the batch be saved completely.

1. The nitration reaction should be carried out in small batches instead of larger ones. This no doubt increases the cost of installation on the number of reactors (required to meet the product demand), but safety is attained. Also even if the reaction goes runway loss is minimised. Thus, it is better to handle a small volume than a large one.
2. If small volumes are handled cooling of the whole volume of the reaction mixture would be rapid. The reactor can be connected to 2/3 heat exchangers supplied with chilled brine when required. The design is so made that the volume of reactor content in emptied almost instantaneously and cooled, bringing in the dissipation of heat rapidly. Thus, the temperature can be brought under control immediately without dilution and thus keeping the batch intact. But, the major disadvantages of this would be the solidification or precipitation of a component in the reaction when cooled, as this may choke the tubes of the exchanger.
3. If dumping is the technique so designed in the plant, then the reactor should be a multi discharging reactor; that is, instead of one bottom discharge, the reactor should have 3 or 4 discharges, so that the rate of dumping would be high.
4. Designing a tubular reactor which can be used in both batch and a continuous manners.

The Concept of Inherent Safety

A process is inherently safe in a rigorous sense, when no disturbance whatsoever can cause an accident. But, in real sense such absolute inherent safety is rare.

The recommendation of Kletz for newer synthetic routes which avoids hazardous reactant materials and conditions, is answered today by Phase Transfer Reactions (PTRs). For example a halo group can be replaced easily by NO_2 using $NaNO_2$ and PTC. The condition of the reaction is mild enough and can be handled without any difficulty, Moreover, such type of reaction would be very economical, but this approach requires extensive investigation.

Azeotropic Distillation in Nitration

The rate of nitration decreases due to the formation of H_2O which accumulates in the process. This leads to the dilution of the whole system and hence reduces the nitrating power of the complete system.

The inefficiency can be reduced and the loss can be minimised if water formed in the reaction is continuously removed azeotropically. The advantages are as follows-

- Avoiding the dilution of the system.
- Using almost the whole amount of HNO_3 without any loss.
- Process is made economic.
- Temperature can be rigidly controlled if the azeotrope boils near or at the temperature of the process.

While nitrating with HNO_3 with azeotropic distillation, azeotrope is added slowly or if the substrate itself can form an azeotropic system with H_2O, it should be used in large volume or added slowly so that sufficient amount of substrate always present in the reactor.

In case, the substrate can not azeotrope the H_2O formed, a solvent may be used which forms the azeotrope. Again one has to search for such a solvent which remains inert in the process.

Mononitration of a substrate capable of azeotroping H_2O, if desired to polynitrate, another solvent of azeotropic capacity is a must.

Limitation of Azeotropic Distillation

1. Oxidising behaviour of HNO_3
2. Difference in temperature of nitration and that of the azeotrope boiling point is seen coinciding in few instances. E.g. Nitration of Ph-Cl. Ph-H etc. with HNO_3.

The recent patents claim the nitration by azeotropic distillation of H_2O using the heat of the reaction. Also the system can use, H_2SO_4 as a catalyst maintaining less concentration of HNO_3 in the mixed acid, i.e., without dilution of the whole nitrating system.

Post-Nitration Processes

In the post - nitration process, recovery of the products, by-products and supporting nitrating system (H_2SO_4) or the solvent involved in nitration are important aspects of making the process economic, and eco-friendly.

Several patents are made in these regards and open literature is still not widely available. The recovery process involves ;

- Complete recovery of the nitro product.
- Separation of the isomers.
- Removal of the waste gas from the system (generally carried out simultaneously).
- Recovery & recycle of supporting acid (H_2SO_2) (CH_3COOH), (CF_3COOH),
- Drying of the nitro product when required.

The nitration mixture of very low concentration can be recycled if the nitro products are first boiled off, along with the water at low pressure; the organic substrate then can be charged directly or slowly into the same pan when nitration with mixed acid can be continued by further addition of HNO_3.

In a typical process of nitration of Ph-H, isothermal nitration is carried out with mixed acid and Ph-NO_2 separated at 130 - 195°C under vacuum, concentrating H_2SO_4 sufficiently leads its usage in the next batch.

In the removal of waste gases from the nitration system, in case of gaseous oxides of nitrogen or nitrating agent pose technical problem as oxides of nitrogen are deadly poisonous. The gas thus coming out of the system must be scrubbed in dilute alkali scrubber, made up of polypropylene. The same scrubbing technique can also be applied to the mixed acid nitrating system.

Conclusion

Control of a runaway reaction is easy when the causes of runaway are determined before hand. After knowing these facts, mathematical deductions to the stability of the system are necessary to design the equipment and the controlling systems.

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