CHEMICAL ENGINEERING TRANSACTIONS
VOL. 48, 2016
A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Eddy de Rademaeker, Peter Schmelzer

ISBN 978-88-95608-39-6; **ISSN** 2283-9216
DOI: 10.3303/CET1648061

Emergency Runaway Reaction - What Precedes? What Follows?

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Two runaway reactions occurred in BASF within the last five years, fortunately only with property damage. In one case an intermediate product decomposed during synthesis of a chelating agent. In the second case a polymerization occurred in the semi-batch production of an Epoxy Acrylate. The course of events and causes of the incidents will be presented in detail and lessons learned will be discussed.

1. Background

Runaway reactions are a well-known phenomenon in chemical industry over decades (Kletz, 2009). Nevertheless, it happens all the time with more or less material damages, injuries and fatalities (Urben, 2007). This does not only concern batch plants, but also continuous production processes.

Exothermic synthetic reactions pose safety risks, which are essential to the fact that the dynamics of heat production differ considerably from the dynamics of heat removal. Reactions can get out of control due to wrong dosing of reactants or the cooling failure by loss of cooling or mixing. As a result of the heat released the temperature in the reaction mixture increases and the reaction rate accelerates to a thermal explosion or runaway. Without sufficient pressure relief the vessel will rupture with the consequence of flying debris and potential secondary vapour cloud explosion (Mannan, 2012).

2. Incident 1: Runaway in a Tube Reactor

2.1 Description of the Process

As an intermediate product in a multistage continuous synthesis Nitrilotriacetonitrile (NTN) is formed from Ammonia, Formaldehyde and Hydrogen Cyanide according to Figure 1. The reaction takes place in aqueous sulphuric solution under overpressure and elevated temperature T ≈ 100 °C. Regarding to this material composition NTN is crystallizing below T ≈ 88 °C.

According to Figure 2 the synthesis took place in a three-stage reactor cascade consisting of two stirred reactors (R 512, R 523), two heat exchangers (W 401/W 401) and a subsequent adiabatic tube reactor (C 400) for finishing. This residence time reactor had a capacity of several m³. The NTN solution is directly transferred via the heat exchanger W 401 to the next reaction step (R 525).

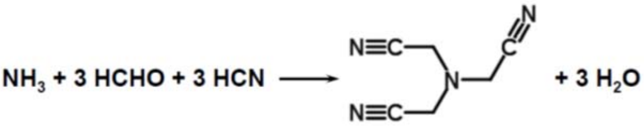

Figure 1: Formation of Nitrilotriacetonitrile

NTN decomposes in a gas forming, self-accelerating reaction above 90 °C with an exothermicity of - 600 J/g. The tube rector C 400 is safeguarded by temperature control at the inlet and outlet in SIL 3 quality triggering a reactor draining to a dump vessel (not shown in Figure 2).

Please cite this article as: Fiedler E., 2016, Emergency runaway reaction - what precedes? what follows?, Chemical Engineering Transactions, 48, 361-366 DOI:10.3303/CET1648061

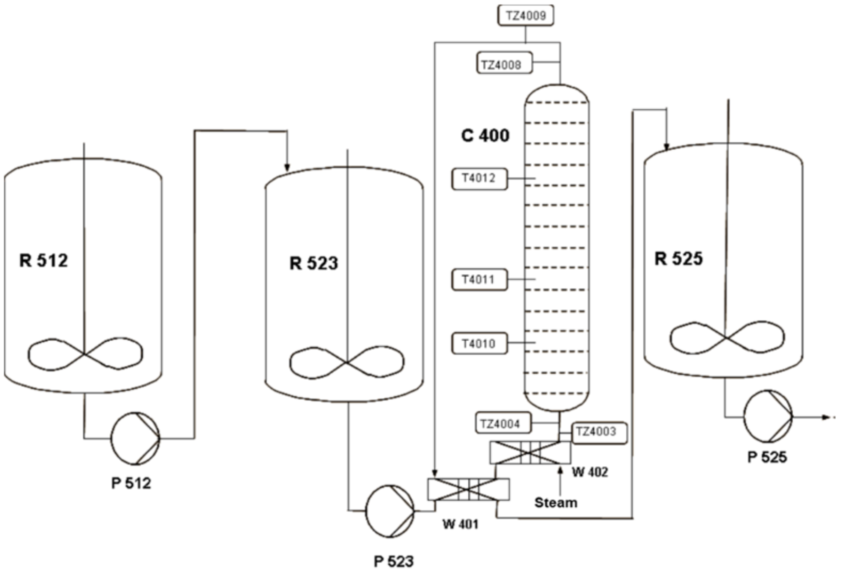

Figure 2: Reactor Cascade

2.2 Description of the Incident

The tube reactor C 400 had been flushed with water routinely and production mode started subsequently. Shortly after restart the feed to C 400 stopped and the cascade was switched to bypass the tube reactor.

