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# **Final degree project**

Study of Protection Strategies Against Explosions and Runaway Reactions in Compliance with Directive 2012/18/EU and Industrial Standards

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In theory, theory and practice are the same. In practice, they're not. Jan L. A. van de Snepscheut

I would like to extend my deepest gratitude to all those who have played a crucial role in the completion of this work and have supported me throughout my academic journey.

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### SUMMARY

The Final Degree Project titled "Study of Protection Strategies Against Explosions and Runaway Reactions in Compliance with Directive 2012/18/EU and Industrial Standards" addresses the critical importance of safety in the industrial sector, specifically within chemical plants. This study focuses on the prevention, protection, and mitigation of major accidents caused by runaway reactions and pressure increases in storage tanks containing hazardous substances, aligning with Directive Seveso III and other relevant industrial standards.

The document examines significant historical cases to highlight the importance of addressing all aspects of industrial production. Explosion protection strategies are evaluated using frameworks and guidelines for pressure relief device design. It further proposes the use of specific protection systems, such as rupture disks, dimensioned according to these international standards, to protect or minimize the impact of such events.

Among the key findings, the analysis highlights three notable accidents. The first is a catastrophic fire in petrochemical storage tanks, which led to a large-scale domino effect due to inadequate safety spacing and the absence of external fire protection systems. Non-compliance with industrial standards exacerbated the consequences, resulting in significant environmental damage, infrastructure destruction, and financial losses. The second case involves a runaway reaction caused by human error and poor pressure relief system design, where improper safety measures failed to contain the rapid pressure increase, leading to catastrophic equipment failure. This highlights the necessity of designing effective safety devices using DIERS methodologies and industrial standards. The third case examines a runaway reaction triggered by insufficient risk analysis and a production batch increase, which overwhelmed the existing pressure relief and cooling systems. The lack of system resizing to handle the increased load resulted in severe overpressure and thermal escalation, causing substantial damage.

This work demonstrates that many industrial accidents are preventable through proper design, regular maintenance, comprehensive training, and strict adherence to safety regulations. Additionally, it emphasizes the necessity of proactive risk management, rigorous personnel training, and adopting advanced safety technologies to ensure the protection of workers, the environment, and the operational sustainability of industrial facilities.

**Keywords:** Industrial safety, explosion prevention, runaway reactions, pressure relief systems, rupture disks, fire protection, chemical process safety, storage tanks, Seveso III Directive, API standards, ISO standards, PED standards.

## RESUM

El Trabajo Final de Grado titulado "Estudio de estrategias de protección contra explosiones y reacciones descontroladas en cumplimiento con la Directiva 2012/18/UE y estándares industriales" aborda la importancia crítica de la seguridad en el sector industrial, específicamente en plantas químicas. Este estudio se centra en la prevención, protección y mitigación de accidentes graves causados por reacciones descontroladas y aumentos de presión en tanques de almacenamiento que contienen sustancias peligrosas, alineándose con la Directiva Seveso III y otros estándares industriales relevantes.

El documento analiza casos históricos significativos para resaltar la importancia de abordar todos los aspectos de la producción industrial. Las estrategias de protección contra explosiones se evalúan utilizando marcos y directrices para el diseño de dispositivos de alivio de presión. Además, propone el uso de sistemas de protección específicos, como discos de ruptura dimensionados según estos estándares internacionales, para proteger o minimizar el impacto de estos eventos.

Entre los hallazgos clave, el análisis destaca tres accidentes notables. El primero es un incendio catastrófico en tanques de almacenamiento petroquímico, que condujo a un efecto dominó a gran escala debido a un espaciamiento inadecuado entre los tanques y la ausencia de sistemas de protección contra fuego externo. El incumplimiento de los estándares industriales agravó las consecuencias, lo que resultó en un daño ambiental significativo, la destrucción de infraestructura y grandes pérdidas económicas. El segundo caso implica una reacción descontrolada causada por errores humanos y un diseño deficiente del sistema de alivio de presión, donde las medidas de seguridad inadecuadas no lograron contener el rápido aumento de presión, lo que provocó fallos catastróficos en los equipos. Este caso resalta la necesidad de diseñar dispositivos de seguridad efectivos utilizando las metodologías DIERS y estándares industriales. El tercer caso examina una reacción descontrolada provocada por un

análisis de riesgos insuficiente y un aumento en el lote de producción, lo que sobrecargó los sistemas existentes de alivio de presión y refrigeración. La falta de redimensionamiento de los sistemas para manejar la carga aumentada resultó en una sobrepresión severa y una escalada térmica, causando daños significativos.

