



Illustration of Typical Scenarios of Fire and Explosion Accidents Caused by Runaway Reactions to Support the Implementation of Risk Assessment in Small and Medium Enterprises

Yoshihiko Sato*, Yukiyasu Shimada, Haruhiko Itagaki

National Institute of Occupational Safety and Health, Japan, 1-4-6 Umezono, Kiyose, Tokyo, Japan

sato-yoshihiko@s.jniosh.johas.go.jp

Unintended chemical reactions involving handled substances are often less understood compared to those involving flammable substances. As a result, risk assessment and corresponding risk reduction measures (hereafter referred to as "RA") may be insufficient in addressing the hazards associated with fire and explosion accidents caused by unintended reactions. Furthermore, conducting effective RA requires extensive knowledge and experience specific to the target process. However, small and medium-sized enterprises (SMEs) often face challenges in identifying and implementing appropriate risk reduction measures due to limited expertise and experience. One practical approach to assisting SMEs is to provide typical scenarios of critical events, such as runaway reactions, along with corresponding risk reduction measures.

Additionally, identifying and prioritizing the most probable scenarios from among the typical cases can help SMEs focus on the most relevant risk reduction measures. To facilitate RA implementation in SMEs, this study developed and consolidated typical fire and explosion accident scenarios caused by runaway reactions into a single scenario diagram. Moreover, past incidents of fires and explosions triggered by runaway reactions were analyzed and mapped to these typical scenarios, allowing the identification of frequently occurring patterns. Risk reduction measures are also provided for the most recurrent scenarios to support effective risk reduction efforts.

1. Introduction

Since 2011, Japan has experienced a series of severe accidents at large-scale chemical plants due to fires and explosions triggered by unintended chemical reactions. A common factor contributing to these accidents was a lack of sufficient risk, primarily stemming from an inadequate understanding of the chemical substances involved (Cabinet Secretariat et al., 2014).

A study by the U.S. Chemical Safety Board (CSB) on accident statistics related to reactive hazards found that more than 60% of reactive accidents for which causal information was available involved inadequate management systems for identifying or evaluating the hazard (US CSB, 2002). The study also noted that while hazard assessment methods exist for identifying dangerous reaction scenarios, they are not specifically designed for reaction hazards and do not adequately address how to manage the unique aspects of reactive hazards (US CSB, 2002).

Unintended chemical reactions involving handled substances are often less understood compared to those of target flammable substances. Consequently, risk assessment and risk reduction (hereinafter referred to as "RA") may be insufficient in addressing the risk of fire and explosion accidents caused by unintended reactions. Therefore, strengthening the implementation of RA is essential for preventing such accidents. Several evaluation methods have been developed to assess hazards associated with abnormal chemical reactions. Among these, two widely recognized methods tailored for small and medium-sized enterprises (SMEs) are The Preliminary Screening Method for Chemical Reactivity Hazards (developed by the Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers (AIChE)): This checklist-based approach helps identify the presence of reactivity hazards, requiring further in-depth assessment for hazardous processes. The

CCPS Chemical Reactivity Evaluation Tool (developed by the Reactivity Management Roundtable (RMR) of AIChE) This tool follows a “what-if” approach, posing questions to identify scenarios in which reactivity hazards may occur. To effectively implement reasonable risk reduction measures, accident scenarios, must be carefully considered—similar to the CCPS Chemical Reactivity Evaluation Tool. However, there is limited information available to support the structured development of accident scenarios based on pre-defined questions. Since SMEs often lack sufficient resources (e.g., skills, expertise, and technological capabilities) to conduct comprehensive hazard evaluations, providing typical scenarios and risk reduction measures for critical events (e.g., runaway reactions) could help them identify risk and implement appropriate risk reduction measures. To facilitate the proper implementation of RA for unintended reactions, it is crucial to extract and prioritize high-probability scenarios from among representative cases. One way to achieve this is by analyzing past incidents of fires and explosions caused by runaway reactions and mapping them to pre-defined typical scenarios. We considered extracting highly likely scenarios by tracing past cases of fires and explosions caused by runaway reactions to the typical scenarios we developed. If certain scenarios appear frequently, it is reasonable to classify them as high-priority accident scenarios, which should be the focus of risk mitigation efforts. Therefore, in this study, we examined past cases of fires and explosions caused by runaway reactions, matched them with representative scenarios, and identified the most recurrent ones to establish priority for risk reduction measures.

