Runaway reactions. Part 2 Causes of Accidents in selected CSB case histories

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Summary

Part 1 briefly discussed the basic thermochemistry of reactive chemicals, the statistics of accidents involving runaway reactions, and general control measures to minimise risk and mitigate the consequences. The present paper highlights the main causes of major accidents from runaway reactions with illustrative case histories to link theory and practice. It also discusses lessons learned from these accidents, which are very similar in the cases studied. The main causes are management deficiencies, inadequate understanding of the process chemistry and thermochemistry, inadequate design for heat removal, inadequate control and safety systems, inadequate operational procedures, including training and human factors.

1 General causes of runaway accidents

A typical runaway scenario involves reactants being charged into a reactor at room temperature and heated with stirring until the reaction temperature is reached. Temperature is held constant to optimise cycle time and yield. On completion, the reactor is cooled and emptied. However, if no provision is made in the process to account for cooling failure at reaction temperature e.g. due to power failure or operator error (forgot to start the stirrer), etc. then unconverted material still present in the reactor may react at an uncontrollable rate proportional to the amount of unreacted material. This may lead to over-pressure in the vessel and subsequent rupture by virtue of the normal reaction exotherm. Alternatively, a secondary decomposition reaction may be initiated and the heat so produced may lead to yet a further increase in temperature and eventual runaway conditions[1].

The prime causes of runaways are associated[2,3] with

- process chemistry
- inadequate design
- substandard operational procedures
- lack of training
- raw-material quality control
- temperature control
- agitation
- mischarging of reactants
- maintenance
- human factors (which may impact all of the foregoing).

2 Case Histories

Case histories illustrate the causes and consequences of accidents involving runaway reactions with lessons learned; space restrictions limit this to the following four cases with additional examples provided in reference 4.

Case 1 – Dye product manufacturing plan [5,6]

A violent explosion and fire occurred in the Morton International, Inc. dye production plant on April 8, 1998 in Paterson, New Jersey, injuring nine employees, two of whom sustained serious burns. On the day of the accident a chemical reaction was ongoing in a 40 years old, 7,500 l carbon steel reactor (2.7 m high). Workers had turned on the steam supply to the reactor, beginning what they assumed would be a routine six to eight-hour production run of a dye used to tint petroleum fuel products. But within less than half an hour, a runaway reaction started, accelerating beyond the heat removal capability of the kettle. The resulting high temperature led to a secondary decomposition reaction causing an explosion. As a consequence, the over-pressure blew the hatch of the reactor, releasing kettle contents ejecting flammable material through the roof of the building, raining down chemicals onto the surrounding community. Residents were confined to their homes, voluntarily sheltering in place for up to three hours while officials evaluated health risks.

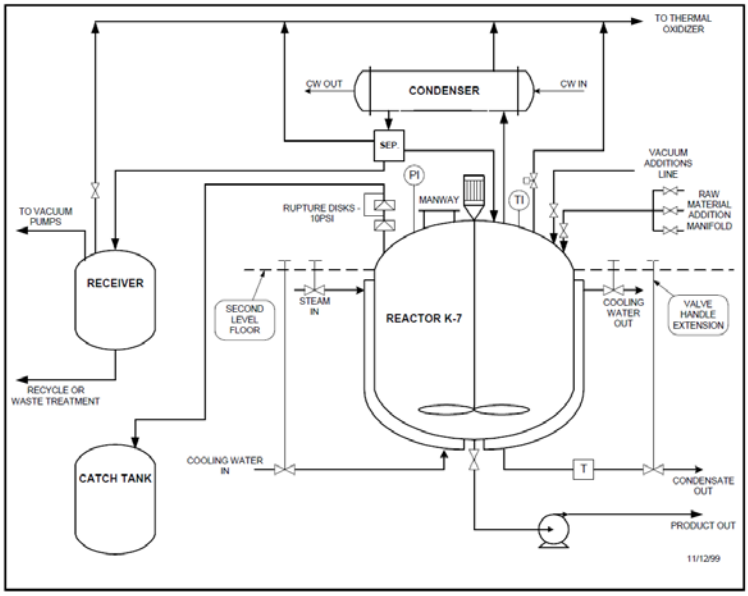

Figure 1: Simplified process diagram (Source: CSB)

Causes and findings

The initial runaway reaction was most likely caused by a combination of factors, such as

- the reaction was started at a temperature higher than normal
- the steam used to initiate the reaction was left on for too long, and
- the use of cooling water to control the reaction rate was not introduced soon enough.