Este trabajo demuestra que muchos accidentes industriales son prevenibles mediante un diseño adecuado, mantenimiento regular, capacitación integral y cumplimiento estricto de las normativas de seguridad. Además, enfatiza la necesidad de una gestión proactiva de riesgos, una formación rigurosa del personal y la adopción de tecnologías avanzadas de seguridad para garantizar la protección de los trabajadores, el medio ambiente y la sostenibilidad operativa de las instalaciones industriales.

Palabras clave: Seguridad industrial, prevención de explosiones, reacciones descontroladas, sistemas de alivio de presión, discos de ruptura, protección contra incendios, seguridad en procesos químicos, tanques de almacenamiento, Directiva Seveso III, estándares API, estándares ISO, estándares PED.

## SUSTAINABLE DEVELOPMENT GOALS

The implementation of effective industrial safety strategies in explosion protection and runaway reactions represents a significant contribution to several Sustainable Development Goals (SDGs), particularly SDGS 3 and 12.



SDGs 3- Good Health and Well-Being: Protecting the health and well-being of workers, communities, and the environment is central to any industrial safety strategy. Reducing the occurrence of major accidents, such as explosions or toxic leaks, lowers the risk of occupational and environmental diseases. Furthermore, preventive measures and emergency response plans save lives, prevent injuries, and mitigate impacts on communities near industrial facilities.



SDGs 12- Responsible Consumption and Production: A responsible approach to managing hazardous chemicals reduces major accident risks, minimizing environmental impacts and costs. Systems to prevent overpressure, control temperature, and provide emergency relief ensure safer, cleaner, and more efficient operations, promoting a sustainable life cycle for chemical products.

## **1. INTRODUCTION**

Protection and prevention against major industrial accidents are fundamental priorities to ensure the safety of workers, facilities, the environment, and surrounding communities. The 2012/18/EU Directive, commonly known as the Seveso III Directive, is in force across the European Union, establishing stringent regulations aimed at preventing severe accidents involving hazardous substances or mitigating their potential impacts. In addition to this directive, specific industrial standards provide detailed techniques to identify risks and minimize their consequences.

The industrial sector, aligned with current regulations, technological advancements, and comprehensive studies of industrial protection systems, has significantly expanded the range of devices designed to prevent severe accidents caused by explosions and runaway reactions. These devices also mitigate the consequences when such events are unavoidable. Real-world case studies will be analyzed to highlight the critical importance of both economic and technical investment in chemical plant safety.

### 1.1. PROBLEM STATEMENT

Safety plays a vital role not only in protecting people and the environment but also in ensuring a company's economic stability. A controlled, well-designed industrial process that guarantees both efficiency and safety is fundamental for any plant's success.

My interest grew during an internship at a company specializing in safety systems, particularly pressure relief and explosion protection. This experience deepened my understanding of these systems' importance and inspired me to further explore this critical field.

Despite advancements in technology and industrial knowledge, a lack of awareness persists among professionals, current and future, about the significance of safety regulations and

standards. Many do not fully grasp how these standards protect processes, people, and the environment.

Analysis of industrial accidents shows that most could have been prevented or mitigated with proper safety measures. Common causes include equipment failures, human errors, unsafe conditions, uncontrolled leaks, poor maintenance, and design flaws. These seemingly minor issues can escalate into catastrophic events, highlighting the need for well-trained personnel and strict regulatory compliance.

This study emphasizes the importance of educating industry professionals on safety and the need for rigorous training. By analyzing real-world cases, it aims to identify the root causes of accidents, assess their consequences, and propose response systems that could have minimized their impact. Safety is not an afterthought but a cornerstone of successful industrial operations.

#### 1.2. SEVESO: AN INDUSTRIAL ACCIDENT THAT SHAPED HISTORY

Seveso, an Italian municipality near Milan with 17,000 inhabitants, became infamous for a major industrial accident on July 10, 1976. This event, caused by the release of toxic chemical substances, included the largest recorded human exposure to TCDD (tetrachlorodibenzo-pdioxin). In response, Europe introduced the Seveso I Directive (1982), later amended in 1996 and 2012, to address major industrial accident hazards.

