Analysis of thermal runaway events in French chemical industry

Amine Dakkoune, Lamiae Vernières-Hassimi, Sébastien Leveneur, Dimitri Lefebvre, Lionel Estel

Amine Dakkoune, Lamiae Vernières-Hassimi, Sébastien Leveneur, Dimitri Lefebvre, Lionel Estel. Analysis of thermal runaway events in French chemical industry. Journal of Loss Prevention in the Process Industries, 2019, 62, pp.103938. 10.1016/j.jlp.2019.103938 . hal-02314230

ANALYSIS OF THERMAL RUNAWAY EVENTS IN FRENCH CHEMICAL INDUSTRY

Amine Dakkoune[1,2], *Lamiae Vernières-Hassimi*[1*], *Sébastien Leveneur*[1,3], *Dimitri Lefebvre*[2], *Lionel Estel*[1]

[1]Normandie Univ, INSA Rouen, UNIROUEN, LSPC, EA4704, 76000 Rouen, France,

E-mail : lamiae.vernieres@insa-rouen.fr

[2] Université Le Havre – GREAH, 25 rue P. Lebon, 76063 Le Havre, France.

[3] Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland.

1. Introduction

Thermal runaway represents a serious threat in the chemical industry. This dreaded phenomenon can lead to dangerous consequences to humans, environment and equipment (Jiang et al., 2016a). From a chemical engineering point of view, thermal runaway occurs when the heat-flow rate released by reactions exceeds the heat-flow rate exchanged with the surroundings. Hence, thermal accumulation increases and the reaction temperature keeps rising, which speeds up the heat-flow rate released (Jiang et al., 2016b).

Thermal runaway, well known event by chemists, can result in an explosion or a high quantity of gas and/or vapor emission that can be flammable and/or toxic. The outbreak of the reactor and the explosive combustion of the gases emitted, may lead to the destruction of buildings and the formation of secondary fires, which can aggravate the overall consequences via the domino effect (Hemmatian et al., 2014).

The cause of the biggest industrial disasters in history like Seveso (1976) and Bhopal (1984) was thermal runaway. In the Seveso disaster, the reactor safety disk broke because of an increase in temperature and pressure in the reactor due to an exothermic side reaction. The bursting of the container resulted in the release of a large quantity of dioxins into the atmosphere. The Bhopal disaster leads to a discharge of 40 tons of toxic gases due to a runaway reaction in a pesticide storage facility (ARIA, 2016).

The French chemical industry has experienced many events due to thermal runaway, such as the Saint Vulbas mishap in 1994 where 324 kg of hydrogen peroxide was released due to a runaway reaction in a fine chemistry unit. In addition, the Wingles mishap in 2010 involved a situation of overpressure in a reactor due to a thermal runaway reaction that burst the rupture disc of the reactor and released 3 tons of styrene. Furthermore, the incident at the lubricant additive manufacturing plant in Rouen (2013) involved a prolonged release of a high concentration of mercaptans, a highly odorous and toxic gas, because of a runaway reaction in a storage tank (ARIA, 2016). In our previous study (Dakkoune et al., 2018a), we found that 25% of the events in the chemical industry in France were caused by thermal runaway between 1974 and 2014. Therefore, it is important to examine how these events can be avoided.

The analysis of past events enables a continuous improvement of process safety. Based on an examination of the scientific literature, we found that several research groups have studied the kinetics and the risk analysis of thermal runaway reactions (Liu et al., 2017; Ni et al., 2016; Rakotondramaro et al., 2016; Vernières-Hassimi et al., 2017; Vernières-Hassimi and Leveneur, 2015; Wu and Qian, 2018). However, we noted an absence of work related to thermal runaway events in the French chemical industry despite the significant presence of this risk. This lack of information urged us to look into this problem. In this study, we analyze the events involving thermal runaway reactions in the French chemical industry between 1988 and 2013, as well as their causes and consequences. We focus on data contained in the ARIA database. The results obtained were compared with a similar study carried out in the same period in the United Kingdom about thermal runaway events (Saada et al., 2015). Finally, based on experience feedback, lessons were learned and recommendations were given.

The rest of this paper is organized as follows: Section 2 gives an overview on some means of prevention from process events. In Section 3, we introduce the working methodology that includes the chosen data and event selection. Section 4 is divided in 3 parts. The first one deals with the causes and consequences of thermal runaway events. The second part is dedicated to lessons learned from experience feedback. In the third part, we compare the current results with the ones obtained from the United Kingdom study. The conclusion is presented in Section 5.

2. Prevention of process events.

The prevention of major risks is a social safety necessity. The protection of process plants from unexpected failures and maintaining their continuity is becoming a priority for industries and countries. Theses preventions aim to avoid severe societal and economic crises that may happen. To remedy this problem, stringent industrial risk regulations have been developed, and scientific research effort increases (Khan et al., 2015).

2.1 Regulation aspects

From a political point of view, different laws have been voted upon by the French and European Union parliaments to prevent major chemical risks such as the “Bachelot law” Act No 2003-699 of July 30th, 2003 that was created in response to the AZF plant explosion in September 2001 (ARIA, 2016). This law includes a technological risk prevention plan. This prevention plan should reduce risks at the source, redefine urban and building plans, and reinforce buildings or expropriate the most exposed residences. Alternatively, the Seveso directive, the most well-known European directive on industrial plant risk management, was originally adopted in 1982 following the Seveso disaster in Italy in 1976. It requires that the EU Member States define a policy for the prevention of major industrial risks. These laws require that industries realize risk analysis, in order to demonstrate to authorities and civil society that they are able to control and reduce the risks associated with their field of activity and reinforce their safety.

2.2 Risk analysis aspects

The role of risk analysis is to identify the sources and the degree of risk that can cause damage to humans, environment or property, and to add adequate preventive measures in order to eliminate or to control those risks. The study of accident risk analysis started in the 1970s according to Kletz (1999) following the succession of major accidents and the development of the chemical industry (Planas et al., 2014).

Different methods of risk analysis in the chemical industry are known, such as risk matrices, risk graphs, bow-tie methods, failure mode analysis, effects and criticality analysis (FMECA), and hazard and operability analysis (HAZOP). However, these methods have limitations that make their use critical (Baybutt, 2015, 2014).

2.3 Educational aspects

From an educational point of view, integrating process safety into chemical university programs may be part of the solution. Perrin et al. (2018) demonstrated the importance of integrating safety principles into the educational courses of chemical engineering. Leveneur et al. (2016) and Mkpat et al. (2018) proposed pedagogical education models about this subject. This approach can also be applied to operators and professional training in process safety (Spicer Thomas et al., 2013).