Though reasons for these excursions were not given it is noted that the reactor temperature was controlled by operators manually adjusting the flow of steam and cooling-water piped to the kettle and the positioning of the valves was left to their experience. This could result in different operators adopting different settings which was particularly risky since the operating temperature of 150^{o}C was close to the runaway decomposition temperature of 195^{o}C. Kettle instrumentation measured pressure of reactor and cooling-water and temperature. The latter used a single thermocouple linked to a digital display and recorder chart; the chart could not record temperatures > 150^{o}C. The reactor was not equipped with temperature or pressure alarms, automatic shut-down facility or dump/quenching systems.

Operator batch sheets were vague on instructions to control temperature and did not address the risk or runaways nor had operators or supervisors been trained to deal with such emergency. (The Company's MSDS contained inaccuracies including listing the boiling-point for Yellow 96 Dye as 100 ^{o}C but subsequently shown to be 330^{o}C i.e. above the decomposition onset temperature of 195 ^{o}C).

Further to these, the investigation revealed that the company did not adequately evaluate or control hazards and the reactor, therefore, was not provided with sufficient cooling capacity or adequate emergency shutdown or venting systems. In 1989 the Company's research unit recommended tests to determine the rate of chemical reaction under worst conditions, determine the rate of decomposition of finished product, and establish pressure rise data to size vents. The also recommended control and safety devices such as shut down system. None of these were adopted by the production facility.

Additionally, management had previously introduced changes to the process (to full batch production from the more inherently-safe semi batch process) and scaled-up without following management-of-change procedures. Several previous problems with control of temperature had gone unresolved. The rupture disks were too small to safely vent high pressure in the kettle in the event of either of the two foreseeable runaway reactions. The operator did not provide personnel with adequate training on how to respond to avoid injury if a runaway reaction could not be controlled.

Lessons learned

Safe operations and control measures for reactive processes need particular attention in the design phase. Each individual reactive process requires its own hazard identification to determine an appropriate prevention and mitigation system influencing both process design and equipment decisions. These choices depend on numerous factors, including process parameters and inputs, adjacent and connecting processes and equipment, the volume of potential releases and impacts, as well as potential human and environmental exposure. In this particular case, despite research findings back in 1989, the reactor was not provided with sufficient cooling capacity or adequate emergency shutdown or venting systems.

Reactive processes can be highly sensitive to even the smallest changes in process design, operations, maintenance, and equipment. For this reason, any potential change to the process should be evaluated as a candidate for the MoC procedure. If there are any doubts raised about the safety risks involved, a full MoC procedure should be implemented.
This accident also violated several safety management system norms, in particular:

- Ensuring that the process hazard analysis is fully documented with appropriate training before operation start-up;
- Ensuring full documentation and training of all relevant personnel on operational procedures and operating parameters, including how to respond to deviations and emergency situations;
- Systematic investigation and analysis of near misses, and unsafe process deviations and follow-up (implementation, documentation and communication to all involved staff of any resulting recommendations).

Awareness of the state of art of knowledge in chemical reactivity can also help to prevent accidents. Good practice guidelines such as the Lees' Loss Prevention in the Process Industries or those published by the Centre for Chemical Process Safety were available in connection with reactive chemical processes. However, the company's process safety management program did not require adherence to those publications.

Case 2 - Polymerisation batch reactor[7]

In January 2006 the production department began preparing a 6,080 pound acrylic polymer batch the day before the incident, using approximately 12 % more material than would normally be made in a single batch as it was ordered by the company. Plant managers scaled up the recipe and added all of the monomers required. The plant superintendent determined the quantities of solvent, monomer, and initiator needed for the batch. The day shift operators then blended the solvents and used some of the blend to prepare the initiator solution. They added the balance to the 1,500 gallon reactor. The second shift operators, in accordance with written instructions, added some of the monomer to the reactor and held back the remainder for use later in the reaction sequence but unfortunately nearly all of the additional monomer for the larger batch had been included in the initial charge. The day shift arrived on the morning of January 31 and added steam to the reactor jacket to heat the reactor to the temperature specified on the batch sheet, then shut off the steam. The senior operator took the final step to start the reaction by pumping initiator solution into the reactor. Presumably because of poor instrumentation he then visually checked the flow of solvent through the condenser sight glass and use judgement to monitor the rate of reaction. While the reaction initially did not proceed as vigorously as he expected, the rate of flow of condensed solvent later increased and appeared to be in the normal range. Several minutes later, the senior operator heard a loud hissing and saw vapour venting from the reactor manway. The irritating vapour forced him out of the building. Three other employees were also forced from the building by the release. The senior operator re-entered the building wearing a respirator, and was able to start emergency cooling water flow to the reactor jacket. However, the building exploded less than 30 seconds after he exited. The increase in the batch size increased the quantity of monomer in the reactor at the point of initiation by 45%; and the concentration of monomer by 27%. These factors together increased the maximum heat output by at least 2.3 times the normal amount. Unknown to the site management at the time, the condenser was significantly fouled on the cooling water side. There was no evidence that the condenser had ever been inspected or cleaned of sediment, scale and rust in its 30 years of service.

