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Escalation Scenarios Triggered by Thermal Explosions in Batch and Semi-Batch Reactors

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In the present paper, a methodology for the determination of inherent safety distances for escalation and layout optimization has been introduced. A survey of past domino accidents triggered by thermal explosions have been carried out and analysed with the aim of a deeper understanding of the possible primary scenarios and related escalation vectors.

1. Introduction

Runaway reactions (or thermal explosions) are the result of the loss of thermal control in a reactor undergoing an exothermic process. They are characterized by extremely high rates of temperature increase (hundred degrees per minute) that might lead to the formation of gaseous reaction products and/or vapours deriving from the boiling of the reactor contents, as experimentally demonstrated in several recent papers (e.g. O. Reyes Valdes et al. 2015; O. J. Reyes Valdes et al. 2015). This is particularly true for the case of batch and semi-batch reactors, in which heat accumulation is more likely to occur (Copelli et al. 2013, Casson Moreno et al. 2015).

The main consequence of runaway reactions is the pressurization of the reactor. If the emergency relief system and more in general preventative and mitigation barriers are not properly designed, the internal pressure may become higher than the failure pressure and the equipment explodes. Thus, a runaway reaction can trigger a domino scenario: the loss of containment of the reactor (solid, liquid, or biphasic) can occur along with the formation of fragments and shock waves, which in turn may constitute the escalation vectors for the domino effects (Cozzani et al., 2007; 2009), according to the definition proposed by Reniers and Cozzani (2013): "an accident in which a primary unwanted event propagates within an equipment ("temporally"), or/and to nearby equipment ("spatially"), sequentially or simultaneously, triggering one or more secondary unwanted evets, resulting in overall consequences more severe than those of the primary event".

Figure 1 shows the possible paths in which thermal explosions can trigger a domino accident by generating escalation vectors. In the plot, the escalation vectors are signed in red colour, with the exception of flash fire and release of toxic substance, which are not intended to be able to escalate (Cozzani et al., 2013; Reniers and Cozzani, 2013).

Starting from this generalisation, the present study addresses the need for the assessment of the expected intensity of escalation vectors generated by thermal explosion. To this aim, a survey of domino accident triggered by runaway reaction is presented. Accidents have been analysed in terms of causes, scenarios, type of industry and reaction involved, and final consequences in terms of human losses. Some literature case histories of runaway reactions characterized by domino effects are also presented.

2. Approach to the assessment of domino effects triggered by thermal explosions

Due to the complexity of domino scenarios, there is not a unique approach to their assessment, especially for what concern the definition of threshold values for damage and escalation distances (Alileche et al. 2015). Still the approach based on threshold values is very useful to identify secondary scenarios as it allows defining the minimum intensity of the primary scenario necessary to have escalation.

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For the quantification of the physical effect of the escalation vectors, there are many models relating the intensity of the escalation vector and the structural characteristic of the target to the potential damage to equipment available in literature (the equipment vulnerability models, Reniers and Cozzani, 2013). Below a description of those of interest for the case of domino scenarios caused by thermal explosions and reported in Figure 1.

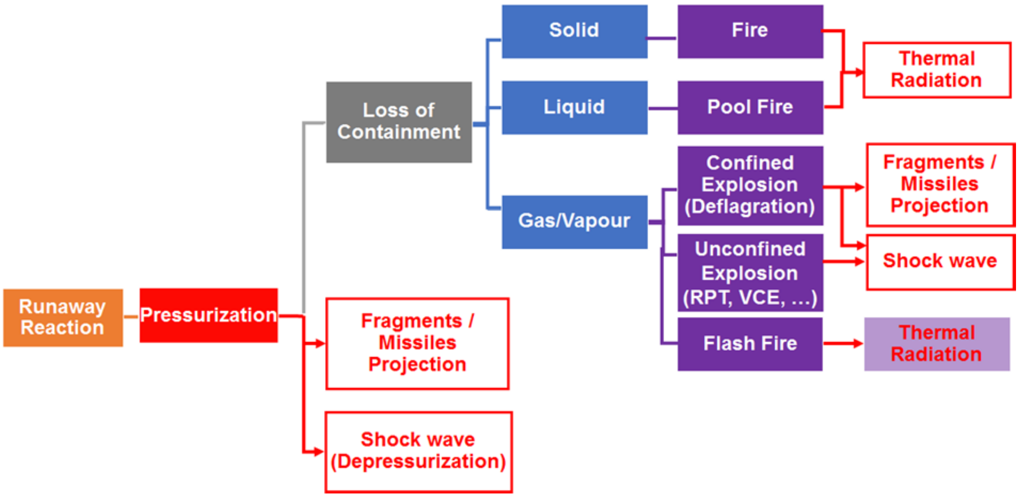

Figure 1: The path of domino effect triggered by runaway reaction (or thermal explosions) in batch and semi-batch reactors. Escalation vectors are signed in red.