2. Development of typical scenarios (scenario diagram) for runaway reactions

Runaway reactions, which typically occur in batch or semi-batch processes due to an imbalance between heat generation and heat removal within the reaction system, were the focus of this study. Various typical scenarios related to runaway reactions were identified using findings from Fault tree analysis (FTA) (Rajagopal and Jain Col, 1994; Kao and Hu, 2002; Banerjee, 2003), event tree Analysis (ETA) (Ka and Hu, 2002), hazard and operability (HAZOP) study (Crawley and Tyler, 2015), bow-tie analysis (Paltrinieri and Khan, 2016) and cause-and-effect diagrams (Coker, 2007) applied to past batch operations, which are often used as logical scenario identification methods in chemical process safety assessment,. These selected scenarios were integrated into a single scenario diagram. For each identified scenario, examples of risk reduction measures were considered and incorporated into the scenario diagram. Additionally, past cases of fires and explosions resulting from runaway reactions were examined to refine the scenario development. For each identified scenario, examples of risk reduction measures were considered and incorporated into the scenario diagram. Risk reduction measures were classified according to the multiple protection concept (AIChE/CCPS, 2008), which consists of (A) containment and control, B) preventive safeguards, C) mitigative safeguards, and D) detection methods. Furthermore, the order of implementation and reliability of these risk reduction measures were structured according to occupational health and safety standards (OHSAS 18001:2007, 2007, OHSAS 18002:2008, 2008) as follows: (a) inherent safety measures, b) engineering controls, c) administrative controls, and d) personal protective equipment.

Figure 1 presents an excerpt from the scenario diagram. The initiating event for development is the breakdown of thermal equilibrium, where the heat generated by the reaction exceeds the heat removed from the reaction system. The sequence of events leading to accidents is summarized as follows:

- (i) Thermal Equilibrium Breakdown: An imbalance between the heat generation and heat removal increases both the temperature and gas generation rate in the system as the reaction progresses. The resulting pressure rise in the reactor may cause structural failure, potentially leading to reactor damage. A significant temperature increase may also ignite the reactor's contents.
- (ii) Reactor Failure and Its Consequences: If the reactor ruptures, shock waves and fragments may be generated. Fires and explosions can occur if the released material is flammable. If the material is toxic, its release can pose significant risks to health and the environment.
- (iii) Root Causes of imbalance in heat generation and removal: An increase in the exothermic rate or a decrease in the cooling rate may cause thermal runaway. Possible causes of an increased exothermic rate include Incorrect reactant temperature, Uncontrolled addition of reactants, Reactant accumulation, Hot spot formation, and Re-stirring after two-phase separation of reaction contents. The causes of the reduced cooling rate may include failure of mixing and Reduced cooling efficiency. Each failure mechanism (e.g., “Reactant temperature too high” in Figure 1) expands to include both operational failures and equipment-related failures.

To effectively implement RA for fire and explosion prevention, it is crucial to systematically identify all possible runaway reaction scenarios. However, exhaustive scenario identification requires extensive expertise and process-specific knowledge. In cases where SMEs or operators lack sufficient knowledge and experience, the typical runaway reaction scenarios illustrated in the scenario diagram may serve as a reference. It is important to note that this scenario diagram presents only common scenarios and does not encompass all possible cases.