Figure 2: Synthron facility after the explosion (CSB report[6])

Causes and findings

The main causes relate to Company failings

- lack of knowledge/hazard recognition including that used in scale-up from laboratory to production and between production batches)
- poor documentation
- poor practices (e.g. manway bolting procedures entailed securing the manway using only 4 of the 18 clamps, thereby allowing solvent vapour to escape well below reactor's maximum allowable working pressure)
- lack of staff training
- lack of preventative maintenance
- inadequate plant design/safety features including automatic safeguards
- flawed emergency plan
- inadequate corporate oversight.

Lessons learned

Lessons parallel many of those for the other reported case histories including the need for experienced staff at all levels (the majority of staff had been in the job for much less than a year). Patterson[8] highlights the main lesson as the need to manage change to both staff and process; crossing a shift boundary is a known risk factor (e.g., Piper Alpha). Safe operations and control measures for reactive processes need particular attention in the design phase. Each individual reactive process requires its own hazard identification to determine an appropriate prevention and mitigation system influencing both process design and equipment decisions. These choices depend on numerous factors, including process parameters and inputs, adjacent and connecting processes and equipment, the volume of potential releases and impacts, as well as potential human and environmental exposure. In this particular case, the reactor was not provided with automatic safeguards that could prevent or mitigate the effects of loss of control over the reaction. The investigation revealed that another critical aspect, the corporate oversight of process safety seemed inadequate; management should have a clear understanding of the process and they should detect hazards of a scale-up and understand the thermodynamics to avoid accidents. Reactive processes rely on strict process control to avoid accidents. A successful scale-up can be achieved if the different characteristics of the process, such as reaction kinetics, thermal dynamics and mixing characteristics of the reactor are understood[9]. As such, all necessary measures should be in place to minimize deviation from the "recipe" and its operating parameters, including temperature, pressure, sequence of procedures, input volumes, input concentration, and other parameters as may be important to the process. For this reason, it is essential to provide an appropriate level of training on all procedures and equipment prior to staff assigned to reactive process units. Redundancy measures, such as control room display and overrides of critical parameters, can also be considered as additional layers of protection.

Case 3 - Plastic production plant[10]

The BP Amoco Polymers plant in Augusta, Georgia produced plastics, including *Amodel*, a hard but mouldable high-performance nylon. The process entailed passing a solution of di-amines and di-carboxylic acids through a series of reactors. The reaction was completed in an extruder to give material of required molecular weight and then pelletised, cooled and stored. A polymer catch tank received partially reacted waste *Amodel* diverted from a chemical reactor during periods of start-up and shutdown.

On March 13, 2001, an attempt was made to start the production unit. After approximately 1 hour, the start-up was aborted due to problems with the extruder downstream of the reactor but not before an unusually-large amount of partially-reacted material had been sent to the polymer catch tank. Hot molten plastic inside the polymer catch tank continued to react and also began to slowly decompose, thereby generating gases and causing the contents to foam. The material expanded as foaming continued, and eventually the entire tank was filled. The material then forced its way into connecting pipes, including the normal and emergency vents. Once in the pipes, the plastic solidified as it cooled. A hardened layer of plastic 3 to 5 inches thick also formed around the entire inner wall of the tank but the core of the plastic mass remained hot and molten, and likely continued to decompose over several hours, generating gases that pressurized the vessel. More than the normal amount of hot plastic entered the polymer catch tank during the aborted start-up and the tank was filled beyond its working capacity. Twelve hours after the initial attempt to start the production unit 3 operators began to open the catch tank, unaware it was pressurized. They were killed when the partially unbolted cover blew off the vessel, expelling hot plastic. The force of the release caused some nearby piping to break and hot fluid ignited, resulting in a fire.

