International Journal of Safety and Security Engineering
Vol. 15, No. 9, September, 2025, pp. 1949-1959
Journal homepage: http://iieta.org/journals/ijsse

Quantitative Assessment of Thermal Runaway Risk in a Chemical Reactor: Hybrid Approach

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https://doi.org/10.18280/ijsse.150918

Received: 19 August 2025
Revised: 19 September 2025
Accepted: 27 September 2025
Available online: 30 September 2025

Keywords:
thermal runaway, exothermic chemical reaction, polymerisation reaction, HAZard and OPerability analysis, fault tree analysis, event tree analysis, cost-benefit analysis

ABSTRACT

Thermal runaway of a chemical process is a dangerous phenomenon that threatens human life, equipment, installations, and the environment. The aim of our work is to propose a methodology for analyzing and quantitatively assessing the risk of thermal runaway in a polymerization reactor. Firstly, HAZard and OPerability analysis (HAZOP) is used to determine the most critical deviations likely to occur in the polymerization reactor under study and leading to the thermal runaway phenomenon. The various accident sequences are determined and evaluated using event tree analysis (ETA). The causes of the failure of safety barriers implemented in the reactor to prevent the runaway phenomenon are determined using fault tree analysis (FTA). Finally, an economic analysis is carried out to show the economic impact of safety failure barriers on the company. Application results of the proposed methodology show its relevance as a decision-making tool for good industrial risk management. The novelty of this hybrid approach lies in its systematic workflow. Qualitative identification (HAZOP) directly informs quantitative frequency estimation (ETA), which in turn relies on detailed reliability analysis (FTA) to assess safety barrier performance. This integrated methodology not only provides a quantitative risk frequency but also identifies the most critical safety barriers and offers an economic rationale for investment decisions through cost-benefit analysis (CBA), thereby bridging the gap between technical risk assessment and managerial decision-making

1. INTRODUCTION

Insufficient control of chemical processes involving hazardous substances can lead to the release of products that may be flammable, toxic, or explosive, threatening people, equipment, and the environment. Flixborough, Seveso, Bhopal, and other major accidents are disasters with extremely serious consequences that marked the history of the chemical industry. One of the most dangerous phenomena in the chemical industry is thermal runaway risk. Thermal runaway in chemical reactors remains a critical process safety concern. Approximately 120 journal articles per year over the last decade have included thermal runaway as a keyword [1]. Thermal runaway involves the loss of temperature control in a chemical process. This causes the reaction medium to heat rapidly, leading to serious consequences.

Chemical process safety is therefore a major concern for the chemical industry. The thermal runaway phenomenon was studied in relation to various themes, such as feedback and database exploration, experimental methods use, polymers and reactors, digital simulation, and risk analysis methods combination. In the feedback field and basic data exploration, several works were presented [2]. Analysed 169 events that occurred in the chemical industry in France between 1974 and 2014, which were collected and selected from the ARIA database. A quantitative analysis based on frequency and consequence analysis was established, and this study showed that 25% of these events were caused by thermal runaway risk [3]. Analysed accidents involving thermal runaway reactions in the chemical industry that occurred in France between 1988 and 2013, showing that these events were mainly associated with polymerisation and decomposition reactions [4]. Studied 271 thermal runaway incidents in the Chinese chemical industry between 1984 and 2019. The results obtained show that most runaway incidents are linked to the production process, which remains sensitive to operators' behaviour, equipment condition, and environment. According to this study, there are many causes of runaway, including thermal and physical causes, as well as human, organisational, and material causes. In the study by Olivares et al. [5], data relating to accidents caused by thermal runaway risk in the biodiesel industry during the period 2003 to 2013 were developed. According to this study, the accident process follows three stages, namely, accident causes, safety measures, and finally accident consequences [6]. Established modelling using a deterministic and probabilistic approach. The results of applying this methodology to a storage tank containing highly hazardous chemicals show a significant difference between conventional quantitative analysis and the dynamic failure assessment approach. Several works were presented relative to the non-linear prediction theme [7]. Obtained data useful for designing and developing lithium batteries with safety features against thermal runaway risk, as well as the development of an effective thermal management system to prevent this phenomenon initiation. Similarly, research [8] studied the thermal runaway scenario of a styrene polymerisation reaction using extended Kalman observation (EKO) to provide online estimates of reaction parameters. According to this study, the use of the EKO algorithm helps in the safe control of chemical reactions. A brief review of classical thermal runaway prediction criteria was proposed by Yang et al. [9] to distinguish between runaway and non-runaway states of reactors. The proposed approach is relevant to three research areas, namely, process safety assessment, process monitoring optimisation, and process control. In the previous study [10], the prediction of thermal runaway scenarios was developed in a semi-batch reactor where two operating modes were considered. In the first case, reactants are charged and preheated to avoid accumulation, while in the second case, only the heat produced by the reaction heats the reactor. Some of the work concerned the use of experimental methods [11], which adopted calorimetric analysis to quantify the risk of runaway reaction of styrene in contact with a series of contaminating substances. One of the possible causes of runaway risk is contamination of styrene monomer by incompatible species. On the other hand, Zhang et al. [12] investigated the synthesis of three nitro 1, 2, 4 triazole one (NTO) compounds using differential scanning calorimetry (DSC). The results showed that heat release in the nitrification process is mainly centred in the feed phase. It is therefore essential to control the feed rate to ensure safe dosing. On the other hand, Cui et al. [13] were interested in combining experimental and theoretical methods to explore in depth the characteristics of thermal hazard. Bulk polymerisation was studied using a combination of thermodynamic and theoretical kinetic methods. Study results showed that the presence of an initiator presents an undesirable thermal risk. The thermal runaway phenomenon was studied by determining the secondary products profile caused by operating conditions drift [14]. In the risk prioritisation context [15], a kinetic model using reaction and a set of parameters, such as temperature, heat released by reaction, and reaction maximum speed were studied. The aim of this study is to measure online thermal runaway risk associated with an exothermic chemical reaction by controlling the temperature inside the reactor. The fuzzy prioritisation process was used by Wang et al. [16] to quantitatively assess thermal runaway risk in lithium-ion batteries (LIBs). This study allowed obtaining parameter data through experiments and combining it with theoretical methods to determine risk. In the numerical simulation field, Berdouzi et al. [17] used dynamic simulation (Aspen Plus Dynamics) to identify hazardous scenarios that could lead to accidents. Several studies involved the use of matrix methods. Xu et al. [18] assessed severity and probability of thermal runaway risk by calculating typical safety reaction parameters. Among studies that focused on polymers and micro reactors, Allen [19] highlighted several materials and polymers as well as appropriate methods of use to prevent thermal runaway risk in lithium-ion systems, while assessment and comparison of thermal runaway risk occurring in stirred tank reactors and micro reactors, using a cloud model, was developed by Chen et al. [20]. This study's results showed that damage radius can characterise thermal runaway severity, and that application of micro reactors can considerably reduce the severity of thermal runaway risk, which was reflected in the benzene nitration process. Finally, several studies were carried out on the use and combination of risk analysis methods for assessing and preventing thermal runaway in chemical processes. Rathnayaka et al. [21] used an approach based on a combination of fault tree and event tree methods to assess safety in an installation (LNG). The main results provided by this work are a description of the accident, identification of potential consequences, and finally identification of possible causal factors. On the other hand, in the previous study [22], the event tree method was used for potential accident identification scenarios, and then, based on fault tree and possible fault data, final state probabilities were estimated. A new approach called HAZOP4.0 was developed by Mokhtarname et al. [23]. This approach is intended for complex processes and is based on the fusion of a mathematical modelling tool with the conventional HAZard and OPerability analysis (HAZOP) method, in order to evaluate the failure amplitude and duration. An approach based on a combination of analysis methods, namely, fault tree, event tree, and bow-tie, was developed by Attwood et al. [24] for the study and comparison of accident scenarios caused by thermal runaway risk. The aim of this work is to propose a methodology for analysing and quantitatively assessing thermal runaway risk in a polymerisation reactor, based on a risk analysis approach. This hybrid approach involves a combination of risk analysis methods. The HAZOP method is used to determine causes and consequences of various deviations in polymerisation reactor operating parameters that could lead to thermal runaway. Accident scenarios are developed and estimated using the event tree method. The fault tree method is used to determine causes and estimate the failure probability of safety barriers. Finally, in order to improve the performance of these barriers, an economic (cost-benefit) analysis is carried out. While each individual method (HAZOP, ETA, FTA, CBA) has been extensively applied in process safety, their integrated use as a hybrid methodology offers distinct advantages for comprehensive risk assessment. The proposed approach provides a systematic workflow where qualitative identification directly feeds quantitative frequency estimation, which in turn relies on detailed safety barrier performance. This sequential integration avoids analytical redundancy by ensuring that each step addresses a specific aspect of risk: scenario identification, consequence development, barrier reliability, and economic prioritization.