3. Material and methods

3.1 The database

The exploitation of one or more databases is essential to searching for past events and identifying the information necessary to conduct risk analysis. Several databases exist on industrial chemical events such as:

ARIA: Analyse, Recherche et Information sur les Accidents (France);

CSB: Chemical Safety Board (United States);

FACTS: Failure and ACcidents Technical information System (Netherlands);

MARS: Major Accident Reporting System (European Union);

MHIDAS: Major Hazard Incident Data Service (United Kingdom);

RISCAD: Relief Information System for Chemical Accidents Database (Japan);

ZEMA: Zentrale Melde- und Auswertestelle für Störfälle und Störungen in verfahrenstechnischen Anlagen (Germany).

The ARIA database is one of the available European databases. It has been used in several studies to describe different technological accidents (Casson Moreno et al., 2016; Casson Moreno and Cozzani, 2015; Okoh and Haugen, 2014; Ramírez-Camacho et al., 2017; Kirchsteiger, 1999; Trávníček et al., 2018).

The ARIA database, managed by the French Ministry of Ecology since 1992, is an open database that compiles an inventory of past technological and industrial events. It includes information and experience feedback related to these events. This database contains a search engine that can extract events according to specific criteria such as the type of events or the area of activity. In addition, the public can access the data in the ARIA database by visiting the ARIA website (ARIA, 2016).

The ARIA database describes roughly 42,000 events occurring in France and roughly 6,000 events occurring abroad. About 71% of these events concern classified installations. The other events concern the transport of hazardous materials by roads, rail, waterways or pipeline; the distribution and domestic use of gas, mines and quarries; and hydraulic structures.

3.2 Data selection

In the ARIA database, there are two ways to record events:

- Summary form that presents key information.
- Detailed fact sheets that provide more information about the events, their circumstances, consequences, measures taken over the short or medium term, proven or suspected causes, and follow-up or lessons learned.

In our study, to properly analyze the causes and consequences of thermal runaway events, we worked with the detailed fact sheets. Fig. 1 shows the procedure that we followed to select thermal runaway events.

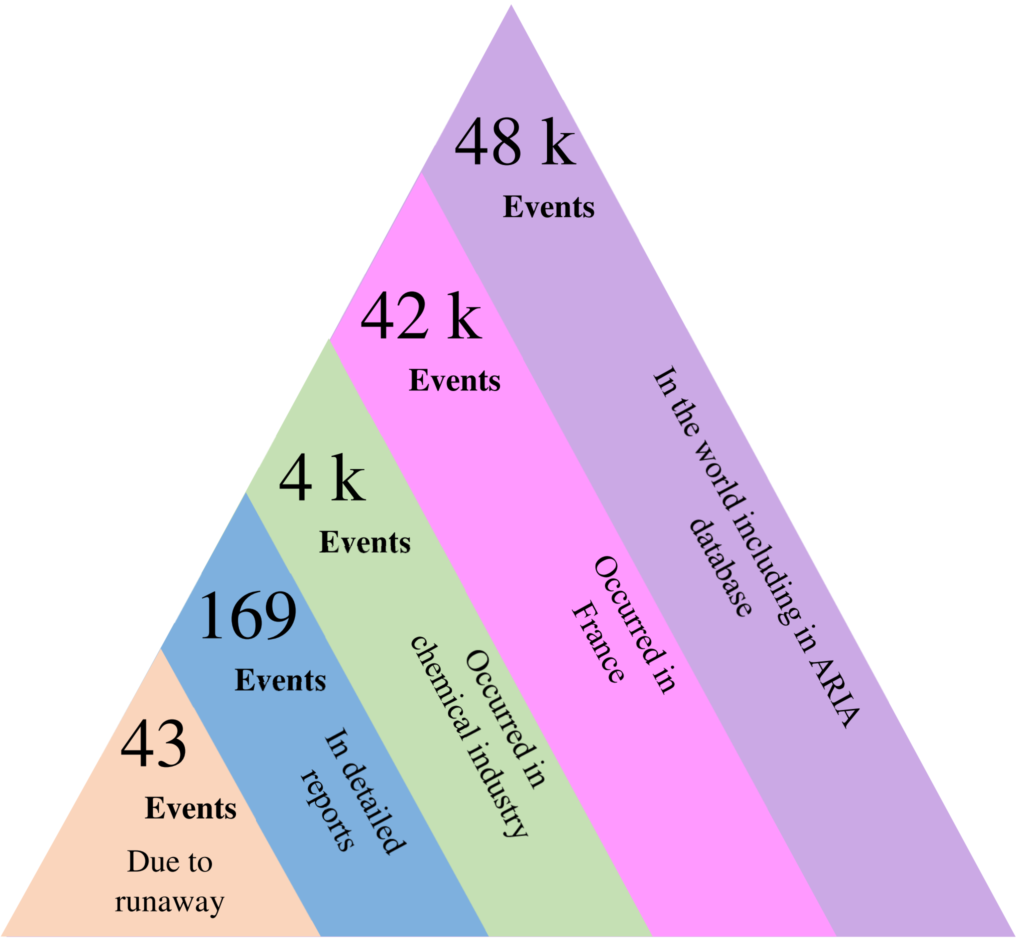

Fig. 1. Structure of events selection in ARIA database.

Among the 42,000 events occurring in France and described in the ARIA database, more than 4,000 occurred in the French chemical sector. Among these 4,000 events, 169 are sufficiently documented and are associated with very precise fact sheets. Among these detailed fact sheets, 43 events due to thermal runaway occurred between 1988 and 2013. This study focuses on these 43 detailed events.

Using the definition provided by Rathnayaka et al. (2011), the events illustrated in this work were classified into five categories :

- Near miss: an event with no consequences observed on health, damage for environment or property and loss of production. It has the potential to result in a loss but does not usually happen.
- Mishap: an event that could cause a minor impact on health, minor damages to property and environment, and loss of production.
- Incident: an event that could cause major injuries, localized damage to property and environment, and a considerable loss of production.
- Accident: an event that may cause massive human fatalities or permanent disabilities, considerable damage to property and environment, production and huge financial loss.
- Disaster: an event that may cause massive fatalities, extensive damage to property and environment, massive loss of production and temporary or permanent plant shutdown.

These definitions are summarized in the Table 1.

Table 1.

Definition for each event class.

Events	Consequences				
	Human	**Environment**	**Production**	**Property**	**Reputation**
Near miss	No injuy	No impact	No loss	No effet	No impact
Mishap	Minor health effects	Minor impacts	Production loss / work hours loss	Minor impacts	Minor impacts
Incident	A major health effect or injury	Localized damage	Considerable loss / work days loss	Localized damage	Considerable impact
Accident	One or more fatalities or permanent major disabilities	Considerable effects	Heavy financial loss.	Considerable damage	Report in national media
Catastrophic accident or disaster	Multiple fatalities	Massive environmental effects	Extensive damage / may cause a shutdown of the plant	Extensive damage	Report in international media

Considering the 43 events, we didn't find any disaster or near miss events due to thermal runaway. Fig. 2 shows the repartition of the events due to thermal runaway, in this study more than half of these events were incidents.