The accident occurred at the ICEMSA plant in Meda, which produced 2,4,5-trichlorophenol (TCP) (see figure 1), an intermediate for disinfectants and herbicides. During a production process halted due to regulations requiring weekend shutdowns, residual ethylene glycol was not fully removed from an intermediate reaction. The mixture remained at 158°C, below the thermal reaction threshold of 230°C. However, with the reactor inactive and unsupervised, a runaway reaction ensued, causing a temperature and pressure spike. The rupture disk released 6 tons of chemicals, including 1 kg of TCDD, contaminating 17 km<sup>2</sup>. [1]

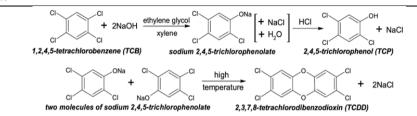


Figure 1: Reactions occurring in the production of the TCP substance

The accident revealed critical gaps in emergency planning and a lack of understanding of the effects of such substances. Evacuations for the 736 residents of Zone A (TCDD concentrations >50  $\mu$ g/m<sup>2</sup>) were delayed by days. Zones B (5–50  $\mu$ g/m<sup>2</sup>, 4,700 residents) and R (<5  $\mu$ g/m<sup>2</sup>, 31,800 residents) were not evacuated (see figure 2). The incident resulted in 250 cases of chloracne, 450 chemical burns from NaOH, and extensive agricultural and urban damage. [1]

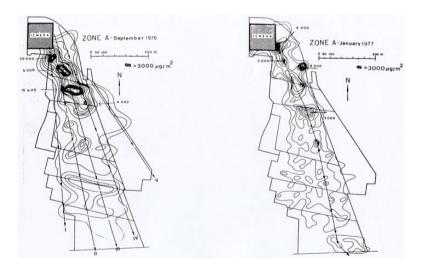


Figure 2: Representation of Zone A- TCDD concentration in the soil greater than 50 μg/m<sup>2</sup>, with 736 residents; Zone B- TCDD concentration in the soil between 5-50 μg/m<sup>2</sup>, with approximately 4,700 residents; Zone R- TCDD concentration in the soil less than 5 μg/m<sup>2</sup>. Source: Seveso Accident (Italy) (Oct 18, 2024) This event drove significant improvements in industrial safety. It underscored the importance of thoroughly investigating chemical processes to identify thermal risks, establishing operational limits, and designing pressure relief systems with proper containment. Although there were no fatalities, the Seveso accident transformed industrial risk management and urban planning to better safeguard populations and the environment.

#### 1.3. SEVESO DIRECTIVE AND INDUSTRIAL REGULATIONS

The 1976 Seveso accident marked a turning point in industrial safety, prompting the creation of legislation aimed at controlling risks associated with hazardous chemicals. In response to this event, the Seveso I Directive (82/501/EEC) was introduced in 1985 to establish a regulatory framework promoting preventive measures and protocols to minimize the likelihood and impact of major accidents in industrial facilities. This directive became a cornerstone of industrial safety policy in Europe and served as the basis for similar legislation adopted in other countries worldwide.

Over time, and informed by lessons learned from other industrial accidents, such as those in Bhopal, Toulouse, and Enschede, the directive evolved. The Seveso II Directive (96/82/EC) introduced significant improvements, followed by the Seveso III Directive (2012/18/EU) in 2012. The latest version adapted the framework to changes in European legislation on chemical classification and expanded citizens' rights to access information and seek justice in the event of incidents. [2]

The Seveso III Directive classifies industrial establishments into two tiers based on the quantities of hazardous substances present. Lower-tier establishments handle quantities specified in Column 2 of Annex I of the Directive, but below those listed in Column 3. Upper-tier establishments possess hazardous substances in amounts equal to or exceeding the thresholds established in Column 3 of the Directive (see Figure 17 and 18 presented in Appendices 1). This classification allows for tailored requirements and obligations for each type of facility, ensuring that measures are proportional to the risks they pose. The Directive also establishes specific requirements for operators and authorities to prevent major accidents, mitigate their potential consequences, and reduce the risk of cascading effects, particularly

when facilities are located close to one another, increasing the likelihood of compound accidents. Operators are required to develop a Major Accident Prevention Policy (MAPP), a document detailing measures to control risks associated with their activities, including appropriate safety management systems. They must also submit detailed safety reports, design and implement robust safety management systems, prepare internal emergency plans, and collaborate with authorities on external emergency planning.

The directive emphasizes public participation in the planning and management of regulated facilities. Member States must ensure that the public can provide input during the development or significant modification of external emergency plans. Moreover, potentially affected individuals must have the opportunity to submit comments and observations before final decisions are made on specific projects.