The remainder of this article is organised as follows: the next section presents the proposed methodology. Section 3 deals with the application of our approach to a polymerisation reactor. Section 4 details the thermal runaway risk assessment, Section 5 the economic analysis, Section 6 discusses results, and Section 7 conclusion.

2. METHODOLOGY

2.1 Principles of the hybrid approach

The core rationale of the proposed hybrid methodology lies in the sequential and complementary application of well-established risk analysis tools, each addressing a specific facet of the risk assessment process. The logical sequence is designed to transform qualitative hazard identification into a quantitative risk estimate, and finally into an economic decision-making framework. This structured progression eliminates redundancy by ensuring that each method builds upon the output of the previous one, without revisiting or duplicating its core analysis.

- HAZOP serves as the qualitative foundation. Its strength is the systematic, creative identification of potential deviations and hazardous scenarios. However, it is inherently limited in providing quantitative risk metrics.
- Event tree analysis (ETA) provides the quantitative scaffolding. It takes the initiating events identified by HAZOP and logically develops the sequences of events that lead to various consequences. Its effectiveness, however, depends entirely on accurate probabilities for the success or failure of the safety barriers within the tree.
- Fault tree analysis (FTA) acts as the reliability engine for the ETA. It is specifically employed to calculate the probability of failure (P_jP_j) for each complex safety barrier (e.g., the inhibition system) featured in the event tree. By decomposing a barrier's failure into its basic components and human failures, FTA provides the rigorous, quantitative inputs that ETA requires.
- Cost-benefit analysis (CBA) constitutes the decision-support layer. It utilizes the final risk frequencies (output of ETA) and consequence severities (in monetary terms) to evaluate the economic efficiency of safety barriers. It answers the pragmatic question of where limited resources for safety improvements should be prioritized.

The interfaces between these methods are explicit and critical:

1. The Initiating Events and List of Safety Barriers from HAZOP define the starting point and the branching nodes for the ETA.
2. The Probability of Failure for each safety barrier, required to solve the ETA, is calculated through a dedicated FTA for that barrier.
3. The Resulting Accident Frequencies for each consequence scenario (output of ETA) and the Monetized Consequence Costs are the essential inputs for the CBA to compute the benefit-cost ratios (BCR).

This flow of information (HAZOP, ETA-FTA, CBA) ensures complementarity and avoids overlap. Each tool has a distinct, non-replaceable role within the integrated framework.