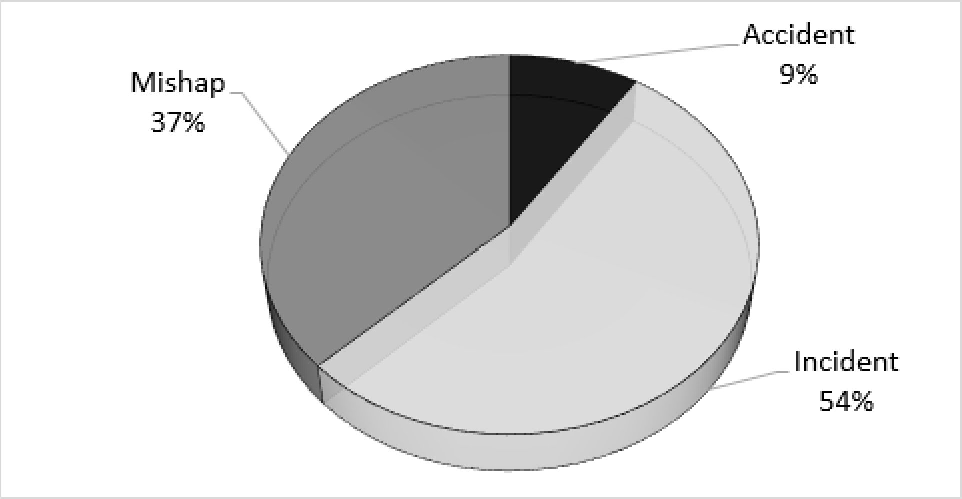

Fig.2. Repartition of the 43 events due to thermal runaway in France

4. Experience feedback results and discussion

4.1 Evolution of events over time

The 43 chemical events in France involving thermal runaway reactions between 1988 and 2013 were grouped and distributed over successive periods of four-year (Fig. 3). The number of past events increased from six over the period 1988–1993 to eleven over the period 1999–2003; the “accident” category disappeared after 1998. On the other hand, the number of incidents and mishaps increased from 1988 to 2003. These increases took place despite the presence of safety laws like:

- The French law of 1976 relating to classified installations in terms of industrial risks.
- The European regulations such as the Seveso 1 directive of 1982, which requires that member states identify industrial sites presenting risks of major events, and maintain a high level of prevention in these sites. In 1996, the new Seveso 2 directive was promulgated in order to introduce some novelties like the notion of prevention and the classification of installations according to two thresholds: “high threshold Seveso” and “low threshold Seveso”. In addition, the new directive reinforces the control of urbanization around high-risk sites and the need to inform the public.

After 2003, the number of events decreased slightly to eight during the period 2004–2009. The number of events then increased to 10 over the last period (2009–2013). In this period, a new French law has been promulgated, known as the “Bachelot law”, whose goal is to reduce the risks of Seveso high-threshold sites. Furthermore, the enactment of the Seveso Directive 2 into French law in 2000 establishes a correspondence between the Facilities Classified for Environmental Protection (ICPE) and the Seveso Directive.

The risk law was modified in 2012 to reinforce the management of major industrial risks by introducing the development of technological risk prevention plans and a more detailed approach to the study of hazards. The third Seveso Directive, which reinforces the requirements already imposed on industrialists to control major events involving chemical products, was entered into force on 2015.

These laws can intervene to reduce these risks. However, it remains necessary to look for the main causes that lead to this critical scenario, and find technical solutions to prevent or reduce the occurrence of similar events.

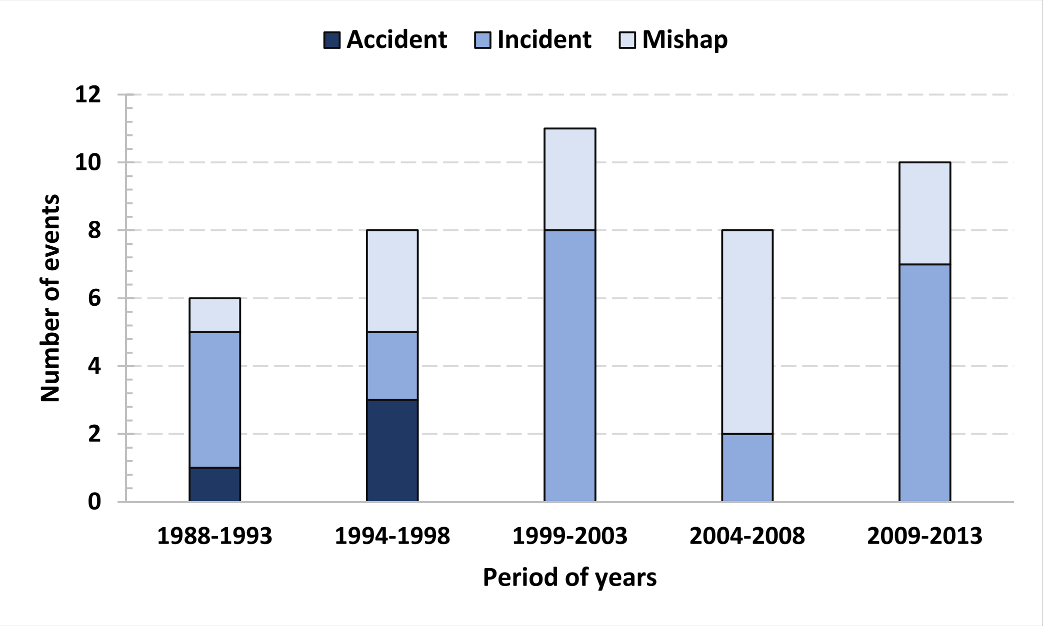

Fig. 3. Distribution of events related to thermal runaway for chemical industry in France from 1988 to 2013.

4.2 Reactions and industries

As shown in Fig. 4, the thermal runaway events occurred in three main kinds of reactions. We found that 34.9% of the reported events concerned polymerization reactions as the first responsible reaction. Decomposition reactions represented 18.6% of the reported events, and nitration reactions represented 9.3% of the reported events. We also noted several other types of exothermic reactions that were lower than 5% (e.g., hydrogenation, oxidation, etc.). Most of these reactions are characterized by a large quantity of heat and gaseous products.

For the events due to decomposition reactions, we identified two different types:

- Decomposition in purpose: the goal of the process was the separation of a single chemical compound into other desired chemical compounds. During this process, the temperature was not controlled and thermal runaway occurred. For example, an incident took place in a paint manufacturing plant in France in 1998. The weakly exothermic reaction at this plant was typically controlled. However, due to a lack of process control, a succession of exothermic chemical reactions produced in the reactor caused an explosion and a fire in the plant (ARIA N°17740).
- Decomposition by accident: the decomposition reaction is not the goal of the chemical process. However, a failure results in the temperature not being controlled and thermal runaway occurs. For example, in a fine chemical unit in France, a runaway reaction took place in a reactor in 1994. This accident was due to an operator who stopped the agitator of the reactor without noticing (ARIA N°5900).