Causes and findings

- Amoco did not adequately review the conceptual process design to identify chemical reaction hazards and there was no systematic procedure specifically for identifying and controlling hazards from unintended or uncontrolled chemical reactions.
- Design documentation did not adequately describe the *Amodel* process which led to misunderstandings. The maximum fill level was not clearly specified. It seems that no warnings were provided about the consequences of overfilling.
- Several problems in design of the polymer catch tank became apparent with operating experience but operations management did not ensure that deficiencies were corrected in a timely manner:
    - Workers were unable to follow established company policies for lockout/tagout and equipment opening because the plugged drains on the polymer catch tank prevented them from verifying the absence of pressure in the tank.
    - Previous occurrences of overfilling and plastic entrainment into connected piping indicated that the polymer catch tank was too small to handle foreseeable process upsets.
    - The level indicating device for the polymer catch tank was unreliable, prone to false indications and often broke when waste plastic was removed.
    - Spring-operated pressure relief valves on the polymer catch tank and the reactor knockout pot were intended to protect the vessels from overpressure. But neither relief valve was shielded from the process fluid by a rupture disk upstream of the inlet.
    - Equipment opening procedures did not specify what actions to take when safety precautions could not be met.
- The Augusta site system for investigating accidents and near misses did not adequately identify causes or related hazards. For example:
    - Sound technical theories were not developed to explain the spontaneous ignition of waste plastic or the phenomenon whereby lumps of waste plastic burst.
    - Accidents and near misses tended to be treated as isolated events. Management did not have a review system to detect trends and patterns.
    - The polymer catch tank had been overfilled and the vent lines plugged on other occasions. Apparently, no effective measures were developed to prevent recurrence.
    - Fires occurred at the extruder on numerous occasions but no effective countermeasures were developed.
- Operations management did not update the documentation to reflect changes in procedures and practices.

Lessons learned

Credible scenarios should be identified to have understanding about the polymer catch tank could become overfilled. Establishing management systems are essential for avoiding human error and preventing technical failure leading to runaway accidents. Responsibilities include establishing the hazards and risks, training, documentation, plant design, maintenance, reviewing near misses and past accidents (to identify cause, examine trends, and rectify short comings). Reactive processes can be highly sensitive to even the smallest changes in process design, operations, maintenance, and equipment. For this reason, any potential change to the process should be evaluated as a candidate for the MoC procedure. If there are any doubts raised about the safety risks involved, a full MoC procedure should be implemented. Awareness of the state of art of knowledge in chemical reactivity can also help to prevent accidents.

Case 4 – Decomposition in a distillation column[11]

First Chemical Corp (FCC), a major producer of aniline and nitrotoluene intermediates and derivatives used in a variety of industries, was located in Pascagoula, Mississippi with several other chemical plants in close proximity. Mononitrotoluene (MNT) is produced by reacting toluene with nitrating acid. The resulting MNT, residual acid, toluene, and water—is sent to a separator, where the spent acid is concentrated and recycled. The rest of the is washed and then sent to a toluene stripper to remove residual toluene. The resultant purified MNT liquid flows to a three-column distillation unit to separate ortho-, meta-, and para-MNT. The first column (C-501) and associated equipment is shown in Figure 3. The column operates under vacuum at bottom temperature ca 177°C. The accident occurred in the plant's continuous MNT production process.