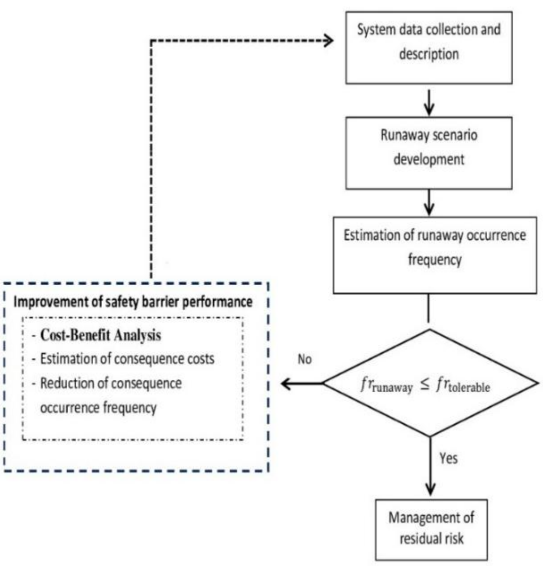


Figure 1. Workflow of the proposed hybrid methodology for quantitative thermal runaway risk assessment

The diagram Figure 1 illustrates the sequential integration and logical interfaces between the HAZOP, ETA, FTA, and CBA methods, ensuring a non-redundant analysis where the output of one stage becomes the input of the next.

2.2 Development of runaway scenarios

HAZOP method is particularly useful for examining thermal-hydraulic systems, where parameters such as flow rate, temperature, pressure, level, concentration, etc., are particularly important for installation safety. HAZOP study is a systematic and structured technique used to identify potential hazards and evaluate problems associated with systems [25]. HAZOP is based on the theory that dangerous events result from deviations from design and operational targets. Such deviations are easily identified using a set of “guide words” as a systematic list of divergent perspectives [26]. The study includes HAZOP as a qualitative risk assessment tool for systematic identification of hazardous situations and operational issues that may arise from deviations in expected behavior, and could result in unintended (abnormal) consequences [27] The main outcomes are tables listing critical deviations (e.g., "HIGH TEMPERATURE"), their causes, immediate consequences, and existing safety barriers designed to prevent or mitigate them.

2.3 Runaway events frequency estimation

To begin with, and in order to estimate the occurrence frequency of the runaway scenario, it is important to systematically list all ‘initiating events’ causes that could be at the origin of this scenario. These events are determined by the HAZOP method and can be external events, material failures (linked to equipment), or human failures. Initiating events are estimated by assigning them occurrence frequencies (or probabilities). In order to estimate the occurrence frequency of these initiating events, various estimation techniques are used, such as experience feedback, test and control operations, expert judgment, and so on. Then, safety barriers put in place to prevent, protect, and mitigate runaway risk are identified, and their failure probabilities are estimated using the FTA method. Finally, the occurrence frequency of the runaway scenario is estimated using the ETA method and Eq. (1):

$$f_i^C = f_i^I \times \prod_{j=1}^{J} P_{ij} \tag{1}$$

where:

f_i^C: Frequency of consequence C for the initiating event i.

f_i^I: Frequency of initiating event i.

P_{ij}: The failure probability of the j^{th} safety barrier protecting against consequence C of initiating event i.

The frequency calculated will be compared with the tolerable risk frequency defined beforehand to ensure that this scenario is tolerable. However, if the adverse event frequency is higher than the tolerable frequency, a risk reduction is necessary.

2.4 Safety barriers performance improvement

In order to improve the performance of safety barriers put in place to prevent, protect against, and mitigate the risk of runaway and to achieve or maintain tolerable risk, CBA for improving the performance of safety barriers is proposed. The frequencies of undesirable consequences (F(Ci)F(Ci)) from the ETA are multiplied by their estimated costs ($C_{accident}$) to determine the annualized risk cost. The reduction in this cost, achieved by improving a barrier's reliability (via a reduced of probability failure from FTA), defines the annual benefit. Comparing this benefit to the cost of improvement yields the BCR, enabling ranked investment priorities for the improvement of safety barriers performance and consequently the reduction of thermal runaway risk.

3. CASE STUDY

In order to illustrate the applicability of the proposed methodology and to estimate the occurrence frequency of runaway risk and assess the performance of safety barriers implemented to prevent and control this phenomenon, our case study focused on one of the most sensitive systems in a petrochemical complex (CP2K Skikda, ALGERIA). This is a polyethylene polymerisation reactor, which in a runaway event could have critical, even catastrophic human, material and environmental consequences [28].

3.1 Reactor description

The system is designed to produce polyethylene from ethylene. The production process involves several stages, such as treatment of raw material, activation and addition of catalyst, and polymerisation in a chemical reactor. The polymerisation reaction taking place in the reactor is exothermic and is accompanied by the release of 800 Kcal/Kg of polyethylene formed. Formation heat of polyethylene must be removed from the reactor in order to maintain the temperature of the reaction medium at an acceptable level, thus avoiding runaway risk. The main reactor operating in continuous operation is a loop-shaped pipe made up of four vertical sections joined by horizontal sections, with vertical sections having insulated jackets for cooling. Reaction heat is removed by a reactor refrigeration system, designed to both heat and cool the system. The coolant circulates through the jackets of four vertical legs of the reactor. The polymerization reactor includes several equipment items. One key component is the reactor feed system, which injects reagents including isobutene, hydrogen, ethylene, and hexene. The reactor design Figure 2 follows standard loop-reactor configurations for polyethylene production as documented in the literature [29, 30]. The specific parameters, dimensions, and safety system layouts are based on the plant's technical documentation, which provides detailed mechanical and process specifications [31].

The flow rates of these compounds are controlled by indicators and alarms (for low flow rates). The reactor also includes a device for monitoring operating parameters. The pressure in the system is monitored by means of a pressure controller indicator (PIC-16147) with indication on DCS and a pressure alarm. The temperature in the reactor is also monitored by means of a TIC-17169 controller with an indicator on DCS. A safety device is connected to the reactor, consisting of a reactor cooling system and 4 safety valves with a set pressure of 56.3 and 59.12 kg/cm^2.g. These valves are designed to ensure reactor safety in the event of an accidental or uncontrolled rise in pressure. The safety system also includes a deluge system that is triggered automatically in a fire event. A reaction inhibition system is in place to inhibit the reaction if necessary.