2.1 Explosion related shock waves

The intensity of shock wave produced by explosion is related to the amount of energy that can be released during the accident. The determination of the amount of energy requires the knowledge of the type and quantity of substances and the details on the reaction taking place in the reactor at the moment of the thermal explosion. Based on this data, the calculation of the energy can be solved either by experimental approach (e.g. adiabatic calorimetry) or via theoretical calculations of thermochemical properties and reactive chemical hazards.

In the case of shock waves, the fundamentally correct approach for the calculation of the effect (both static and dynamic) would involve the application of finite elements methods, which requires a very detailed knowledge of the explosion scenario. On the other hand, the approach based on threshold values allows overcoming these difficulties and can largely simplified the analysis. Besides, Probit models are able to relate the main intensity parameter of the explosion (the overpressure) to the probability of damage for different categories of equipment (Cozzani and Salzano, 2004a, 2004b; Salzano and Cozzani, 2005), thus allowing the estimation of safety distances (according to Cozzani et al., 2007).

2.2 Explosion related fragments/missiles projection

For what concerns fragments/missiles formation, most of literature available is focused on the probability of impact of the fragment on target, rather than the target damage itself (Alileche et al. 2015). In the last case, the knowledge of the mass, shape and velocity of the fragments is required. Some important related considerations are that industrial explosions are usually characterised by fragments with moderate velocity (up to 500 m/s) and with non-perforating shape (Salzano and Basco, 2015), and that thermal explosions are characterised by very different pressurization rates. Because of this, the number of fragments and missiles formed, which is related to the fracture mechanism of the material, can be high in the case of brittle fracture of the material, or low when associated to ductile fracture (Reniers and Cozzani, 2013).

Recently Salzano and Basco (2015) proposed a simplified method to evaluate the effect of both shock waves and fragment projection based on fundamentals equations that will be tested to the case of thermal explosions. In this case, the calculation of the safety distances can be done according to Gubbinelli et al. (2004).

2.3 Thermal radiation

In order to determine the likelihood of the escalation, the time to failure (the time lapse between the start of the fire and the failure of the target equipment, Reniers and Cozzani, 2013) has to be predicted. This depends on the time exposure to fire, so to the duration of the fire itself, which is determined by the mass of flammable substance available to burn. The fire load interact with the target equipment by lowering its mechanical resistance, creating a local thermal stress, melting plastic components and increasing the internal pressure. The modelling of thermal radiation as an escalation vector is very complicate; in literature semi-empirical correlations, simplified criteria, distributed or lumped parameter models are available for the determination of time to failure (Reniers and Cozzani, 2013). Again, in order to save computational time and the need for data, simplified approaches based on Probit functions for the assessment of damage probability of vessels under fire load (Landucci et al., 2009). In this last case, the safety distances can be evaluated based on the work of Cozzani et al. (2007).

2.4 Survey of domino accidents triggered by thermal explosions

The first step of this study was the collection of data on past accidents in which a domino effect was triggered by a runaway reaction. Several studies in literature analysed on the past accidents involving domino scenarios (Abdolhamidzadeh et al., 2012, 2011; Clini et al., 2010; Hemmatian et al., 2014; Kourniotis et al., 2000; Ronza et al., 2003) but none of them focuses on thermal explosions as a cause. It is worth noting that Clini et al. (2010) studied domino accidents involving hazardous materials and runaway reactions were found to be responsible for the 3.5 % of the accident of their analysis, whereas Hemmatian et al. (2014) identified that thermal explosions caused the 8.5 % of the domino accidents happened in the last 50 years.

In general, the analysis of past accident is the only available experimental data on domino effects, even if retrieving detailed information from the analysis of past accidents is intrinsically difficult, due to a general lack in the reporting systems, as also confirmed also by the present survey.

The survey was carried out by consulting the ARIA Database (French Ministry of Ecology, 2015), the Loss Prevention Bulletin (IChemE, 2015), the JST Failure Knowledge Database (Hatamura Institute for the Advancement of Technology, 2015), the eMARS databse (Joint Research Center, 2015) and the CBS website (U.S. Chemical Safety Board, 2015). In addition, a web research was performed by coupling the words “runaway” and “domino”.

A total of 20 accidents entries were collected and analysed. The time span cover by the accidents is of 30 years, from 1982 to 2012; 10 events happened in Europe (50 %), 7 (35 %) in the U.S. and 3 (15 %) in Asia. As shown in Figure 2, the trend of domino accidents triggered by thermal explosions is slightly linearly increasing. The most interesting case study has been summarised in section 4 of the present paper.

