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Loss of Control of a Chemical Reaction and Release of Hydrogen Chloride

Jordi Bosch, Alexis Pey
[a]Swissi Instituto Suizo de Seguridad. c/Lope de Vega 30, Entlo. 08005 Barcelona, Spain
jordi.bosch@swissiesp.com

In this paper an accident caused by the loss of control of a chemical reaction is analysed. Though the loss of control did not generate an extreme temperature and pressure increase, the reaction produced Hydrogen Chloride, which was released at a high rate from the reaction mass and finally released to the atmosphere.

The aim of this study is to describe the triggering causes, to assess the consequences of the toxic dispersion and to propose the safety measures that should have been in place to prevent the accident.

The reaction of interest had been studied during its development stage and carried out in the past in another production site of the same company with no incidents.

Despite the knowledge available, the accident took place. These facts show the importance of the process design and the Management of Change (MOC) procedures.

1. Introduction

In the last decades, achievements on process safety allow to assess the triggering causes of accidents and their consequences [Stoessel, 2008], and hence to design safe processes and mitigation systems.

However, accidents on process industries still occur. Accidents evaluation in the past on batch reactors showed that basic causes are the lack of proper understanding of the process chemistry, inadequate engineering design for the heat transfer and inadequate control systems and safety back-up systems[Barton and Nolan, 1991].

In addition to these facts, management of change protocols and procedures become of high importance in the industry due to the fact that globalization pushed many companies to reorganise productive processes among their sites in a continent of even globally. This paper illustrates these facts taking the accident described as a case study.

2. The accident

2.1 Safe process design

The reaction of interest is a condensation reaction between Cyanuric Chloride and an organic amine (quoted as Reactant A because of industrial secrecy). The reaction results in the desired product and hydrogen chloride.

Since the condensation reaction is exothermic, during the development phase calorimetric tests were conducted in order to assess the thermal risk. Therefore, it was well known that at the desired process conditions the synthesis developed at high reaction rate releasing a significant amount of energy.

The main principle on the design of a safe process was to proceed with this synthesis as a dosed controlled semi-batch reaction, where the amine had to be dosed carefully over the cyanuric chloride solution prepared short before starting the dosing, keeping the temperature between 0 and 10°C by providing the necessary cooling.

The reaction had been carried out this way for a long time in another production site of the same company with no incidents.

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2.2 What was done?

On the morning of the accident, production personnel prepared the reactants and the equipment to proceed with the condensation reaction.

The final desired reaction mass was about 1200 kg, but as there were no reactors available of this size in the industrial site, the reaction was planned in a 10m^3 ebonited reactor equipped with a 6m^3 feed tank.

The feed tank was connected to the reactor through a DN50 pipe fitted with a manual ball valve.

Because of the exothermicity of the reaction and the fact that the reactor had no cooling system, the cooling had to be provided by the ice loaded initially while preparing the Cyanuric Chloride, water and ice solution and the addition of further ice through the manhole as the reaction was performed.

With this purpose, two carts loaded with ice, where ready next to the reactor manhole to be added manually during the reaction to keep reactor temperature within the established procedure margins, i.e. below 10°C.

The feed tank reactor was loaded with 464 kg of Reactant A to be dosed within 2,5 hours.

The dosage of Reactant A from the feed tank started with reactor contents at 1°C, the stirrer turned on, the reactor vent connected to two acid scrubbers and the reactor manhole open to enable the ice addition during the reaction.

Approximately two minutes after the start, a fast increase of temperature was noticed and the dosage of Reactant A was stopped. The temperature increased to 106°C in about 4 minutes causing the reaction mixture to boil.

2.3 Consequences

Already during the temperature increase and before reaching the boiling point, Hydrogen Chloride was released from the reaction mass and started to leave the reactor through reactor vent and the manhole, which was kept open with the idea of adding ice to cool down the reaction.

Due to the release of Hydrogen Chloride through the manhole and the fact that personnel present was not equipped with the necessary protective equipment to face the presence of Hydrogen Chloride, the area had to be evacuated immediately and no ice could be added to the reaction mass.

Some minutes later, with the emergency plan already activated, actions were taken to stop the reaction by adding ice through the manhole; at this point the temperature fell to 0 °C.