Within the following 30 h several attempts to flush the reactor, which was blocked by crystallizate at several positions, failed. Over a long time operations didn't realize that the reactor was filled completely with (solid) material. As they recognized the fact the temperature at sensor T 4010 reached 140 °C.

As the manual triggered emergency dump also failed and the temperature increased rapidly the fire brigade was alarmed. They secured the surrounding of the plant and were prepared to knock down toxic gases like HCN.

A flange of a differential pressure measurement was opened using hazmat suits. In the meantime temperature reached 180 °C (Figure 3), close to a final runaway with potential bursting of the reactor.

Fortunately the reactor was drained and was brought in a safe condition within a short time.

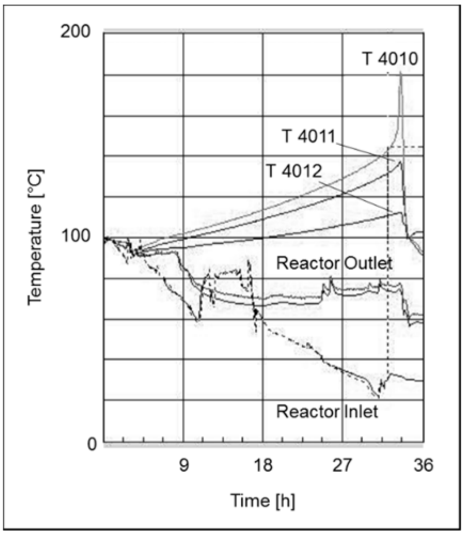

Figure 3: Temperature Profile of Tube Reactor C 400

2.3 Causes of the Incident

The reactor was blocked by crystallization (Figure 4). Due to cold feed from reactor R 512 during restart of the tube reactor C 400 the temperature in R 523 decreased below 88 °C. In combination with a higher concentration of Ammonia and Water the Nitrile precipitated contrary to operational experience. Because of massive crystallization all flushing and draining connections were plugged. All attempts for flushing failed. Misleadingly the operators presumed only a blockage in the reactor outlet and an empty reactor. Therefore the temperature high alarms in the tube reactor were interpreted as false alarms and no one informed the plant management.

Due to a confusing report at shift change the subsequent shift crew acted under the assumption that the outlet was cleaned and the reactor was in filling mode. They didn't realize that the inlet was also plugged. In a former HAZOP-study the observed scenario of reactor plugging was considered very unlikely. The HAZOP team assumed that precipitated NTN would be dissolved by heating-up in the steam heated heat exchanger W 402. Therefore only the temperature measurements at the reactor inlet (TZ 4003, TZ 4004) and the reactor outlet (TZ 4008, TZ 4009) were part of a safety instrument function to detect a starting runaway reaction.

The fire brigade had been alarmed 10 h too late for emergency support

Figure 4: Plugged Reactor Inlet C 400 (left) and Plugged Reactor Feed Line (right)

2.4 Measures

After long considerations and discussions it was finally decided to take the tube reactor C 400 out of service and to run the synthesis only with both stirred reactors. Organizational measures were improved in cooperation with the shift supervisors (especially information content of shift handover protocol). Additionally the design of the emergency dump system was modified by low dead zone connections and a drain line in the feed pipe to to now directly connected vessel R 525.

3. Incident 2: Runaway in a Semibatch Reactor

3.1 Description of the Process

A second runaway reaction occurred during a semibatch synthesis of the Laromer type Epoxy Acrylate 1,4-Butanediol-Diglycidilether-Diacrylate (BDEA), a modified resin for the production of radiation-curable coatings for paper, wood, wood-based materials, plastics and printing inks. The simplified reaction scheme is shown in Figure 5:

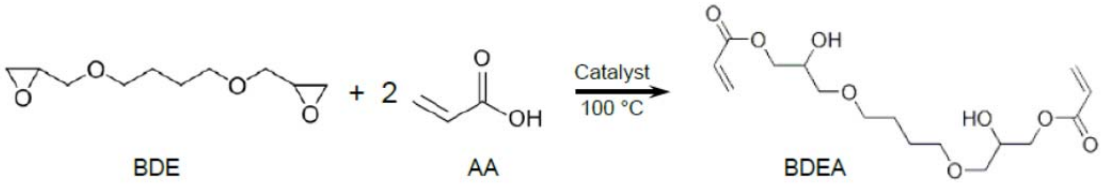

Figure 5: Formation of 1,4-Butanediol-diglycidilether-diacrylate (BDEA)