The directive establishes rigorous inspection standards to ensure effective implementation of safety norms and enforce sanctions for violations, encouraging compliance. Preventive measures outlined in Seveso III range from land-use planning to ensure safe distances between new and existing industrial installations, to the application of technical methods to prevent explosive atmospheres and protect against potential ignitions. These measures aim not only to prevent major accidents but also to mitigate their consequences and facilitate recovery in affected areas. The Seveso Directive is recognized as the first intercontinental legislation in the field of industrial safety, serving as a model for subsequent regulations. By establishing clear prevention, risk management, and recovery measures, it protects people and the environment while strengthening the culture of safety in industry. Through strict standards, collaboration between operators and authorities, and public engagement, the Seveso Directive remains a cornerstone of industrial regulation, particularly in protecting against explosions, fires, and other industrial emergencies. [2]

The Seveso Directive has been a key driver in promoting a culture of industrial safety, establishing essential standards to prevent and mitigate major accidents in industrial facilities. Complementing this directive, other industrial standards address critical aspects of overpressure protection and the design of essential safety equipment. Among these, the standards API (American Petroleum Institute), ISO (International Organization for Standardization), and the Pressure Equipment

Directive (PED) play a fundamental role in ensuring the safety and reliability of industrial systems. These regulations provide comprehensive guidelines for designing, manufacturing, installing, and maintaining devices such as pressure relief valves and rupture disks.

The API standards provide detailed criteria for designing and selecting pressure relief systems to ensure reliability in critical conditions:

- <u>API 520</u>: Specifies methods for sizing and selecting pressure relief devices to protect vessels and pipelines from overpressure. [3]
- <u>API 2000</u>: Focuses on the design, manufacturing, and testing of pressure and vacuum relief valves for atmospheric storage tanks, optimizing internal pressure management. [6]

ISO standards complement API guidelines by detailing testing and design requirements for pressure relief equipment:

- <u>ISO 5208</u>: Defines pressure testing methods for metallic valves, including leak assessment procedures. [3]
- <u>ISO 14313</u>: Sets the requirements for valves used in the oil and gas industry, ensuring safe and long-lasting designs under extreme conditions. [3]
- <u>ISO-4126-7</u>: Standard, developed by the European Committee for Standardization (CEN), is a key reference in the design and implementation of overpressure protection devices. It provides specific guidelines for the design, selection, installation, and maintenance of rupture disks, to ensure effective performance during overpressure events. [7]

The Pressure Equipment Directive (PED) establishes safety requirements for the design, manufacturing, and use of equipment operating at pressures exceeding 0.5 bar within the European Union, ensuring compliance with safety benchmarks to reduce risks associated with overpressure and harmonizing technical specifications to facilitate safer and more reliable operations in industrial facilities. [8]

The implementation of API, ISO, and PED standards ensures that critical equipment operates with high reliability and safety under extreme conditions by reducing the risk of failures, enhancing global compatibility through harmonized guidelines, and extending the operational life of materials. Compliance with these standards is essential in industrial environments as it

protects personnel and the environment, ensures operational continuity, and supports the longterm sustainability of facilities.

### 1.4. TYPES OF ACCIDENTS UNDER THE SEVESO III DIRECTIVE

The Seveso III Directive defines a major accident as any event, such as leaks, fires, or explosions, resulting from an uncontrolled process in industrial facilities. These incidents pose significant risks to people, property, and the environment. Their analysis and prevention are essential due to their severe social and economic consequences, particularly when hazardous substances are involved. [2]

Thermal accidents are common in industrial facilities, with fires being the primary source of severe thermal effects. These events generate intense heat, which can damage organisms, materials, and infrastructure and the extent of damage caused by these fires is typically assessed through the thermal radiation flux emitted. Fires are categorized as follows: [2]

- <u>Jet Fire</u>: The immediate ignition of flammable gases or vapors escaping from tanks, pipelines, or process equipment.
- <u>Pool Fire:</u> Occurs when a flammable liquid forms a pool and ignites upon reaching its flash point, spreading fire across horizontal areas and endangering nearby structures.
- <u>Flash Fire</u>: Results from the rapid ignition of a dispersed flammable cloud in the atmosphere.
- <u>Fireball</u>: A longer-duration fire typical of combustible liquids stored under conditions that allow for vaporization. Fireballs release intense thermal radiation and can affect a wide area.