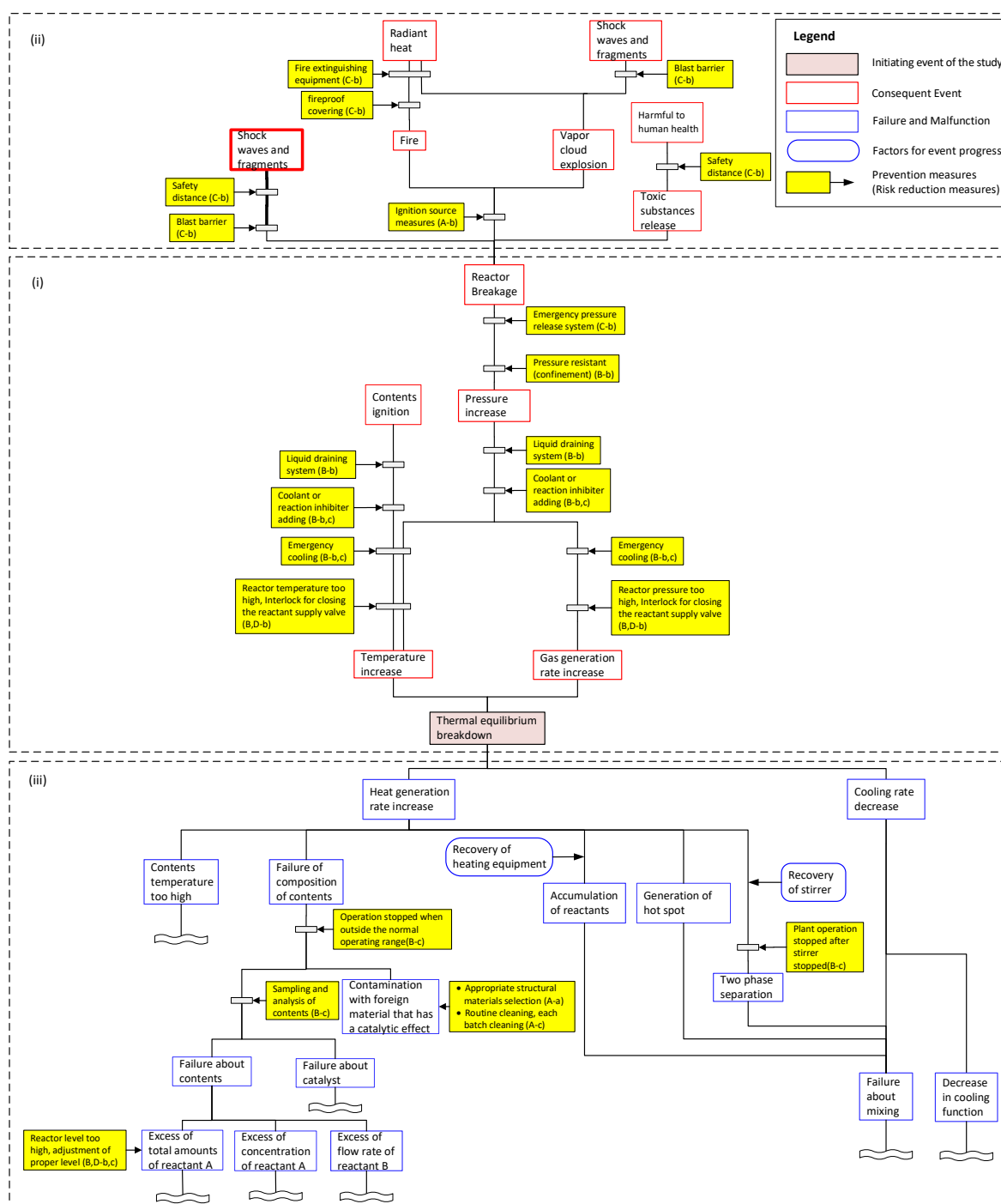


Figure 1: Developed scenario diagram (excerpt).

3. Extraction of frequently occurring scenarios from past cases

Using the developed scenario diagrams, we identified frequently occurring scenarios in the past of fire and explosion accidents caused by runaway reactions. These frequent scenarios were extracted by analyzing past accident cases where accident scenarios had already been investigated. The accident cases used for this analysis were sourced from the Relational Chemical Accident Database (RISCAD) (AIST, 2002), which includes accident data analyzed using progress flow analysis (PFA) (Wada, 2014). Additionally, cases of fires and explosions caused by runaway reactions were documented in the "Handbook of Chemical Substance and Plant Accident Examples" (Tamura, 2006) were considered. A total of 27 accident cases were included in this study.