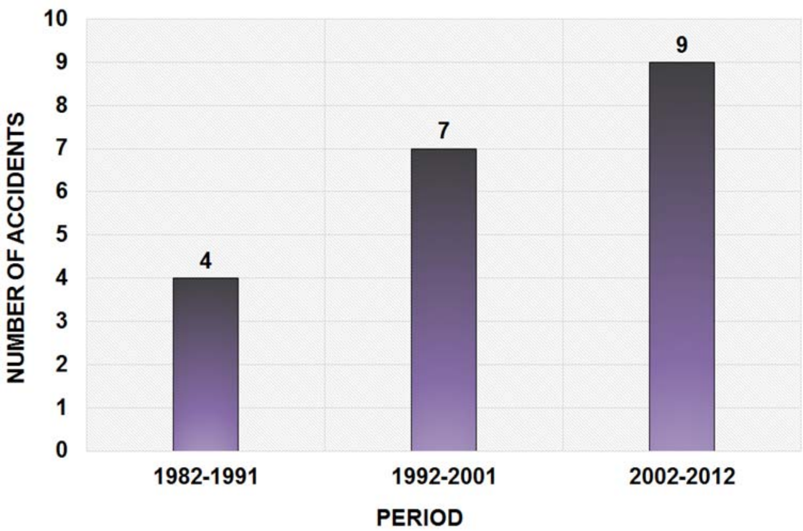

Figure 2: Triennial trend of domino accidents triggered by thermal explosions.

Investigating the primary causes of accidents (Figure 3-a), design error was found to be the most likely to occur, followed by equipment (i.e. cooling system) failure and operational error (principally dosing errors).

For what concerns scenarios (Figure 3-b), three main categories have been identified:

1. explosion + fire (55 % of the cases);
2. explosion + fragments (25 % of the cases);
3. explosion + fragments + fire (20 % of the cases).

For the accidents here analysed, type 1 and 2 can be classified as simple propagation effect, in which a single primary scenario trigger a single secondary scenario. Type 3 is an example of multilevel propagation leading to two different domino chains. According to the categorization proposed by Reniers (2010), all the domino events in our analysis are internal, i.e. they completely evolved inside the same chemical plant.
Statistics about the type of activity and of the reaction involved in these domino accidents are summarized in Figure 4. In most cases, the accidents occurred in polymerisation and decomposition processes. Saada et al. (2015) have recently confirmed this same aspect of thermal explosions. It has to be noted that 19 out of 20 accidents happened during process or storage, just one during transportation of hazardous materials.
Several authors (Kourniotis et at. in 2000, Clini et al. in 2010, Abdolhamizdeh et al. In 2011 and 2012) have demonstrated that accidents involving domino scenarios are characterized by higher consequences in terms of human losses with respect to conventional scenarios. Associated to the 20 accidents in our analysis, 338 injuries and 28 fatalities happened.

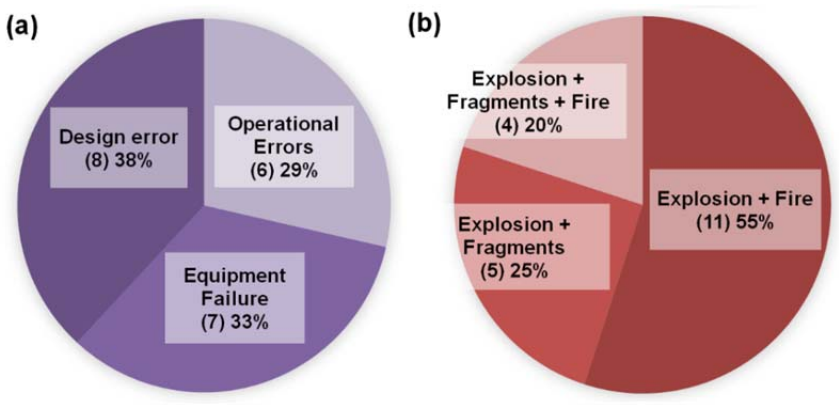

Figure 3: Primary causes (a) and scenarios (b) of domino accidents triggered by thermal explosions.