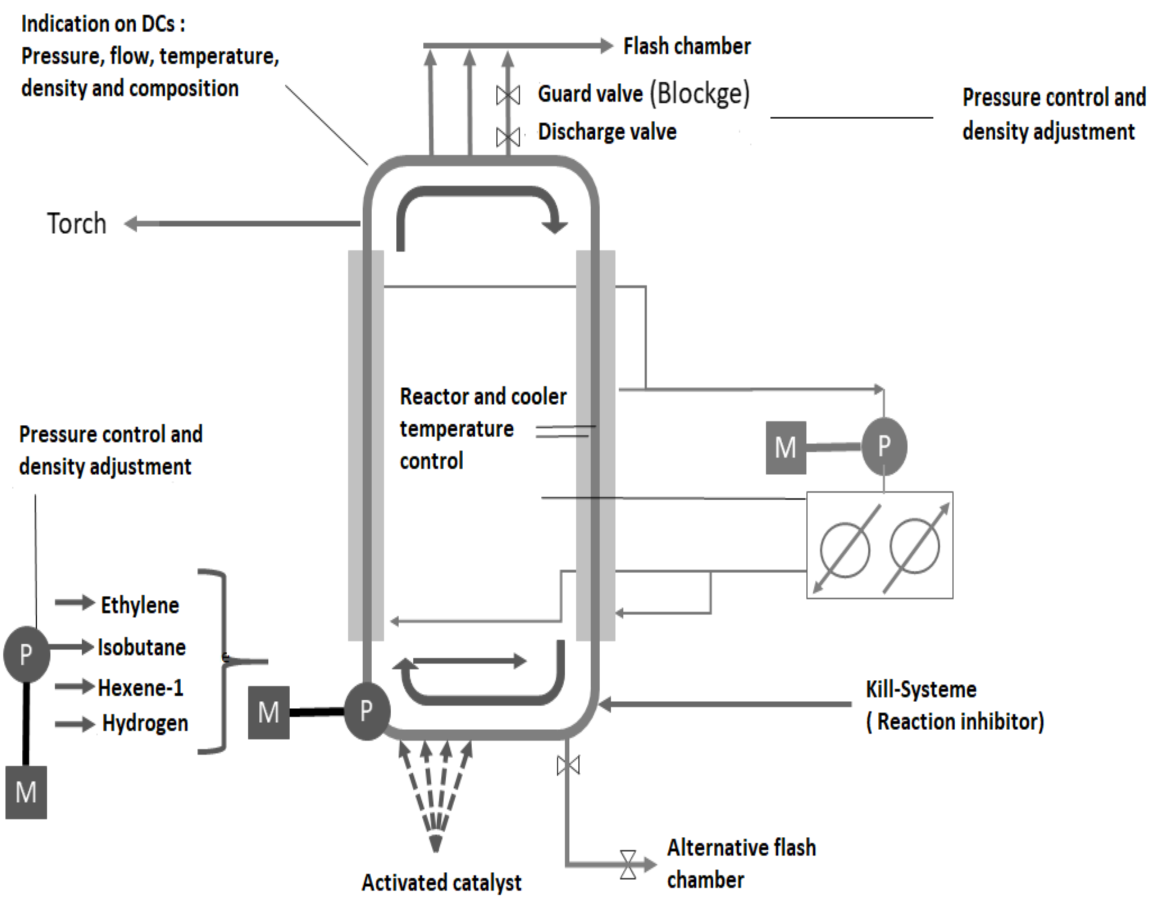


Figure 2. Schematic diagram of polyethylene polymerisation reactor [29]

3.2 Development of runaway scenarios

In the context of this work, we are interested in scenarios with the potential to cause thermal runaway phenomena and lead to dangerous situations. The company chose a value of 10^{-5}/year as the maximum tolerable frequency of accident scenarios that could cause a thermal runaway phenomenon.

An analysis using the HAZOP method is carried out to identify representative scenarios, with corresponding causes and consequences summarised in Table 1 [32, 33].

Table 1. Accident scenarios for the polyethylene polymerisation reactor

No.	Guide Word	Element	Deviation	Possible Causes	Consequences
1	HIGH	Temperature in the reactor	High temperature in the reactor	1- Loss of coolant 2- Cascade control system not correctly synchronised 3- Uncontrolled reaction 4- Polymer deposit on reactor control thermocouple (fouling)	- THH alarm and pump stop alarm triggered - Drop in coolant flow - **Runaway** - Alarm triggered and pump stopped - **Runaway**
2	LESS	Coolant flow	Less coolant flow	Coolant flow drops in the buffer tank - Electrical or pump failure - Flow restriction	High temperature in the reactor - Pump stop alarm triggered - **Runaway**
3	HIGH	Level of solids	High level of solids in the reactor	- Excessive reactivity - Catalyst too active - Insufficient isobutane flow - Decantation legs failure	**Runaway** if decantation legs clog
4	HIGH	Pressure in the reactor	Increased pressure in the reactor	- One or more settling lugs are clogged - Production too high for the number of legs in service - Obstruction on the transfer line - Cycling time too long - Leak in the product discharge valve body	- Temperature rise if the cooling system fails - **Runaway**

3.3 Consequence analysis

In order to reduce thermal runaway risk generated by the representative accident scenarios selected, several safety barriers are implemented to prevent runaway or minimise its consequences. These barriers include a chemical inhibition system, control systems, and systems for mitigating consequences by evacuation, as described in Table 2.

Table 2. Safety barriers for the polyethylene polymerisation reactor

Safety Barrier	Description (Function)
Reaction inhibition system	In the event of extreme situations (such as a shutdown of the cooling system, or insufficient output from it, or a power cut), the reaction inhibition system intervenes to kill the chemical reaction by injecting a reaction inhibitor such as water.
Reagent injection stop (Ethylene)	The Ethylene reagent injection stop system is designed to control the flow of Ethylene to the chemical reaction.
Emergency stop system	The depressurisation system and the emergency stop valve are used to empty the reactor and lower the pressure of the reaction medium in the event of a malfunction of the discharge valve, which can lead to an exponential rise in the pressure of the reaction medium and, in the event of thermal runaway.
Safety valve	In the event of an increase in pressure in the system beyond operating conditions, the safety valve intervenes. It opens to let gases escape from the reactor into the atmosphere and thus maintain the pressure in the system at normal levels.
Rupture discs	In the event of an undesirable rise in pressure in the reaction medium, the rupture disc deteriorates, releasing the excessive pressure to the atmosphere. The operation of the rupture disc is linked to that of the safety valve; between the two barriers, there is a pressure switch which, if the bursting disc opens, sends a signal to the safety valve, which will crash.