However, since multiple causes were often associated with a single accident, each contributing scenario was traced separately. As a result, The total number of scenarios related to the cause of the imbalance between heat generation and heat removal was 32. When multiple loss events occurred in a single case, each event was also traced separately, leading to a total of 29 scenarios that described the progression from heat generation and heat removal imbalances to accidents. The scenarios outlining the cause of heat generation and heat removal and the progression from the imbalances are presented in Tables 1 and 2, respectively.

Table 1: Scenarios from cause to imbalance between heat generation and heat removal

No.	Scenario	Number of events
1	Stirrer malfunction → Poor mixing → Failure about mixing → Cooling rate decrease → Thermal equilibrium breakdown	6
2	Failure of stirrer → Poor stirring → Failure about mixing → Two-phase separation → Recovery of stirrer → Heat generation rate increase → Thermal equilibrium breakdown	4
3	Failure of stirrer → Poor stirring → Failure about mixing → Cooling rate decrease → Thermal equilibrium breakdown	2
4	Refrigerant supply valve/pump malfunction → Refrigerant shutdown/low flow → Decrease in cooling function → Cooling rate decrease → Thermal equilibrium breakdown	2
5	Failure of refrigerant supply pump → Refrigerant supply pump stops → Refrigerant stops/flow rate is low → Decrease in cooling function → Cooling rate decrease → Thermal equilibrium breakdown	2
6	Heating medium temperature too high → Jacket temperature too high → Contents temperature too high → Heat generation rate increase → Thermal equilibrium breakdown	2
7	Catalyst supply too high/low → Failure about catalyst → Failure of the composition of contents → Heat generation rate increase → Thermal equilibrium breakdown	1
8	Catalyst degradation → Reaction rate decrease → Accumulation of reactants → Heat generation rate increase → Thermal equilibrium breakdown	1
9	Failure of stirrer → Poor stirring → Failure about mixing → Accumulation of reactants → Heat generation rate increase → Thermal equilibrium breakdown	1
10	Heat medium supply valve malfunction → Incorrect closing of heat medium supply valve → Insufficient heating of contents → Contents temperature too low → Reaction rate too low → Accumulation of reactants → Heat generation rate increase → Thermal equilibrium breakdown	1
11	Contamination with foreign material that has a catalytic effect → Failure of composition of contents → Heat generation rate increase → Thermal equilibrium breakdown	1
12	Refrigerant supply valve malfunction → Refrigerant supply valve closes incorrectly/over-closes → Refrigerant stops/flow rate too low → Decrease in cooling function → Cooling rate decrease → Thermal equilibrium breakdown	1
	Other scenarios	8

The scenarios leading to the breakdown of thermal equilibrium—the balance between heat generation and dissipation—are diverse. Among them, a significant number of cases involved a reduction in the cooling rate due to insufficient stirring of the reactor contents caused by stirrer malfunction or failure (e.g., stirrer stoppage or delayed activation) (Scenarios Nos. 1 and 3). Additionally, some scenarios involved stirring interruption due to stirrer failure, followed by reactivation after two-phase separation of the reactor contents (No. 2). The most frequently occurring scenario was Scenario No. 2, in which stirring was stopped due to stirrer failure or malfunction and subsequently restarted after the two-phase separation of the reactor contents, leading to rapid heat generation.

In total, 14 scenarios (more than 40% of the 32 scenarios) were attributed to stirrer failure or malfunction, highlighting its significance as a leading cause of thermal runaway. Additionally, in five scenarios (Nos. 4, 5, and 12), a reduction or stoppage of refrigerant flow—caused by—failure or malfunction of the refrigerant supply valve or pump—resulted in a decreased cooling rate. Given the frequency of these scenarios in past incidents, they should be prioritized as potential future accident risks, and risk mitigation measures should be implemented accordingly.

Regarding accident outcomes, most scenarios ultimately led to fires and explosions triggered by the ignition of released combustibles, or Shock waves and structural fragmentation due to reactor breakage (Scenarios Nos. 1-4, 6, 24 out of 29 total scenarios). This sequence of events aligns with established runaway pathways

(AIChE/CCPS, 1995; Barton and Rogers, 1997; Stoessel, 2020), reinforcing the necessity of comprehensive safety measures for this process.