Despite the reactor vent was connected to an exhaust system which sucked in part of the Hydrogen Chloride generated, the capacity was not high enough to prevent the release of Hydrogen Chloride through the manhole. Besides, because of the quantity and production rate of hydrogen chloride during the accident, scrubbers could not cope with it and, as a result, part of the hydrogen chloride was released to the atmosphere producing noticeable discomfort in the surrounding area of the site.

The accident resulted in no fatalities and no significant damage to the facilities.

3. Analysis of the Accident

In this section accident records and experimental data will be assessed in order to achieve a better understanding of the causes which lead to the accident and its consequences.

3.1 Thermal fingerprint

Next graph shows the temperature records inside the reactor during the accident obtained by three temperature sensors, one located in the bottom and two in the upper part of the reactor.

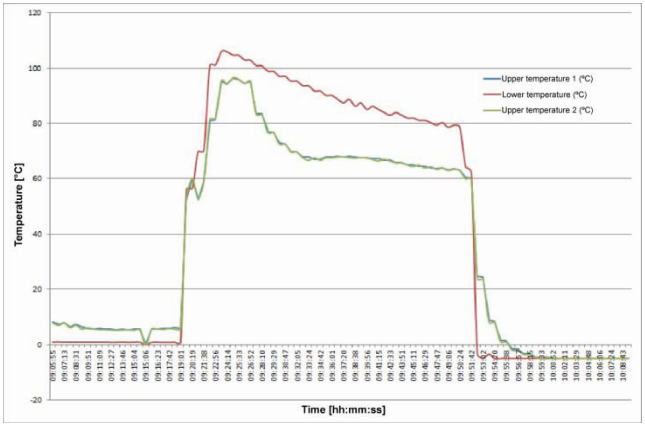

Figure 1: Accident temperature fingerprint

As it can be seen, the temperature profile from the lower temperature sensor is different from the ones placed in the upper part of the reactor. This is produced by the fact that the upper temperature sensors were not in contact with the reactor contents during the entire accident course. Because of this fact, records obtained by the temperature sensor in the lower part of the reactor are considered better for the accident analysis. The temperature evolution showed a very sharp increase at the beginning from 1 °C to 106 °C in approximately 4 minutes when maximum temperature was reached. This fast temperature increase was produced by loss of thermal control of the reaction, a runaway as it will be later shown. Afterwards, the temperature began to decrease slowly until the reactor contents reached 80°C, at this point ice was added to the reactor causing the sharp temperature decrease observed.

3.2 Chemical reactions

The calorimetric tests carried out by the company during the development stage of the process allowed to characterise the properties of the reaction in terms of exothermal potential and reaction rate. Next table shows the most relevant characteristics of the reaction in terms of heat release:

Table 1: Heat potential of the intended reaction

Variable	Units	Value	Reference	Comments
T_p	[°C]	1	Process	Process temperature at the beginning of the dosing
ΔH_r	[kJ/mol]	-192	Calculation	Heat of reaction from calorimetric test results
Q_r	[kJ/kg_{RM}]	-495	Calculation	Heat of reaction considering process concentration
C_p	[kJ/(kg•K)]	4	Calculation	
$\Delta T_{ad,r}$	[°C]	125	Calculation	With 100 % accumulation
MTSR	[°C]	126	Calculation	With 100 % accumulation

As can be seen the MTSR with 100% accumulation is above the observed peak temperature, meaning that the desired reaction has enough heat release potential to generate the observed temperature evolution.

On the other hand, Cyanuric Chloride is unstable in presence of water because of its hydrolysis which leads to the generation of hydrogen chloride as product of this hydrolysis [Urben, 2000]. This fact was already known and a matter of concern by the company. For this reason a safety corporate guideline was edited many years before the accident to clearly describe this risk and the measures to take into account while handling processes where cyanuric chloride was present. One of the measures was to have ice ready to be added to the reactor in case of emergency. The corporate guideline shows that the heat production of the cyanuric Chloride hydrolysis clearly above 2000 kJ/kg of Cyanuric Chloride. Furthermore, it was known that starting at 40°C the time to the maximum rate under adiabatic conditions, $MTSR_{AD}$, of a water and cyanuric chloride in relation 3:1 was 110 minutes. The hydrolysis of cyanuric chloride is fast above 50°C. Finally, it must be taken into account that hydrolysis of cyanuric chloride develops faster in acid media, therefore, the generation of hydrogen chloride by the desired reaction and the cyanuric chloride hydrolysis reaction accelerates the reaction rate of the latter reaction.