Figure 3 presents the event tree for thermal runaway scenarios initiated by cooling system failure. The tree structure shows six safety barriers in sequential order: (1) Reaction inhibition system, (2) Reagent injection stop (Ethylene), (3) Emergency stop system (depressurization), (4) Safety valve, (5) Rupture disc. Each branching point represents a binary outcome (Success/Failure) for the corresponding barrier. The four terminal consequences (C1-C4) represent progressively severe outcomes, with C4 (Runaway/Reactor rupture) requiring failure of all five barriers. The probabilities of failure of safety barriers are shown in Table 3. The various probable sequences have as their initiating event the cooling system failure leading to an increase in temperature in the reactor. The potential causes leading to failures of safety barriers are determined using the fault tree method (Figures 4 (a) and (b)).

FTA is a logical, structured process that can help determine potential causes of system failure before failures occur. In an effort to carry out FTA, firstly, undesired events and the top event need to be examined. In the determination of the top event, causes are determined by classifying faults and sub-faults.

After the build-up of the fault tree, all branches linked to and/or gates and minimal cut set (MCS) are found and evaluated for the top event [34]. A fault tree (FT) is a widely used technique for reliability assessment. Both qualitative and quantitative analyses can be executed in FT. Qualitative analysis of system FT results in a set of MCSs, which are the smallest combinations of events that lead to the occurrence of the top event (TE), i.e., the most undesired event in the system. The quantitative analysis is executed to calculate the TE occurrence probability given the probability of other events, named basic events (BEs) and intermediate events. Thus, failure data requirements of other events are important for the applicability of quantitative analysis [35].

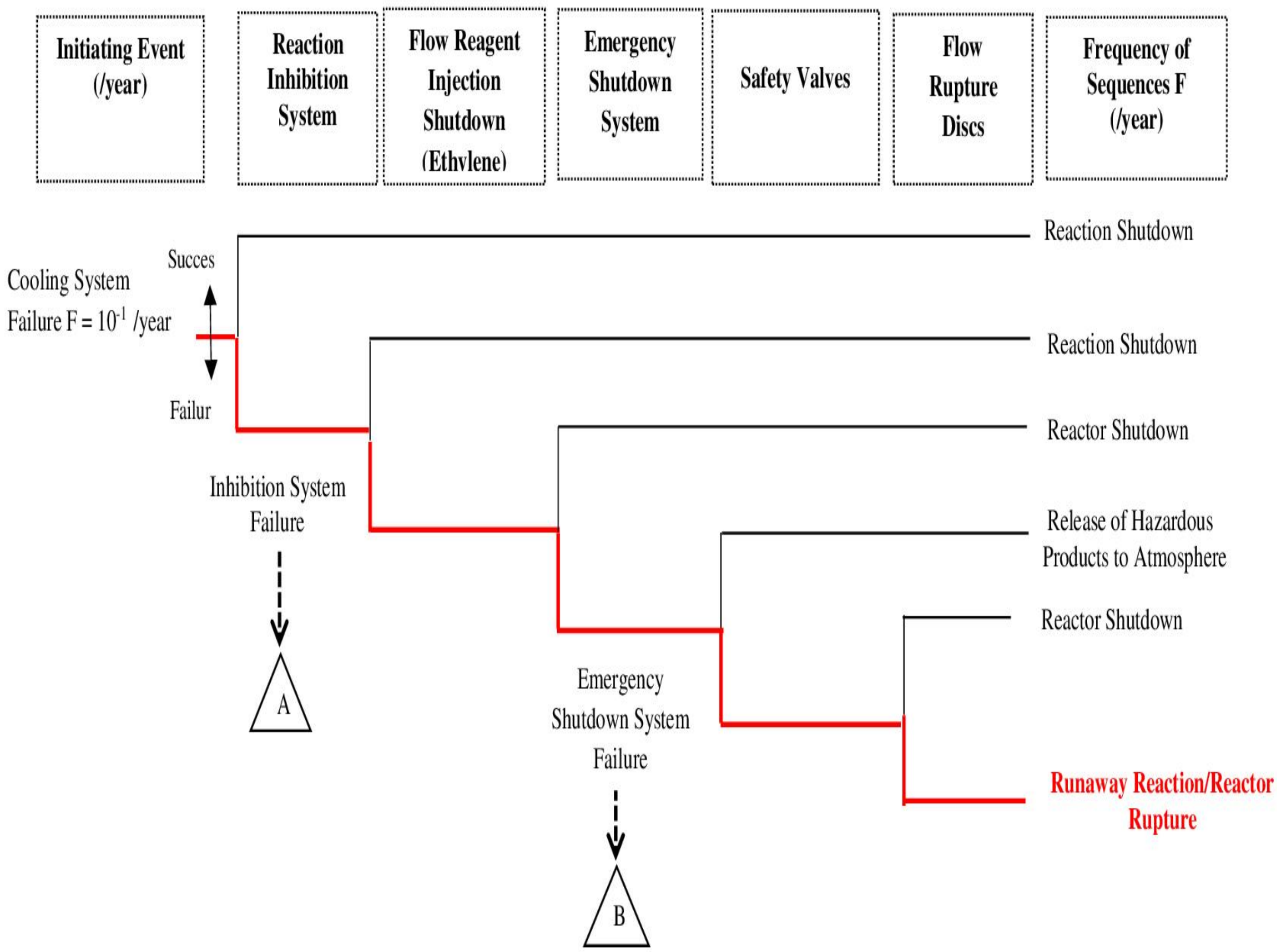
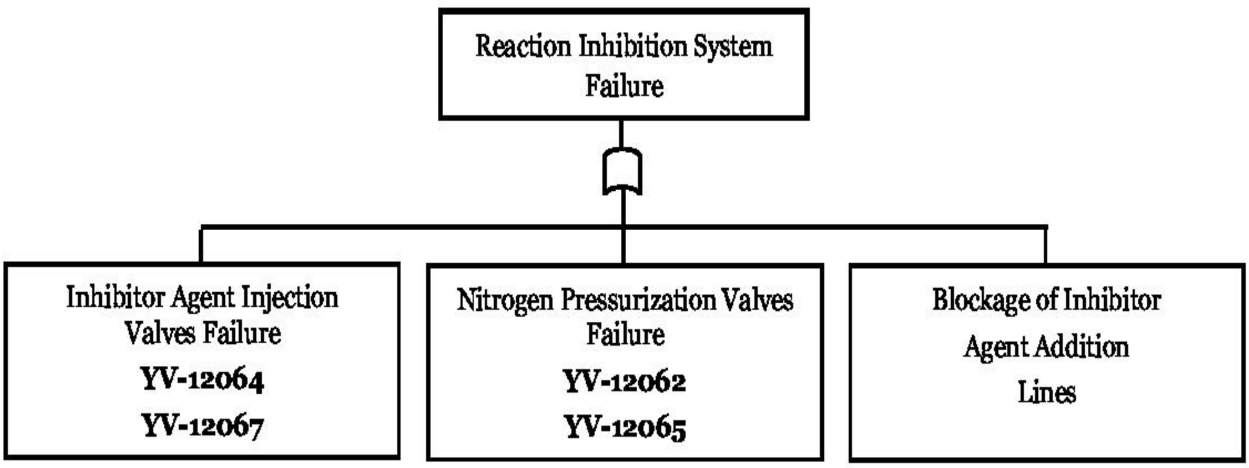