Table 2: Scenarios leading to accidents after an imbalance between heat generation and heat removal

No.	Scenario	Number of events
1	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Vapor cloud explosion	9
2	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Fire	7
3	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Shock wave generation	3
4	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Shock wave and fragment generation	3
5	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage	3
6	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Fragment generation	2
7	Thermal equilibrium breakdown → Temperature increase → Contents ignition	1
8	Thermal equilibrium breakdown → Temperature and gas generation rate increase → Pressure increase → Reactor breakage → Toxic substances release	1

Figure 2 illustrates a scenario diagram of the most frequently occurring runaway reaction (Nos. 1-3 in Table 1 and Nos. 1-4 and 6 in Table 2). Risk reduction measures applicable to each scenario are presented in Figure 2. To prevent the progression of these frequently occurring scenarios, it is essential to implement risk reduction measures based on the multiple protection concept. These measures must be selected by evaluating both technical feasibility and cost considerations to ensure that the target risk level is effectively achieved. However, determining appropriate risk reduction measures requires specialized knowledge, which can be challenging for individuals or organizations with limited technical expertise. In such cases, the examples of risk reduction measures provided in this study can serve as valuable reference points when developing mitigation strategies for runaway reactions. Nevertheless, these examples should be treated only as general guidance. Each risk assessment implementer must design scenario-specific risk reduction measures based on the process characteristics and hazardous properties of the handled substances to ensure effective hazard mitigation.

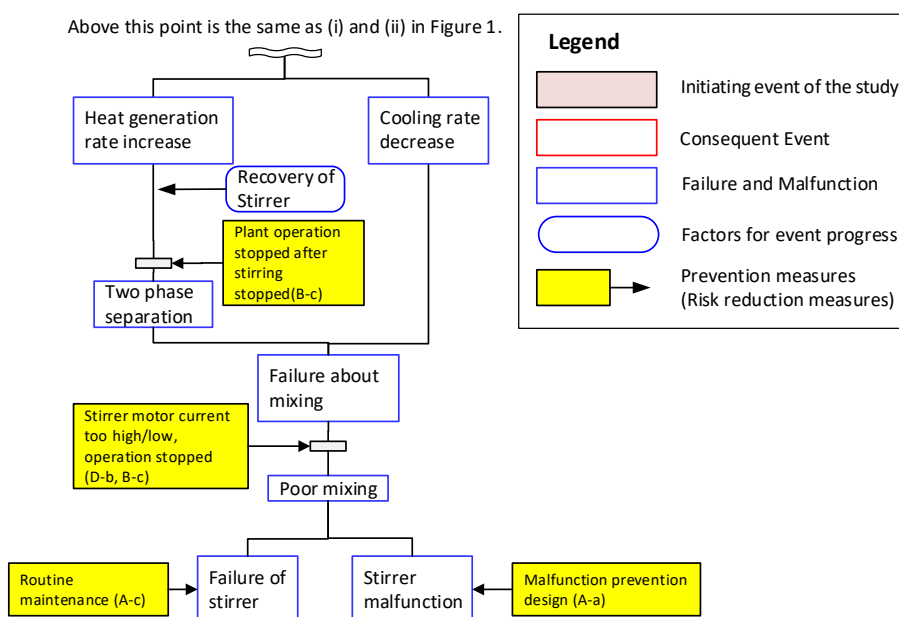


Figure 2: Scenario diagram with excerpts of frequently occurring scenarios.

4. Conclusions

To facilitate the effective implementation of the RA for unintended chemical reactions, this study compiled typical runaway reaction scenarios into a structured scenario diagram. By utilizing these scenario diagrams, frequently occurring scenarios observed in past cases of fires and explosions incidents caused by runaway reactions were identified. Additionally, examples of risk reduction measures were provided for these high-risk scenarios. These scenario diagrams and risk reduction measure examples are expected to serve as valuable tools for risk assessment and mitigation, particularly in cases where organizations lack sufficient expertise or experience in conducting detailed RA. By leveraging these resources, industries can enhance their ability to identify potential hazards and implement effective safety measures to prevent accidents.

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