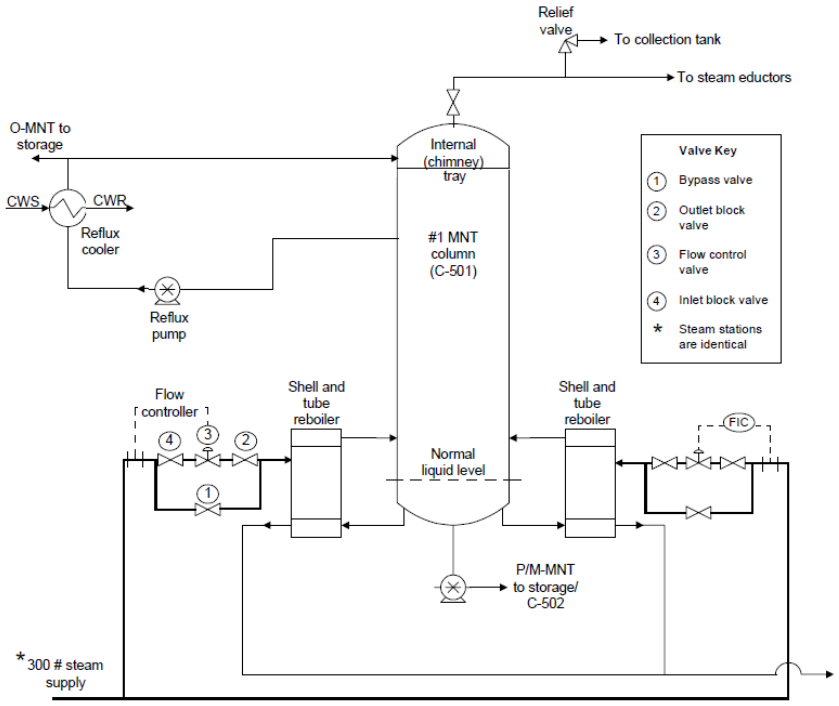

Figure 3: MNT distillation column (C-501) and related equipment

In September 2002 the plant was shut down following a series of incidents including a fire in a hydrogen unit and loss of vacuum in the distillation unit (which contained 1,200 gallons MNT). On 5 October the plant boilers were brought back online and between 5–13 October the temperature steadily increased at column bottom reaching ca 232°C. Vaporising material was carried up the column and accumulated on the chimney tray at the top. On the morning of October 12 this resulted in a high-level alarm for the tray actuating; it was silenced by the operator, but no further action was taken. Early on 13 October rumbling was heard which was followed by an increasingly loud sound described as being similar to a relief valve venting. Operators noticed material venting at a high velocity from an apparent horizontal breach in the upper half of the column. The column ruptured and the force of the explosion knocked down the three operators who were standing just inside the control room door; they received cuts and abrasions from shattering glass. The explosion propelled the top 35 feet of C-501—both the vessel head and approximately 30 feet of the cylindrical shell—offsite. A large column sidewall fragment hit a storage tank approximately 500 feet away, resulting in a fire in and around the vessel containing large quantities of para-MNT. The cooling tower for the unit was also struck by debris and caught fire. The pressure of the explosion damaged a number of buildings onsite, including the control room.

Causes and findings

During the several days of shut down the column bottoms had been inadvertently exposed to steam from leaking valves. Nitrotoluenes are known to decompose instantly when exposed to high temperatures and if exposed to elevated temperatures for extended periods, generating gases which could cause pressure build-up if contained. In fact, in 1996 the company performed thermal testing in a separate batch process within the same facility. The test indicated that MNT should be kept below 370°F (187 °C) to avoid decomposition. As a result, temperature limits were incorporated into operating procedures and an interlock system was installed to prevent the distillation equipment from overheating. These procedures clearly warned operations personnel not to exceed 395°F (201°C) in the still pot for more than an hour due to “production breakdown”. Since the test was done in a batch process the company did not integrate these findings nor suggested any modifications to the operating procedures in the continuous process, although the same chemical was used. The column was equipped with temperature indicators these were not fitted with alarms. The silencing of the high-level alarm by operators with no follow-up action accidentally worsen the situation and contributed to the accident. The consequences of this incident were also exacerbated by inadequate evaluation of the location and structure of the control room, and poor community notification.

Further to these causes the followings also contributed to the accident:

- Inadequate understanding of the potential hazard of thermal decomposition in continuous processing equipment.

- Insufficient instrumentation to allow monitoring and control of the process to prevent a catastrophic release (alarms, interlocks, overpressure protection).
- Lack of a system to ensure isolation of heat sources.
- Inadequate preventive maintenance, which allowed leaks in isolation valves.

Lessons learned

Proactive identification of the hazards based on literature and review of internal company batch operations. Good working practices and training would have prevented steam leakage on to column, monitoring column temperature during shutdown, investigating relevance of high-level alarm. Facilities handling dangerous substances, especially those that are prone to explode should be designed with multiple safety layers of protection. Given the fact,that the MNT left in the column when the unit was shut-down and not verifying positive isolation of the heat source made the conditions in the vessel similar to those in batch operation. In those cases, high temperature interlock should be in place.

3 Conclusions

Accidents stemming from runaway reactions are not rare and can be devastating. Underlying causes surround inadequate design, ignorance of hazards and risk, lack of emergency procedures, poor management, inadequate training and a host of human factors. For example, in all of the above cases, inadequate design of heat removal, lack of awareness of hazards or knowledge in chemical reactivity, lack of operational procedures and adequate training showed up. Also in majority of the cases emergency shutdown systems were absent, inappropriate formula was used or the scale-up was not successfully achieved and management of change procedures were lacking Some human factor issues were evident e.g. mischarging of dangerous substances, lack of control of the process parameters before start-up, operators failed to follow protocol or good working practice, and poor management.

Even though processes involving reactive chemicals are hazardous activities, they produce valuable products for industry and consumers. They can be conducted safely if good practice is adopted and the processes are undertaken by trained staff at all levels, and monitored. These two papers provide a brief overview of the subject. More detailed information is given in the references[12]. Videos and simulations on runaway reactions[13] are available from the US CSB and the UK HSE together with a training package from the IChemE[14].

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