The synthesis took place in a stirred reactor by charging the vessel from the top with bifunctional 1,4-Butanediol-Diglycidilether (BDE) and heating up to 90 °C. After adding of several inhibitors, especially Hydroquinone-Monometyhlether (MEHQ), which requires the presence of small amounts of oxygen, the lean air supply to the bottom of the reactor was opened. Subsequently Acrylic Acid (AA) was fed in the in the temperature range of 95 °C - 100 °C. After dosing of 5 % AA a catalyst was added to the reaction mixture. According to the recipe the batch had to finish over several hours at 110 °C. After cooling down to 50 °C the reactor had to be discharged.

3.2 Description of the Incident

During the batch finishing phase of a trial run an uncontrolled polymerization was observed (Figure 6). Short stopping with additional MEHQ after increase of temperature and viscosity failed due to loss of lean air. After 2.5 h water was added via an meanwhile opened manhole without immediate success. The fire brigade was alerted 30 minutes later. They initiated a partial evacuation of the plant, alarmed the close proximity and ordered shelter-in-place or evacuation of several office buildings on the site. After two additional hours the BASF crisis committee for emergency response was convened. In the meantime the temperature in the reactor increased to maximum 270 °C. Fortunately 5.5 h after starting runaway the temperature in the vessel decreased to 100 °C (normal condition) and half an hour later all-clear could be given.

After the incident the upper part of the reactor was filled by polymer, the bottom part showed a liquid phase of unreacted BDE (Figure 7).

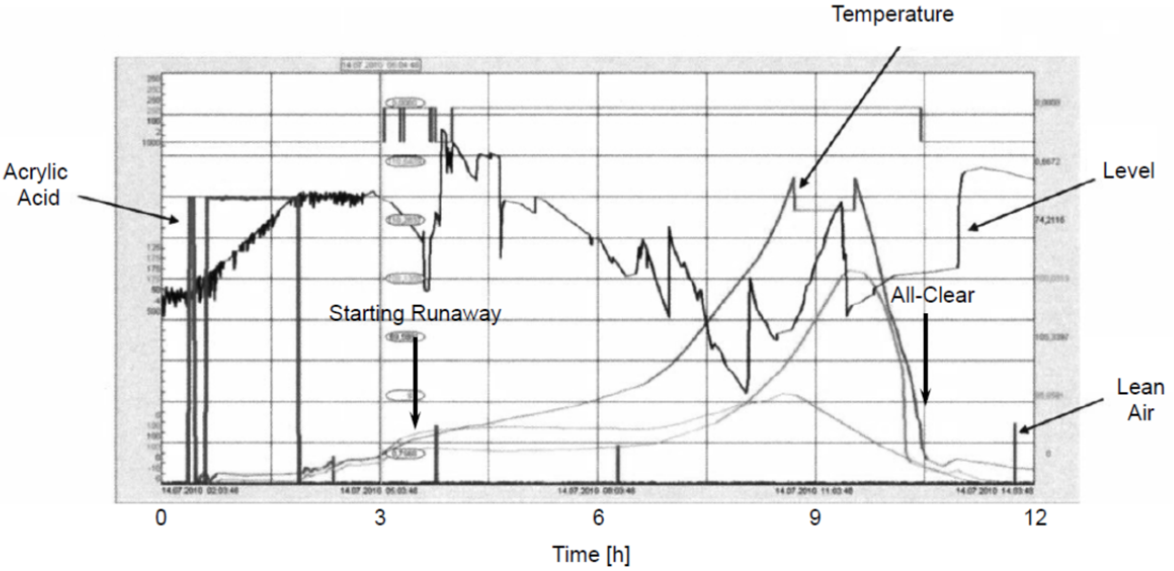

Figure 6: Temperature Profile of BDEA Synthesis in Agitated Vessel

Figure 7: View through the open manhole of the reactor after the incident, showing massive polymerization (left) Pieces of Polymer from the reactor (right)

3.3 Causes of the Incident

Due to customer request the common stabilizer Phenothiazin was substituted by MEHQ. MEHQ stabilized acrylic systems are requiring a sufficient oxygen supply by lean air to keep the stabilizer in function. In the present case the lean air supply was insufficient. Due to a blocked check valve in the line the lean air flow became low with the consequence of loss of stabilizer activity and subsequent starting polymerization of BDEA after conversion of 90 % acrylic acid. Fortunately the temperature in the reactor didn't exceed the extrapolated maximum temperature of 270 °C (Figure 6) due to evaporative cooling by the added water and depressurizing via the open manhole. Safety data of the reaction system had shown gas forming, self-accelerating decomposition above 300 °C.