Polymerization and decomposition reactions are more significant in terms of damage, and they are responsible for more than half of the thermal runaway events recorded in France. These observations were also found in the works of Saada et al. (2015) in the United Kingdom. This type of reactions often produces a rapid increase in heat and pressure that produces large amounts of energy and can cause fires, releases of gas and/or vapor or explosions if the reactor cooling system cannot eliminate the excess energy (Zhu et al., 2015). These reactions can occur in several chemical sectors shown in Fig. 5.

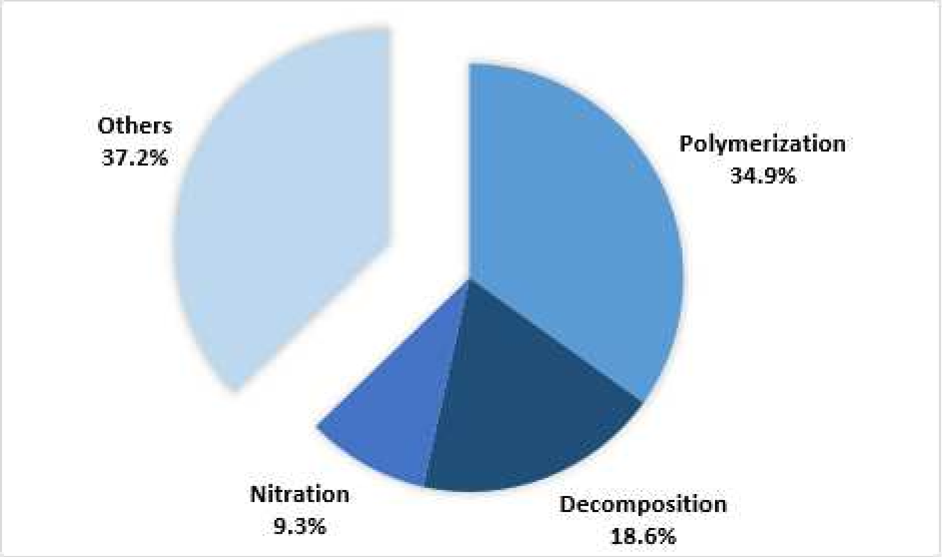

Fig. 4. Repartition of reactions responsible of thermal runaway events in France

Fig. 5 shows the categories of industries affected by thermal runaway events. Manufacturing of paints and adhesives accounted for 23.3% of the total number of reported events. Organic chemical industries accounted for 20.9% of the total number of reported events. Plastics and rubber products industries accounted for 18.6% of the total number of reported events. Pharmaceuticals industry followed with 16.3% and inorganic chemicals industry accounted for 13.9% of the total number of reported events. Refinery industry accounted for 2.3% of the total number of reported events. Other chemical industry categories include industrial activities such as manufacture of fertilizers and manufacture of explosives. Together, these industries accounted for 4.6% of the total number of reported events.

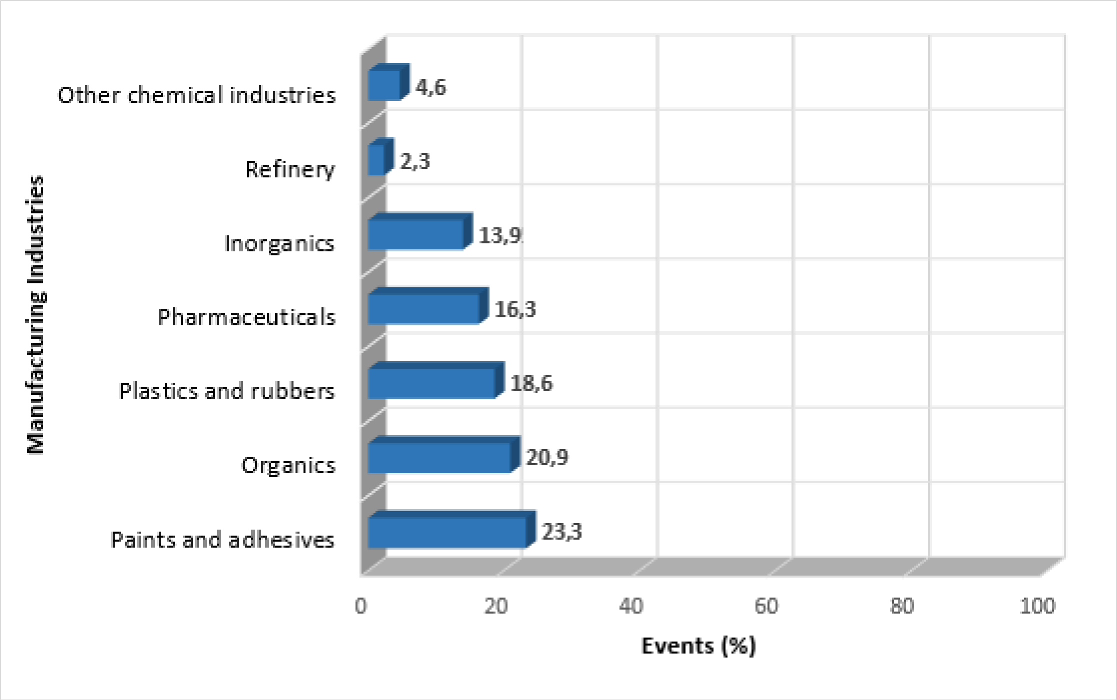

Fig. 5. Percentage of events in the various chemical industries in France

4.3 Human consequences of thermal runaway

The consequences of thermal runaway events vary from one event to another. In one case, thermal runaway caused an explosion and a fire of a hydrogenation reactor in a plant dedicated to toluene di-amine (TDA) (ARIA N°7956). This event resulted in the death of one employee and injuries to three other employees. In addition, several substances were released during the explosion (hydrogen, isopropanol, nickel, TDA, etc.). In another case, an exothermic runaway reaction caused an explosion and a fire in a reactor in a pharmaceutical plant (ARIA N°7069). This event was responsible for the death of an operator and the emission of toxic gases. Injuries of six operators and property damages estimated at roughly 2.13 M€ resulted from another event (ARIA N°4708). In an event, thermal runaway caused the release of 690 kg of formaldehyde and 36 kg of phenol from a polymerization reactor (ARIA N°7135). In another case, thermal runaway caused the release of 58.5 tons of styrene in a copolymerization reactor (ARIA N°17740).

In order to illustrate the degree of severity of these events, we have opted to focus on human consequences. We found that 40% of the runaway events in this study caused injuries or fatalities to operators or the general population. Table 2 lists the number of injuries and deaths due to thermal runaway events in each chemical industry.

Table 2.

Number of injuries and deaths due to thermal runaway events in France for each chemical industry sector from 1988 to 2013.