Taken into account the last mentioned facts, if the reactant A dosage is controlled and reactor contents are kept below 10 °C, the process under study may be categorized as class 2 by the thermal risk classification scale described by Stoessel (1993) shown in next figure. However if reaction is carried out bachwise, the same process should be categorized as class 5, i.e. the worst case. Nevertheless, the hydrolysis reaction may be triggered by the desired reaction if thermal control is lost, and the boiling of the reacting mass can not be considered as a safety barrier against the secondary reaction since it is triggered at a lower temperature.

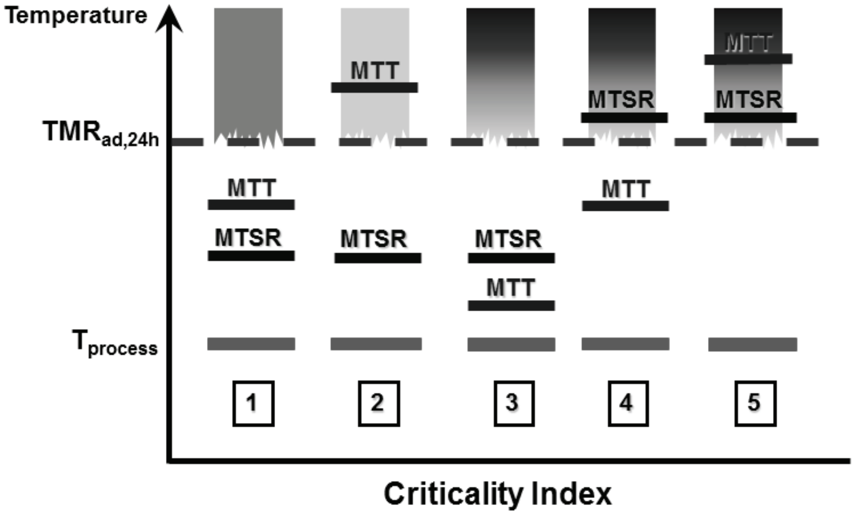

Figure 2: Stoessel scale for thermal risk assessment of discontinuous chemical processes

3.3 Equipment and control system

The reaction was carried out in a 10 cubic meter ebonited reactor with no cooling system despite it was known that the conducted reaction was exothermic and the company safety concerns on the handling of Cyanuric Chloride. Reactor was fitted with temperature and pressure sensors whose signals where available on field. Reaction control was intended to be through the reactor temperature and the dosing flow. To cool the reactor contents, ice was manually added through the reactor manhole according to the temperature measurements. Reactant A dosage was manually controlled by the operator on a ball valve attending to the reactor temperature and the operator knowledge since there was no flow or volume measurement available. Besides, the selected reactor was clearly oversized for the quantities involved, the total reacting mass was approximately 1400 kg which results in a filling grade lower than the 15%. Consequently, the existing pipe among the reactor and the feed tank had been designed to deal with large volumes according to the reactor volume. Considering the pipe flow capacity from its diameter, Reactant A might have been dosed in less than six minutes if the valve was completely open. This time is clearly below the 150 minutes of dosing time of reactant A

3.4 Management of Change

The reaction under study had been conducted in another site of the company with no incidents. When production was moved to the new site, production procedure was adapted to new site capabilities but with no significant changes of the reactants involved.

As in the accident reactor, an ebonited reactor was used in the former site. However the reactor had a pneumatic system to introduce ice inside the reactor controlled by the reactor temperature. This system is noticeably better than the manual ice addition used in the accident scenario regarding the temperature control. Additionally, Reactant A was not dosed from a feed tank but from an Intermediate Bulk Container (IBC) through the reactor manhole. Again there was no flow or volume measurement, but operator could visually estimate the added volume from the IBC and the dosage flow was constricted by the IBC valve which is more in accordance to the manipulated quantities than the feed tank valve of the accident reactor, a DN50 pipe.

To summarize, the change of site resulted in a worst control of the temperature and dosage of reactant which has been proved to be critical for thermal control of the reaction under study. This facts resulted in an evident poor Management of Change where the key measures to control reaction where lost when production was moved from site.