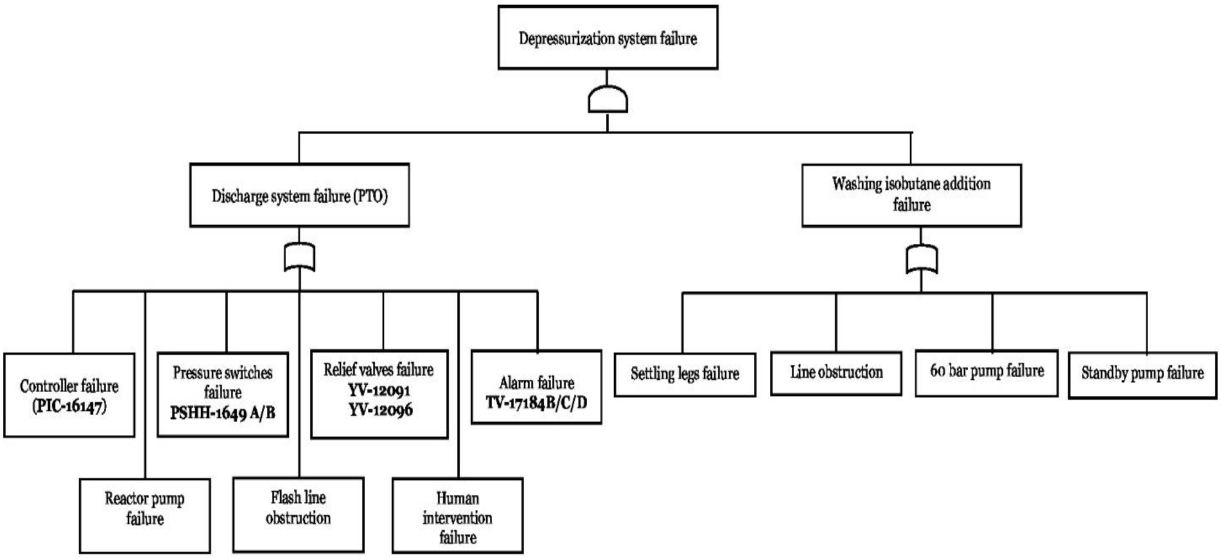
Figure 3. Event tree for thermal runaway scenarios in the polyethylene polymerisation reactor

Table 3. Safety barriers failure probability

No.	Safety Barrier	Probability of Failure
1	Reaction inhibition system	2.1 10^{-3}
2	Reagent injection system	4.5 10^{-3}
3	Emergency stop system (depressurisation)	4.75 10^{-2}
4	Safety valve	10^{-2} (ICSI)
5	Rupture disc	10^{-2}



(a)



(b)

Figure 4. (a) Failure of the reaction inhibition system; (b) Depressurisation system failure

4. THERMAL RUNAWAY RISK ASSESSMENT

To calculate occurrence frequency of thermal runaway, Eq. (1) is applied, which in our case becomes:

$$f_{Runaway} = f(EI) \times \Pi_{i=1}^{5} \qquad (2)$$

With:
$f(EI)$: Cooling system failure frequency.
P_i: Failure probability of barrier j.

Probabilities of safety barriers failure and consequences frequencies are given in Tables 3 and 4, respectively. The frequency of initiating events and failure probabilities of safety barriers are calculated using the FTA method.

In Table 5, different basic events of the two FTA developed are defined with their probabilities of occurrence.

The frequency of initiating event (failure of cooling system): 10^{-1}/year [6].

It can be seen that the 'Thermal runaway' scenario caused by failure of the cooling system is estimated to have a frequency of 4.49 10^{-12}. This scenario is considered acceptable, and to maintain this level, continuous improvement in the performance of safety barriers is required.