Chemical Industry	Number of injuries	Number of deaths
Paints and adhesives	25	0
Inorganics	17	1
Pharmaceuticals	15	1
Organics	12	1
Plastics and rubbers	7	0
Other chemical industries	1	0
Refinery	0	0
Total	77	3

According to our data, the paints and adhesives industry experienced the majority of reported injuries (25 people) followed by the inorganics industry (17 injuries), the pharmaceuticals industry

(15 injuries) and the organic manufacturing industry (12 injuries). These last three industries also suffered one death each.

Deaths constitute almost 4% of people affected by runaway events. The deaths of three people were reported due to an explosion following a thermal runaway reaction. Roughly, half of injuries (53%) were caused by projectiles or toxic releases and 41% of injuries were caused by explosions. The remaining injuries (6%) were caused by fire.

The largest number of injuries were reported for two events: the first one was an extended release of Mercaptan at a paints and adhesives chemical plant in 2013 (ARIA N°43616). Individuals displaying symptoms of nausea, headaches and irritated upper respiratory tracts required 20 medical consultations. The other event was an explosion at an inorganic chemical plant in 2003 (ARIA N°24819), a technician sustained a throat injury due to shattered glass; 13 other employees experienced shock.

4.4 Causes of thermal runaway events

Based on the experience feedback events, 17 different causes related to the thermal runaway events were found in the French chemical industry between 1988 and 2013. These causes were classified into three major groups: technical and physical causes, human and organizational causes, and natural causes.

Table 3 lists the different causes and their appearance rates for the 43 thermal runaway events in the French chemical industry studied here. Because most of the events recorded in this study have multiple causes, it was difficult to distinguish the initial cause from secondary causes. For this reason, the causes identified in this Table regroup all initial, secondary, etc. causes.

Causes of thermal runaway events in the United Kingdom chemical industry will be compared with causes of thermal runaway events in French chemical industry in the section 4.6.

Table 3.

Possible causes responsible of thermal runaway events in French and United Kingdom chemical industries.

Possible causes of events		**% of cause in each country**	
		France	***United Kingdom***
Technical and physical causes	*Stirring / Cooling*	8.5	9.1
	Quality: impurity, particle size	7.7	3.4
	Technical failure: mechanical / electrical	6.9	12.5
	Detector malfunctioned	6.9	0.0
	Unexpected exothermic reaction	5.4	5.7
	Power cut	3.8	1.1
	Reactor sizing	3.1	4.5
	Leakage	0.8	2.3
Human and organizational causes	*Operator error*	21.5	27.3
	Poor risk analysis	10.0	4.5
	Reactor charging	6.1	5.7
	Insufficient training	5.4	5.7
	Unsuitable procedures and devices	5.4	14.8
	Maintenance operations	3.1	1.1
	Inadequate Cleaning	2.3	2.3
Natural causes	*Temperature*	2.3	0.0
	Storm	0.8	0.0

Based on Table 3, one can see that the most frequent technical causes of thermal runaway are related to stirring and cooling problems in a reactor (11 events; 8.5%). This cause can be initiated by the same group of causes such as power failures due to technical problems (ARIA N°28416, N°30199, N°44071) and poor stirring (ARIA N°8056, N°32419, N°6980), or by another group of causes like storms (ARIA N°38617), stirring stoppage due to human error (ARIA N°5900, N°13520) and leakages of cooling water (ARIA N°17740).

The second most important factor was the quality of the reactants introduced into the reactor (10 events; 7.7%). For example, the accidental addition of water (an impurity) in the reaction mixture caused $SOCl_2$ hydrolysis with the production of SO_2 and HCl and led to an increase in the pressure in the reactor (ARIA N°7069, N°4708). In addition, the presence of impurities favors decomposition reactions and initiates thermal runaway (ARIA N°30323, N°40496, N°29752, N°29082, N°16213, N°2375). Finally, the size of particles also plays an important role in the reaction stability (ARIA N°24819).

The third factor is shared between technical failures and detector malfunctions (9 events for each; 6.9%). For example, fault indication of the actual temperature within a tank due to poor positioning of the temperature sensor (ARIA N°43616), a communication fault between the temperature sensor of the dryer and the controller regulating the temperature (ARIA N°41305) or an incorrect value provided by the detector (ARIA N°21994). Furthermore, technical failures like the failure of the automated control mechanism subsequent to a short circuit (ARIA N°16424), the failure of the control of a pneumatic drainage valve (ARIA N°18339), or the failure of a safety card (ARIA N°27001, N°3536) can also cause thermal runaway events.

Another major factor is the problems associated with the accidental presence of an exothermic reaction (7 events; 5.4%). For instance, the slow decomposition of a chemical species in the presence of air (ARIA N°22459) or heat and light (ARIA N°44335) and contact with another chemical species (ARIA N°4460, N°7135). The others technical and physical causes are less prevalent.

Many human and organizational causes are responsible for a large number of thermal runaway events. According to Table 3, operator errors are the most common causes of thermal runaway (28 events; 21.5%). For example, the presence of a contaminant in the reactor (ARIA N°30323, N°7069), an error manipulation due to a lack of focus (ARIA N°5900, N°38617) or a manipulation by an operator for the first time (ARIA N°4708), can also cause thermal runaway. In addition, a lack of respect for reagent quantities or handling steps (ARIA N°40496, N°36630) and poor interventions by the operators on the system (ARIA N°25952, N°33561, N°3536), also contribute to thermal runaway events. Poor risk analysis (e.g., inadequate or absent devices or safety instructions (ARIA N°7135, N°4708, N°8056, N°30323, N°29082, N°22693) and insufficient risk analysis (ARIA N°44071, N°22693)) was the cause of 13 events (10.0%). Additionally, reactor charging contributed to eight runaway events (6.1%). For example, overcharge of chemicals in the reactor (ARIA N°40328) and the rapid introduction of reactants in the reactor (ARIA N°36794, N°7135, N°36630) favors the reaction drift.

Other human and organizational causes play minor roles in thermal runaway compared with the three factors noted above. A lack of communication between employees, insufficient operator training, poor response to emergency or training, leaking, poor control of maintenance operations, inadequate procedures, and the use of unsuitable devices are all contributing causes.

Natural phenomena such as storms and environmental conditions such as high temperatures have been directly responsible for four thermal runaway events. For example, a storm that causes a reactor to lose power (thereby ceasing stirring and cooling) resulted in thermal runaway by domino effect (ARIA N°38617). Also, an extremely high outside temperature contributed to thermal runaway by transferring heat through the reactor, which was poorly insulated (ARIA N°25952).

Through these results, we noted a strong presence of human errors involved in thermal runaway events in the French chemical industry. This finding was also reported by Saada et al. (2015) for the United Kingdom. Cacciabue (2000) confirmed that human errors contribute to an increase in accidents. However, it is difficult to estimate human reactions to an accident because human behavior changes from one human to another. In addition, interaction between humans, and between humans and machines/organizational structure make the problem more complex. Nivolianitou et al. (2004) confirmed that the pronounced complexity of mechanical and electronic systems is one of the factors that complicates the role of humans in a plant.