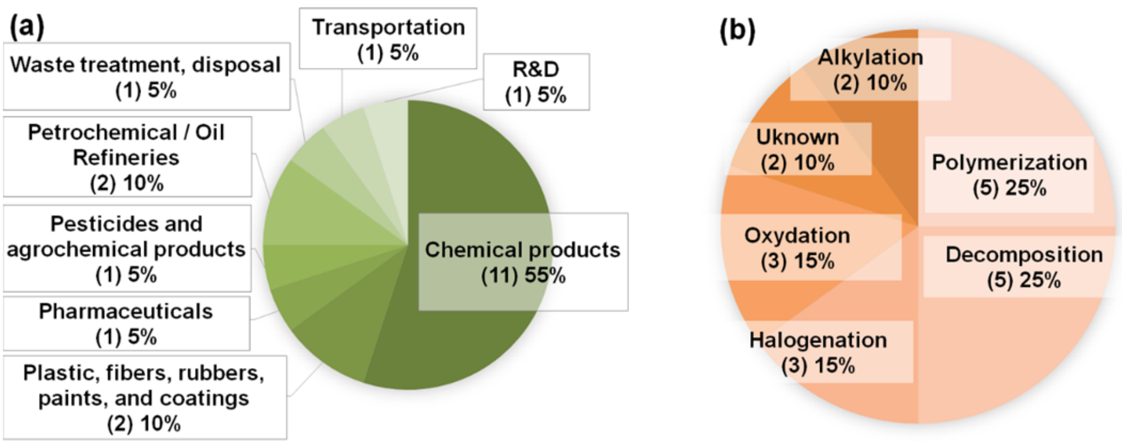

Figure 4: Type of activity (a) and reaction involved (b).

3. Case studies

As previously mentioned, some significant accidents have been selected to represent the path that escalation vectors generated by a runaway reactions can follow when generating domino events.

3.1 Explosion + Fire: VCE in a European petrochemical industry, March 20th 1990

The plant was producing difluoronitrobenzene (DFNB) by reacting dichloronitrobenzene (DCNB) with potassium fluoride at a temperature of 165°C and atmospheric pressure. DFNB was purified by centrifuge and distillation and was subsequently hydrogenated to difluoroaniline (DFA), an intermediate for the pharmaceutical industry. Probably because of the presence of water in the reaction (contamination) the reactor underwent a runaway reaction, the products vented, and vapours were seen to ignite at the top of the reactor. A VCE occurred, followed by a serious fire. A storage tank of xylene was ignited and prolonged the fire (Joint Research Center, 2015).

3.2 Explosion + Fragments: accident in Cork (Ireland), August 6th 1993

In a pharmaceutical industry, an explosion occurred in a batch reactor containing waste solvents, pharmaceutical intermediates, and by products. The explosion was caused by a runaway reaction producing too much gas and vapours for the pressure-relieving device to vent the reactor safety. Debris from the ruptured chemical reactor punctured storage vessels in the process building and storage tanks in bunded areas adjacent to it resulting in another explosion and subsequent fires.

Two employees received minor injuries from debris. Firewater run-off contaminated harbour waters and foreshore. Water distribution to the community was interrupted for 24 hours. The process equipment were decontaminated and the building dismantled. Damages and associated costs were estimated in about 20 million Euros (French Ministry of Ecology, 2015).

3.3 Explosion + Fragments: accident in Freeport (U.S.), September 13rd 2002

An isothermal container of hazardous waste catastrophically ruptured at a transfer station of a chemical company. The origin of the thermal explosion was the excessive heating the of the tank to permit the transfer of the waste (94 % cyclohexanone oxime, 4% water, and 2% cyclohexanone) that started to self-decompose, causing an over pressurization of the tank. As a consequence, 28 people received minor injuries, and residents living within 1.5 kilometres of the accident site had to shelter in theirs place for more than 5 hours. The force of the explosion propelled a 134 kg tank car dome housing about 500 meters away. Two storage tanks near the transfer station were damaged releasing 2.5 m^3 of oleum (fuming sulfuric acid and sulfur trioxide) (French Ministry of Ecology, 2015).

3.4 Explosion + Fragments + Fire: accident in Himeji (Japan), September 29th 2012

In a chemical industry, a runaway polymerization caused the release of a white smoke through the vents on an intermediate storage tank containing acrylic acid. The highly exothermic reaction led the product to boil; this caused over pressurization leading to cracks in the shell and subsequent leaks. Eventually a BLEVE burst the tank. Fragments and overheated polymers were projected within a 70 meters radius. Five adjacent tanks damaged during the blast, leading to the loss of acrylic acid and toluene, originating a pool fire in the retention basin. The explosion resulted in 37 victims: one fire fighter burned to death, five were seriously injured, and another 31 responders sustained slight injuries. Two of the three rescue vehicles were destroyed and over 500 employees in neighbouring companies evacuated. The unit affected was closed for 9 months, causing a 10% drop in the world’s acrylic acid production capacity. Production losses amounted to 450 million $, while property damage was assessed at 15 million $ (French Ministry of Ecology, 2015).

4. Conclusions

In the last 30 years, the trend of domino accidents triggered by thermal explosions is linearly increasing, although slightly. The survey revealed that in 20% of the cases multilevel propagation happened, leading to two different domino chains: the first due to the projection of fragments and missiles, the second due to fire. Some case histories were presented, being representative of the different domino propagation patterns. An approach for the assessment of escalation vectors triggered by thermal explosions was introduced.

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