3.5 Accident analysis

Inspection after the accident shown that the 37 % of Reactant A which should be dosed in 2,5 hours had been dosed in approximately 2 min. Furthermore, since the heat required to cool the reactor contents from ambient temperature to 1 °C is analogous to the cooling effect of the ice initially loaded into the reactor, initial ice was already melted into water when reaction started and hence no reaction heat was removed with ice. Consequently, thermal control of the reaction was lost due to the fast addition of Reactant A into the reactor and the lack of cooling capacity which triggered the hydrolysis of Cyanuric Chloride.

Additionally, the secondary reaction was enhanced by temperature and hydrogen chloride evolved from the desired reaction.

Regarding the atmospheric release of hydrogen chloride, the accident survey showed that scrubbers solution had been depleted during the accident. Moreover, the survey showed that the scrubbers maintenance was poor and not systematic in the site. This fact resulted in a greater hydrogen chloride release due to the reduced absorption capacity of scrubbers as it will be later shown in consequences analysis.

3.6 Consequences analysis

As a result of the accident, a large temperature increase was observed in the reactor which resulted in the reactor contents boiling. However, the main consequence of the accident was the release of hydrogen chloride outside the reactor which produced notable discomfort and irritation to people exposed to the release outside the production site.

Analysis carried on the reactor contents after the accident combined with the mass balance of the products involved indicate that over 40 kg of hydrogen chloride were released from the reactor during the accident.

Hydrogen chloride could escape from the reactor in three different ways:

- Trough the reactor manhole that was open to the production building where it was confined and later treated.
- Trough the reactor vent and neutralized by scrubbers afterwards.
- Trough the reactor vent to the scrubbers which could not neutralize it and thus was released to the atmosphere.

Consequently, observed effects outside the site are related to the hydrogen chloride that was not neutralised by scrubbers.

Analysis on the scrubbers solution show that it was depleted during the accident. However as the situation of the scrubbers solution before the accident is unknown, one can not estimate the quantity of hydrogen chloride neutralized by scrubbers. Dispersion modelling calculations have been carried out to determine the amount of hydrogen chloride required for the observed effects considering the following points:

- Atmospheric conditions on the day of the accident.
- Release point position: Scrubber height.
- Gas concentration: AEGL 1 of hydrogen chloride as observed effects outside the site correspond to those related to AEGL1, notable discomfort and irritation.
- Release period: From temperature evolution of reactor contents it is assumed that main gas release took place for a period of 5 minutes.
- Distance where hydrogen chloride release was noticed outside the site.

Calculations concluded that the about 10 kg of hydrogen chloride were released to the atmosphere, and hence about 75% of the release remained confined inside the production building or was neutralized by scrubbers.

Considering the hydrogen chloride released inside the building no significant and the scrubbers design characteristics results that the scrubbers operated below the 50 % of the design capacity. However, as part of the hydrogen chloride was released inside the production building, the scrubbers operated to an even lower capacity. This fact was result of the poor maintenance of the scrubbers noticed during the accident survey.

3.7 Safety proposals

Causes analysis has shown that the chemical process under study has sufficient thermal potential to trigger a secondary reaction if temperature or reactant dosing are not controlled properly. To improve the process, the thermal potential should be reduced -for instance by diluting reactant A with water- to reduce the reaction heat and increase the heat capacity of the reaction mass, and dosing rate should be constrained to a maximum flow in accordance with the cooling capacity of the reactor which could be accomplish by using dosing pump or a constriction plate. Moreover, as hydrolysis of Cyanuric Chloride is enhanced in acid media, dosing should be interlocked to pH and it should be assessed to conduct the reaction at a higher pH.

On the other hand, consequences analysis has shown that poor maintenance of emergency equipment leads to lower operation capacity and hence to greater consequences. Therefore, maintenance of emergency equipment should be rigorous and systematic. In addition, when introducing new processes, it should be verified that emergency equipment capacity is in accordance to the foreseen effects of known accidental scenarios.

4. Conclusions

In this work the analysis of causes and consequences of an accidental release of hydrogen chloride was presented. The accident causes analysis point out the importance of process design to lead to inherent safe processes and the management of change to ensure that process modifications do not reduce the process safety or results in new hazards.

On the other hand, consequence analysis shows the importance not only of the design of emergency devices but also of their maintenance to ensure their operability when required.

Safety proposals are made taking into account identified causes of the accident, and also its consequences.

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