Future research that focuses on events related to thermal runaway must take into consideration problems related to the human factor. This issue must be studied further in order to help staff working in chemical industries determine the best solution to reduce thermal runaway risks. The information resulting from experience feedback by using ARIA database can subsequently provide lessons and recommendations to reduce the frequency of similar thermal runaway events in the future.

4.5 Lessons learned

The study of past events (experience feedback) has an important role in preventing the same event or an event with the same causes. This importance is reflected in the lessons learned from each event that occurred before. The analysis of thermal runaway events in France indicates that these events are mainly caused by the lack of knowledge of the reaction system, technical and maintenance problems, operator errors as well as insufficient risk management.

- Lack of knowledge of the reaction system: in order to prevent thermal runaway events, firstly, it is essential to have a deep knowledge on thermal behavior of the reaction medium such as thermodynamic and kinetic constants. This knowledge can be obtained through various laboratory techniques such as differential scanning calorimetry and adiabatic calorimetry. Although the theories go back at least 50 years (Aris, 1969) and events have been recorded at least as long ago (Lees, 1980), basic safety precautions such as adiabatic calorimetry measurement or analysis of potential side reactions are not taken into account. Thus, it is important to use modeling tools to evaluate the risks of thermal runaway. The models must be reliable, explicit and simple to obtain key parameters of safety according to the operating conditions. These models may make the intervention more effective in the case of a malfunction (Vernieres-Hassimi et al., 2016) by combining them with detection methods, and / or control methods (Vernières-Hassimi and Leveneur, 2015; Dakkoune et al., 2018b; Dakkoune et al., 2019).

– Technical and maintenance problems: in order to prevent technical and maintenance failures, a study based on experience feedback can be used to identify critical safety equipment. This study would guide the financial investment to improve the resistance of this equipment. For example, in the case of corrosion, an analysis must be performed regarding the compatibility of the substances used with materials of process conception. This analysis can avoid problems of corrosion leading to leaks, incompatibilities between the reaction medium and reactor container / storage etc.

– Operator errors: the chemical industry needs to be more vigilant about risks that are mainly related to human factors, due to the complexity of their behavior. In addition to that, the operator interacts with other external factors such as hardware, management, another operator, etc. In order to reduce the events related to the human factor, a search for methods to improve employee behavior is essential. In fact, it can be interesting to work on improving the ergonomics of several equipment, and the training of operators for process safety. An investigation can also be proposed to improve the intervention of operators. However, it would be difficult to completely eliminate all human errors during an operation.

– Insufficient risk management: a risk management system related to the prevention of runaway is essential. The analysis of past events has shown a deficiency in the application of this system, which is mainly related to the assumptions made in the identification of the events feared and / or the selection of dangerous phenomena. This analysis also showed that in some cases the risk management systems were either non-existent or not updated after a modification of the process or the operating mode.

4.6 Comparison of French, the United States and the U.K industries

In our previous study of events in the chemical industry in France, we found that 25% of these events were caused by thermal runaway (Dakkoune et al., 2018a). In another study conducted in the United States, and related to the causes of major chemical industry events, Balasubramanian and Louvar (2002) found that 26% of major events were due to thermal runaway. According to these two references, France has experienced the same percentage of runaway events as the United States. Saada et al. (2015) also declared that the incidence of events due to thermal runaway was significant in the United Kingdom.

In the following, a comparison involving thermal runaway was carried out between the current study and the study elaborated by Saada et al. (2015). This comparison was interested in causes and consequences of events related to thermal runaway in the United Kingdom in the same period of our study (1988-2013).

This comparison is necessary to situate the position and evaluate the performance and capabilities of the French chemical industry in terms of safety compared to those who are similar economically and geographically. Nevertheless, these comparisons will never be 100% reliable because no system is identical to another.

The results show that the main reactions responsible for thermal runaway events in UK and France were polymerization and decomposition reactions (Fig. 6). These two reactions were responsible for almost half of runaway events in UK.

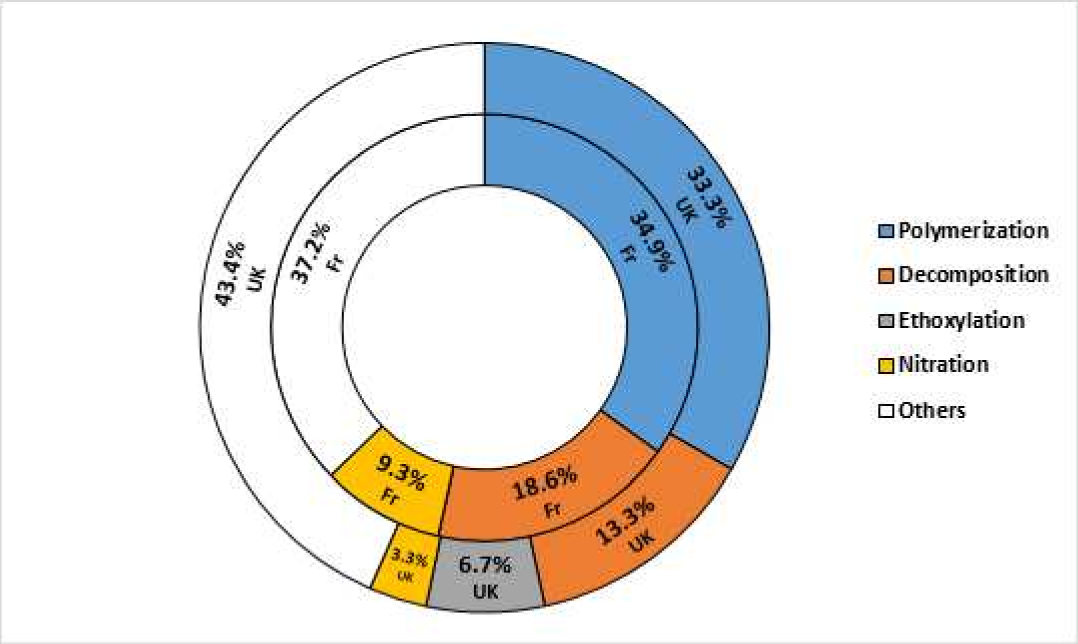

Fig. 6. Comparison and repartition of reactions responsible of thermal runaway events in France (Fr) and the United Kingdom (UK).

On the other hand, industries affected by the highest number of thermal runaway events were also similar with the current study. These industries are the organic chemical industry at first followed by plastics and rubber industries. More details are presented in Fig. 7.