Lean air supply was not safeguarded in SIL-quality as usual but only by organizational measures (checklist). In addition a flow low alarm failed because of a displaced limit value. Aggravating this situation, the process was highly manual with simultaneous low personal presence in the plant.

At the bottom of the agitator vessel mixing was insufficient. Loss of lean air enhanced this effect with the consequence of additional self-polymerization of unreacted BDE.

Short stopping with MEHQ from a separate vessel also failed due to loss of lean air. Furthermore the short stopping solution was injected too late and only on the surface of the reactor content. Due to high viscosity mixing was inadequate.

3.4 Measures

Test trials for the synthesis of BDEA were cancelled immediately, no restart of the process until yet. Charging a reactor with the whole amount of BDE, which can polymerize by itself highly exothermic, is very dangerous. Therefore the process has to be redesigned to an inherently safer approach before any restart of the synthesis.

Nevertheless the plant safety concept for handling acrylic systems in the plant concerned was revised. Under design aspects safeguarding of lean air supply was improved to SIL-quality and the short stopping concept in reactive systems was adapted to BASF requirements. Organizational measures and checklists were improved with focus on safety relevant issues and Management of Change process. Personal presence in the plant and control room was amended and knowledge transfer from R&D to production was improved according to BASF regulations.

The process safety risks of Acrylic monomers arise from the high reaction heat that is generated by polymerization. A BASF expert team was formed after the incident and consists of process technology representatives of all BASF operating divisions that handle acrylic monomers as well as representatives of global process safety. The mission of the team is to create and maintain a guideline relating to the safe handling of Acrylic monomers in processes for all BASF operating units that handle acrylic monomers. Another focus lies on collecting existing best practices in safety technology, to communicate and share these within the BASF community and where needed to further develop these techniques.

The BASF expert team has classified the process safety risk in handling of Acrylics into three categories: storage of acrylics, polymerization of Acrylics and other reactions where the acrylic double bond disappears in reaction (e.g. Michael additions) and reaction of acrylics where the double bond is maintained.

In the first working phase, based on the described incident, the main task was to gather all existing safety concept principles for reactions of acrylics where the double bond is maintained. In addition, it was decided that the storage concept had to be verified. In the second phase, the task is to maintain the knowledge and the expert network/contacts to distribute any new developments in safety concepts within the community.

In case of both described incidents the fire brigade had been alerted too late for emergency response. Therefore the information and cooperation between the affected plant and the fire brigade as well as the direct neighbourhood on the site has to be improved. Particularly helpful are regular emergency drills to train all necessary procedures including the timely and appropriate alarm of the firefighters. Furthermore it's recommended to transmit notably safety relevant process data from the DCS directly to the data network for emergency response on the site.

4. Conclusions

Chemical plants must be designed and operated so as not to endanger people or the environment. To achieve this goal in the best manner, safety and environmental aspects must be taken into account in a logical approach as early as possible, normally during process development, since errors or omissions are very time-consuming and costly to correct later.

In order to be able to prepare a balanced process concept which complies with process and occupational safety as well as environmental aspects, the hazards to humans and the environment that are associated with the process must first be identified. In the next step, the probability that the hazards identified will occur, must be assessed in a step review process, together with the extend of possible damage. Then suitable safety precautions can be specified, which in accordance with the BASF plant safety concept restrict the risks associated with the process to an acceptable level. This applies not only to primary measures within the process itself, but also to secondary measures to handle the so-called nevertheless-case.

The overarching goal for BASF is to maintain these high standards throughout the life cycle of a production facility. This is accomplished through the development and consistent performance of a comprehensive process safety management system within each production facility.

As an important element of the process safety management system BASF has launched a structured program for process safety reviews of existing plants in 2011. Evolved from a less formal program in the mid-1990s for dedicated sites the new approach focuses on broadening and globalizing the program.

A hazard assessment, i.e., the plant safety concept and associated implementation check, is required for all parts of a plant including related auxiliary and infrastructure facilities (e.g., off gas, waste water utility systems). It must be periodically reviewed to keep it up-to-date. The review may focus on changes and lessons learned (revalidation) or in case of the implementation check may be performed as full review ("clean sheet" review).

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