Table 4. Consequences frequency

Consequence	Description	Consequences Frequency (/year)
C1	Reaction stop	10^{-1}
C2	Reactor shutdown	9 10^{-2}
C3	Release of product into flare (Isobutane, hexane, Ethylene)	4.45 10^{-8}
C4	Runaway / Reactor rupture	4.49 10^{-12}

Table 5. Definition of basic events and their probabilities of occurrence

	Basic Events	Description	Probability of Occurrence
Reaction Inhibition System	Ev_1	Failure of inhibitor injection valves YV-12064 / YV-12067	5.02 10^{-3}
	Ev_2	Failure of nitrogen pressurisation valves YV-12062 / YV-12065	8.71 10^{-3}
	Ev_3	Obstruction of inhibitor addition lines	2 10^{-3}
Emergency Stop System	Ev_4	Controller failure (PIC-16147)	2.15 10^{-2}
	Ev_5	Reactor pump failure	1.13 10^{-1}
	Ev_6	Pressure switch failure PSHH-1649 A/B	7.03 10^{-3}
	Ev_7	Alarm failure TV-17184B/C/D	10^{-3}
	Ev_8	Discharge valve failure Y-12091 YV - 12096	5.02 10^{-3}
	Ev_9	Flash line obstruction	2 10^{-3}
	Ev_{10}	Human intervention failure	10^{-1}
	Ev_{11}	Decantation legs failure	10^{-3}
	Ev_{12}	Line obstruction	2 10^{-3}
	Ev_{13}	Pump failure 60 bar	1.13 10^{-1}
	Ev_{14}	Pump failure standby	1.13 10^{-1}
	Ev_{15}	Emergency stop valve failure	10^{-1}à 5.10^{-3} per valve
Safety Valve	Ev_{23}	Safety valve failure	10^{-1} à 1.10^{-3}
Rupture Disc	Ev_{24}	Rupture disc Failure	10^{-3}

5. COST-BENEFIT ANALYSIS

The approach adopted in our work to establish an economic analysis is based on two stages. The first stage consists of estimating the consequences costs generated by the occurrence of an accident due to thermal runaway, in terms of economic losses of accident scenarios (losses linked to production stoppage, equipment repair and maintenance, environmental fines, etc.). The second stage consists of introducing CBA as a parameter for estimating the annual benefit generated by improving the performance of various safety barriers put in place, leading to a reduction in accident frequency.

All monetary values in this analysis are expressed in 2023 U.S. dollars (USD) to ensure temporal consistency. Costs were derived from internal company records, vendor quotations from 2022-2023, and industry benchmarking studies. Economic losses were estimated through consultation with plant managers, safety engineers, and financial officers at the case study facility (complex CP2K Skikda, ALGERIA).

5.1 Estimation of the consequences cost

The aim of this section is to show the economic impact of the thermal runaway phenomenon in a polymerisation reactor. The development of thermal runaway can lead to different types of consequences, as indicated above (Figure 3, Table 4):

- Reaction stop: Consequence (C1)
- Reactor shutdown: Consequence (C2)
- Release of flare product: Consequence (C3)
- Runaway / Rupture: Consequence (C4)

Each type of consequence results in certain types of loss (Table 6)

Loss costs are estimated on the basis of the company's own expert opinions (Table 7).

Table 6. Losses associated with consequences

Consequences	Designation	Associated Losses
C1	Reaction stop	- Loss of production - Loss of products
C2	Reactor shutdown	- Loss of production - Loss of products
C3	Release of flare product	- Loss of raw material - Environmental fines - Decontamination - Environmental analysis
C4	Runaway / rupture	- Human injury costs - Loss of production - Material damage and reconstruction - Loss of products - Pollution

Table 7. Cost of economic losses associated with consequences

Consequence	Description	Frequency (/year)	Associated Loss (USD)	Risk Cost (USD/year)
C1	Reaction stop	10^{-1}	78.769	7.877
C2	Reactor shutdown	$9\ 10^{-2}$	708.923	638
C3	Flare product release	$4.45\ 10^{-8}$	23.359	0.001
C4	Runaway / breakdown	$4.49\ 10^{-12}$	3.564.308	0.00002

5.2 Reduction of the consequence occurrence frequency

Of many methodologies used for economic evaluation, CBA is the most common and widespread. CBA makes it possible to assess the net benefits of specific procedures or products by comparing total benefits with total costs of the procedure as a whole, expressed as a net present monetary value [36]. CBA is particularly relevant for large-scale infrastructure projects, where a systematic assessment is essential to justify investments [37, 38]. CBA is integrated to assess the economic efficiency of safety barriers. It compares the investment and maintenance costs of barriers with the benefits generated by the reduction in risk frequency.

The methodology for calculating economic benefit is based on a quantitative assessment of the reduction in frequency risk as a result of improving safety barrier performance. The annual benefit (B) represents the savings made by reducing accident frequency. It is calculated using the following Eq. (3):

$$B = \Delta F \times C_{accident} \tag{3}$$

where:

ΔF corresponds to a reduction in accident frequency expressed in occurrences per year ($year^{-1}$).

This reduction in frequency is achieved by improving maintenance policy, mainly by reducing MTTR (mean time to repair in the event of failure) of critical systems such as the inhibition system and cooling system. More effective maintenance reduces downtime of safety equipment, thereby reducing the frequency of thermal runaway.

The total cost of consequence ($C_{accident}$) represents all the economic losses associated with an accident occurrence. This cost has three main components. First, the cost of injury to operators, which includes medical and care costs, as well as costs associated with time off work for injured employees. Second, lost production cost, which is calculated on the basis of the length of time the facilities are shut down or the probability of failure of the production system. Third, environmental penalties cost, including fines and sanctions in the event of ecological damage.

The economic efficiency of each barrier is evaluated by BCR, defined as the ratio between the annual benefit generated and the total cost of the barrier (initial investment and maintenance costs). The BCR is expressed by the following Eq. (4):

$$BCR = B / \text{Total cost of barrier} \tag{4}$$

A BCR greater than 1 indicates that economic benefits exceed investment costs, thus justifying the installation or performance improvement of the safety barrier in question.