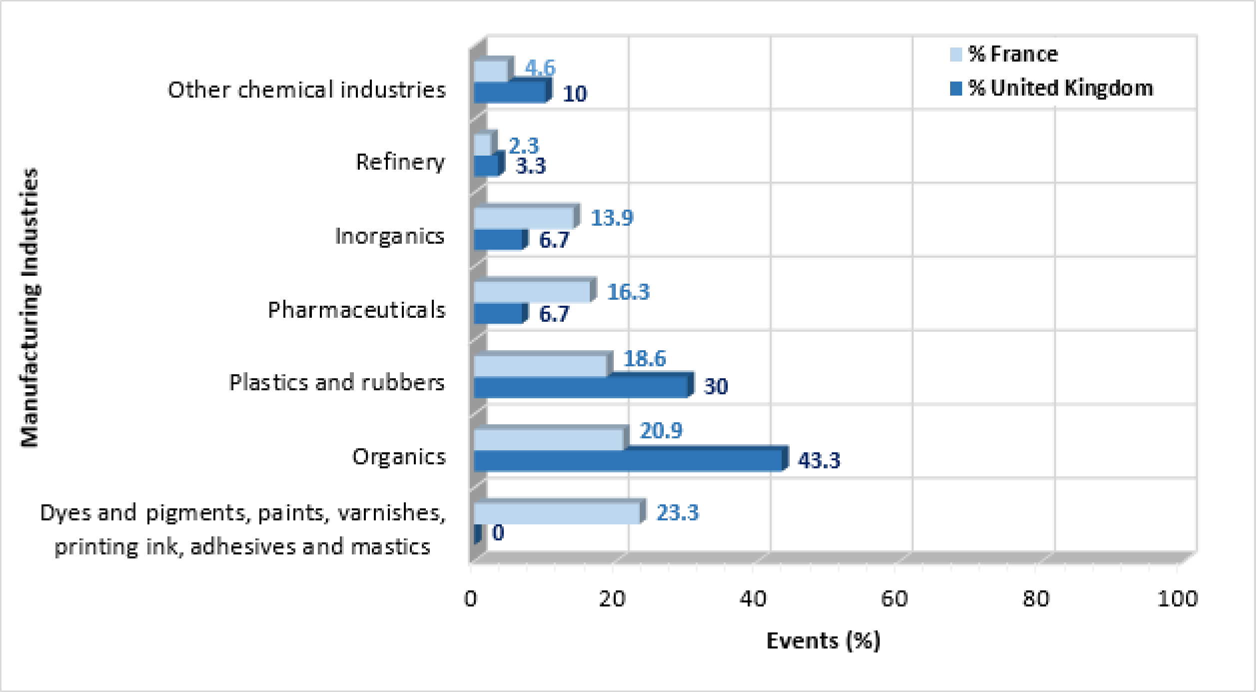

Fig. 7. Comparison of the percentage of thermal runaway events in the various chemical industries between France and the United Kingdom.

In regards to thermal runaway causes, similar results have been observed for the current study and the UK study (Table 3). The main causes were related to operator errors, technical and mechanical failures, unsuitable procedures and devices, stirring and cooling problems.

5. Conclusion

Risk analysis was carried out on 43 selected past events involving thermal runaway in the French chemical industry between 1988 and 2013. Detailed information about these events was obtained from the ARIA database.

In this study, we found that thermal runaway events were primarily associated with polymerization and decomposition reactions. Operator errors were the primary causes of the thermal runaway events and the number of victims was significant. The current events were compared with the runaway events in UK, the comparison confirms some common points like: operator error was the major cause of runaway events, the polymerization and decomposition reactions were the main reactions responsible for this runaway. Based on experience feedback, lessons were learned and recommendations were provided to prevent thermal runaway events in the future.

Thermal runaway events are a significant problem that is still occurring in chemical industry, more than half of the studied events were classified as incidents. From the period of 1999–2003, the number of thermal runaway events increased and these events have remained more or less stable over the last 10 years. This situation raises the question of the real impact of laws related to risk on industries. One could also note that reaction thermodynamic study is a difficult subject. Although it is difficult to eliminate the risk of thermal runaway, and as a result it is not likely that runaway reaction events will disappear. The only remaining measure is to isolate the reactor from the rest of the world and / or to remove employers and residents from the reactor environment in order to avoid the human consequences (death, injury...) and equipment damage.

Acknowledgements

This project AMED has been funded with the support from the European Union with the European Regional Development Fund (ERDF) and from the Regional Council of Normandie.

References

ARIA, 2016. ARIA : Retour d’expérience sur accidents technologiques. URL http://www.aria.developpement-durable.gouv.fr/ (accessed 4.6.17).

Aris, R., 1969, Elementary Chemical Reactor Analysis. Prentice-Hall, Englewood Cliffs, NJ

Balasubramanian, S.G., Louvar, J.F., 2002. Study of major accidents and lessons learned. Process Saf. Prog. 21, 237–244. https://doi.org/10.1002/prs.680210309

Cacciabue, P.C., 2000. Human factors impact on risk analysis of complex systems. J. Hazard. Mater. 71, 101–116. https://doi.org/10.1016/S0304-3894(99)00074-6

Casson Moreno, V., Cozzani, V., 2015. Major accident hazard in bioenergy production. J. Loss Prev. Process Ind. 35, 135–144. https://doi.org/10.1016/j.jlp.2015.04.004

Casson Moreno, V., Papasidero, S., Scarponi, G.E., Guglielmi, D., Cozzani, V., 2016. Analysis of accidents in biogas production and upgrading. Renew. Energy, Special Issue: Biogas as a Renewable Fuel 96, 1127–1134. https://doi.org/10.1016/j.renene.2015.10.017

Dakkoune, A., Vernières-Hassimi, L., Leveneur, S., Lefebvre, D., Estel, L., 2018a. Risk analysis of French chemical industry. Saf. Sci. 105, 77–85. https://doi.org/10.1016/j.ssci.2018.02.003

Dakkoune, A., Vernieres-Hassimi, L., Leveneur, S., Lefebvre, D., Estel, L., 2018b. Fault Detection in the Green Chemical Process: Application to an Exothermic Reaction. 1 67, 43–48. https://doi.org/10.3303/CET1867008

Dakkoune, A., V. Hassimi, L., Leveneur, S., Estel, L., Lefebvre, D., 2019. Model-based fault detection and isolation for chemical processes: Application to the prevention of thermal runaway, IEEE Symposium Series on Computational Intelligence (SSCI), pp. 1352–1358. https://doi.org/10.1109/SSCI.2018.8628709

Hemmatian, B., Abdolhamidzadeh, B., Darbra, R.M., Casal, J., 2014. The significance of domino effect in chemical accidents. J. Loss Prev. Process Ind. 29, 30–38. https://doi.org/10.1016/j.jlp.2014.01.003

Jiang, J., Jiang, J., Wang, Z., Pan, Y., 2016a. Thermal runaway criterion for chemical reaction systems: A modified divergence method. J. Loss Prev. Process Ind. 40, 199–206. https://doi.org/10.1016/j.jlp.2015.12.024

Jiang, J., Yang, J., Jiang, J., Pan, Y., Yu, Y., Zhou, D., 2016b. Numerical simulation of thermal runaway and inhibition process on the thermal polymerization of styrene. J. Loss Prev. Process Ind. 44, 465–473. https://doi.org/10.1016/j.jlp.2016.10.017

Khan, F., Rathnayaka, S., Ahmed, S., 2015. Methods and models in process safety and risk management: Past, present and future. Process Saf. Environ. Prot. 98, 116–147. https://doi.org/10.1016/j.psep.2015.07.005

Kletz, T.A., 1999. The Origins and History of Loss Prevention. Process Saf. Environ. Prot., Developments in Process Safety 77, 109–116. https://doi.org/10.1205/095758299529938

Lees, Frank P., 1980. Loss prevention in the process industries hazard identification assessment and control. Volume 1 Technology & Engineering. ISBN:9780123971890

Leveneur, S., Vernieres-Hassimi, L., Salmi, T., 2016. Mass & energy balances coupling in chemical reactors for a better understanding of thermal safety. Educ. Chem. Eng. 16, 17–28. https://doi.org/10.1016/j.ece.2016.06.002

Liu, S.-H., Lin, W.-C., Hou, H.-Y., Shu, C.-M., 2017. Comprehensive runaway kinetic analysis and validation of three azo compounds using calorimetric approach and simulation. J. Loss Prev. Process Ind. 49, 970–982. https://doi.org/10.1016/j.jlp.2017.05.014

Mkpat, E., Reniers, G., Cozzani, V., 2018. Process safety education: A literature review. J. Loss Prev. Process Ind. 54, 18–27. https://doi.org/10.1016/j.jlp.2018.02.003

Ni, L., Mebarki, A., Jiang, J., Zhang, M., Dou, Z., 2016. Semi-batch reactors: Thermal runaway risk. J. Loss Prev. Process Ind. 43, 559–566. https://doi.org/10.1016/j.jlp.2016.07.024

Nivolianitou, Z.S., Leopoulos, V.N., Konstantinidou, M., 2004. Comparison of techniques for accident scenario analysis in hazardous systems. J. Loss Prev. Process Ind. 17, 467–475. https://doi.org/10.1016/j.jlp.2004.08.001

Okoh, P., Haugen, S., 2014. A study of maintenance-related major accident cases in the 21st century. Process Saf. Environ. Prot., Loss Prevention 2013 92, 346–356. https://doi.org/10.1016/j.psep.2014.03.001

Baybutt, P., 2015. A critique of the Hazard and Operability (HAZOP) study. Journal of Loss Prevention in the Process Industries 33, 52–58. https://doi.org/10.1016/j.jlp.2014.11.010

Baybutt, P., 2014. The use of risk matrices and risk graphs for SIL determination. Process Safety Progress 33, 179–182. https://doi.org/10.1002/prs.11627

Perrin, L., Gabas, N., Corriou, J.-P., Laurent, A., 2018. Promoting safety teaching: An essential requirement for the chemical engineering education in the French universities. J. Loss Prev. Process Ind. 54, 190–195. https://doi.org/10.1016/j.jlp.2018.03.017

Planas, E., Arnaldos, J., Darbra, R.M., Muñoz, M., Pastor, E., Vílchez, J.A., 2014. Historical evolution of process safety and major-accident hazards prevention in Spain. Contribution of the pioneer Joaquim Casal. J. Loss Prev. Process Ind., European Process Safety Pioneers 28, 109–117. https://doi.org/10.1016/j.jlp.2013.04.005

Rakotondramaro, H., Wärnå, J., Estel, L., Salmi, T., Leveneur, S., 2016. Cooling and stirring failure for semi-batch reactor: Application to exothermic reactions in multiphase reactor. J. Loss Prev. Process Ind. 43, 147–157. https://doi.org/10.1016/j.jlp.2016.05.011

Ramírez-Camacho, J.G., Carbone, F., Pastor, E., Bubbico, R., Casal, J., 2017. Assessing the consequences of pipeline accidents to support land-use planning. Saf. Sci., Risk analysis and land use planning: managing safety on the short and long range 97, 34–42. https://doi.org/10.1016/j.ssci.2016.01.021

Rathnayaka, S., Khan, F., Amyotte, P., 2011. SHIPP methodology: Predictive accident modeling approach. Part I: Methodology and model description. Process Saf. Environ. Prot. 89, 151–164. https://doi.org/10.1016/j.psep.2011.01.002

Saada, R., Patel, D., Saha, B., 2015. Causes and consequences of thermal runaway incidents—Will they ever be avoided? Process Saf. Environ. Prot., Bhopal 30th Anniversary 97, 109–115. https://doi.org/10.1016/j.psep.2015.02.005

Spicer Thomas O., Willey Ronald J., Crowl Daniel A., Smades Wendy, 2013. The safety and chemical engineering education committee—broadening the reach of chemical engineering process safety education. Process Saf. Prog. 32, 113–118. https://doi.org/10.1002/prs.11594

Trávníček, P., Kotek, L., Junga, P., Vítěz, T., Drápela, K., Chovanec, J., 2018. Quantitative analyses of biogas plant accidents in Europe. Renew. Energy 122, 89–97. https://doi.org/10.1016/j.renene.2018.01.077

Vernières-Hassimi, L., Leveneur, S., 2015. Alternative method to prevent thermal runaway in case of error on operating conditions continuous reactor. Process Saf. Environ. Prot. 98, 365–373. https://doi.org/10.1016/j.psep.2015.09.012

Vernieres-Hassimi, L., Assoudi-Baikari, R.E., Abdelghani-Idrissi, M.-A., Mouhab, N., 2016. New Analytical Method for Maximum Temperature Assessment in an Exothermic Tubular Chemical Reactor. Chemical Engineering Communications 203, 174–181. https://doi.org/10.1080/00986445.2014.973943

Vernières-Hassimi, L., Dakkoune, A., Abdelouahed, L., Estel, L., Leveneur, S., 2017. Zero-Order Versus Intrinsic Kinetics for the Determination of the Time to Maximum Rate under

Adiabatic Conditions (TMRad): Application to the Decomposition of Hydrogen Peroxide. Ind. Eng. Chem. Res. 56, 13040–13049. https://doi.org/10.1021/acs.iecr.7b01291

Wu, D., Qian, X., 2018. Experimental study on the thermal runaway of hydrogen peroxide with in-/organic impurities by a batch reactor. J. Loss Prev. Process Ind. 51, 200–207. https://doi.org/10.1016/j.jlp.2017.12.012

Zhu, Y., Chen, Y., Zhang, L., Li, W., Huang, B., Wu, J., 2015. Numerical investigation and dimensional analysis of reaction runaway evaluation for thermal polymerization. Chem. Eng. Res. Des. 104, 32–41. https://doi.org/10.1016/j.cherd.2015.07.017

Graphical abstract