6. RESULTS AND DISCUSSION

As mentioned previously, the application of the HAZOP method enabled us to identify accident scenarios that could occur in a polymerisation reactor, as well as their causes, consequences, and safety barriers put in place to deal with these scenarios (Table 4). These scenarios are represented in the form of an Event tree (Figure 3) in order to estimate their frequency of occurrence.

The results of this analysis show that the occurrence frequency of runaway risk (4.4910^{-12}/year) is tolerable and well below the threshold set by the company (10^{-5}/year). Despite this, and in order to maintain this level of reactor safety, an economic analysis was carried out.

6.1 Interpreting economic metrics for safety decisions

The economic analysis reveals significant variation in BCR across safety barriers (Table 8). The inhibition system (BCR = 12.6) demonstrates exceptional economic efficiency, where each dollar invested yields $12.6 in risk reduction benefits. Conversely, the emergency stop system (BCR = 0.16) appears economically unattractive when evaluated solely through this lens. However, this low BCR does not imply the barrier is unnecessary. Rather, it indicates that further investment in enhancing this specific system may not be economically justifiable compared to other options. The emergency stop remains a critical safety function required by design standards and operational procedures.

Table 8. Safety barriers cost-benefit analysis

Safety Barrier	Cost (USD)	ΔFrequency (year-¹)	Annual Benefit (USD/year)	RCB
Cooling system	1.713.37	3.13 10^{-5}	8.846.154	5.2
Emergency stop system	1.4040	1.15 10^{-7}	221	0.16
Inhibition system	7.058	8.32 10^{-6}	88.923	12.6
Safety valve	26,698	4.49 10^{-10}	15	0.51

6.2 Balancing economic efficiency and safety imperatives

Process safety management requires balancing economic feasibility with safety necessity. While CBA provides valuable guidance for resource allocation, it must be applied within a broader decision-making framework that considers:

1. Regulatory compliance: Some safety measures are mandatory regardless of economic return.
2. Risk tolerance thresholds: Societal and corporate risk acceptance criteria may require additional protection.
3. Non-monetized values: Human life, environmental protection, and corporate reputation carry intrinsic value beyond financial quantification.

In practice, a multi-criteria decision approach is recommended, where BCR serves as one input among several, including technical effectiveness, reliability improvements, and alignment with safety culture objectives.

6.3 Practical implications for safety management

The hybrid methodology's key contribution is its ability to prioritize safety investments. For the studied reactor:

- **Highest priority:** Inhibition system improvements (high BCR, direct risk reduction)
- **Medium priority:** Cooling system enhancements (good BCR, preventive function)
- **Maintenance focus:** Emergency stop and safety valves (maintain current reliability rather than major upgrades)

This prioritization enables safety managers to allocate limited resources where they will have the greatest impact on both risk reduction and economic performance.

Integration of cost-benefit ratio analysis reveals significant disparities between different safety barriers, enabling a clear prioritisation of investment. The inhibition system stands out as the most cost-effective barrier, with an exceptional BCR of 12.6, meaning that each Dollar invested in this system generates 12.6 Dollars in savings in terms of accident risk reduction. This remarkable performance is explained by the relatively moderate cost of the system (7.058 USD) compared with the significant impact of its improvement on reducing accident frequency. This barrier is therefore an absolute priority for safety investment.

The cooling system, although requiring a considerable investment of 1.713.373 USD, also presents an attractive profitability with a BCR of 5.2. This performance is justified by the system's major contribution to preventing thermal runaway, generating a substantial annual profit of 8.846.154 USD. Despite its high cost, this system deserves priority attention because of its direct impact on the overall safety of the process and its ability to avoid catastrophic consequences.

In contrast, the Emergency Stop System has a particularly low BCR of 0.16, indicating that the economic benefits generated (221 USD/year) do not offset investment and maintenance costs. This suggests that, although this system remains vital for operational safety, further investment in its improvement would not be economically justified in the current context. It is therefore appropriate to maintain this system in its current operational state without committing additional resources.

The safety valves present intermediate situations with respective BCRs of 0.51. Although this ratio is below the economic break-even point of 1, it is still more favourable than that of the emergency stop system. Despite their functional importance, this equipment does not justify massive investment according to purely economic criteria, but could be the subject of targeted improvements if other technical or regulatory considerations require it.

7. CONCLUSIONS

In this study, developed and applied a hybrid methodology for quantitative thermal runaway risk assessment in a polymerization reactor. The integrated approach combines HAZOP, ETA, FTA, and CBA into a comprehensive framework. It progresses systematically from hazard identification to economic decision support. Key findings indicate:

- The thermal runaway frequency (4.49×10^{-12}/year) is well below the company's tolerable risk threshold (10^{-5}/year).
- The inhibition system represents the most cost-effective safety investment (BCR = 12.6).
- Economic analysis helps prioritize safety investments but must be balanced with regulatory and ethical considerations.

Several limitations warrant acknowledgment and suggest directions for future research:

- **Data uncertainty:** The analysis depends on reliable data and cost estimates with inherent uncertainties. Future work could incorporate sensitivity analysis or probabilistic cost modeling.
- **Static analysis:** The current approach uses static reliability data. Dynamic risk assessment methods could capture time-dependent degradation and interdependencies.
- **Simplified consequence modeling:** The economic analysis simplifies some consequence pathways. More

detailed consequence modeling, including domino effects, would enhance accuracy.

- **Human and organizational factors:** While included in this approach, these factors deserve more systematic treatment through methods like Human Reliability Analysis.

Future research directions include:

- Extending the methodology to batch and semi-batch reactors with different risk profiles.
- Integrating thermodynamic modeling to predict runaway severity under various scenarios.
- Developing software tools to automate the hybrid methodology for industrial applications.
- Incorporating resilience engineering concepts to assess system recovery capabilities.

Despite these limitations, the proposed hybrid approach provides a robust, transparent framework for quantitative risk assessment that supports both technical safety decisions and economic resource allocation in chemical process industries.

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