Leaks represent another common type of industrial accident, often serving as precursors to fires or explosions. These involve the unintended release of toxic or flammable substances, which can create hazardous conditions. Common scenarios include: [2]

 <u>Gas or Liquefied Gas Leaks</u>: Caused by catastrophic container failures or breaches in storage systems.

- <u>Vapor Leaks</u>: Occurring in process equipment handling liquefied gases or volatile liquids.
- Liquid Leaks: Resulting from defects in industrial equipment or pipeline systems.

The impact of leaks is evaluated based on respiratory doses, which combine the concentration of the substance in the air with the duration of exposure. Toxic leaks directly affect health, potentially causing acute or chronic conditions, while flammable leaks can form explosive mixtures if an ignition source is present.

On the other hand, explosions are highly destructive mechanical accidents characterized by the sudden release of energy due to gas expansion. They generate overpressure, displacement, and fragment projection, leading to extensive damage. [4] Common types of explosions include:

- <u>Vapor Cloud Explosion (VCE/UVCE)</u>: Explosions caused by the ignition of flammable vapor clouds, either confined (VCE) or unconfined (UVCE), which often result in widespread destruction.
- <u>BLEVE (Boiling Liquid Expanding Vapor Explosion)</u>: A violent explosion caused by the rapid vaporization of a liquid stored above its boiling point, typically following the rupture of its containment vessel.

Additionally, explosions can often be triggered by runaway reactions, where a chemical reaction becomes destabilized, leading to uncontrolled increases in temperature and pressure. This phenomenon occurs when the heat generated by the reaction exceeds the system's capacity to dissipate it, resulting in thermal and pressure build-up that can rupture equipment or activate relief systems. Runaway reactions are typically caused by errors in reactant loading, impurities, inadequate control system designs, or a lack of understanding of material reactivity.

These reactions highlight the importance of understanding chemical and thermal properties to identify potential hazards within processes. Runaway events can escalate rapidly, posing significant risks to industrial facilities, personnel, and the surrounding environment. Proper evaluation of system vulnerabilities and process stability is critical to reduce these dangers.

#### 1.5. EXPLOSIONS AND RUNAWAY REACTIONS

Thermal runaway events in industrial facilities remain a critical area of study within process safety. The concept of thermal runaway has been extensively analyzed in scientific literature, with research focusing on its variations, underlying causes, and potential consequences. The most severe outcome is the catastrophic explosion of equipment, accompanied by significant damage and risk to human life and the environment.

This phenomenon occurs when the heat generated by a chemical reaction increases exponentially, while the heat removal capacity of the system rises only linearly with temperature. This imbalance creates a critical risk of losing control over the chemical reactions, potentially leading to a runaway event.

In these situations, some reaction components may vaporize or decompose as the temperature surpasses their boiling points, further exacerbating pressure buildup within the equipment. This escalation can culminate in a BLEVE (see figure 3). If the rate of pressure increase exceeds the discharge capacity of the control system or the equipment's design limits, the resulting overpressure can surpass the mechanical strength of the vessel, leading to a catastrophic explosion.

Statistical data highlight the critical importance of industrial safety and effective control systems. Between 1995 and 2004, 12% of BLEVE explosions were caused by uncontrolled reactions. Over a broader historical range, from 1926 to 2004, six BLEVE incidents resulted in 19 fatalities and 171 injuries. Despite significant advancements in understanding thermal runaway and the development of preventive and mitigation technologies, these efforts have yet to achieve a noticeable reduction in associated risks.

Currently, thermal runaway remains a major contributor to industrial accidents. It accounts for 26.5% of incidents in the petrochemical industry and 25% of catastrophic events in the European industrial sector, whether or not they result in fatalities. These statistics emphasize the urgent need for continued innovation in safety practices, more robust control systems, and the

widespread adoption of advanced technologies to mitigate the risks associated with thermal runaway events. Addressing these challenges is essential for ensuring safer and more resilient industrial operations. [5]

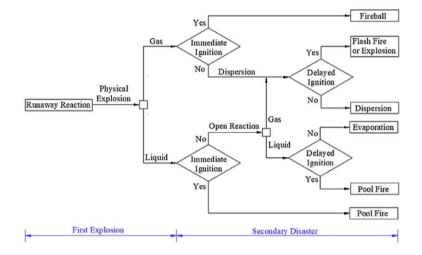


Figure 3: Flowchart of accident sequences due to Runaway reaction. Source: What do we know already about reactor Runaway? (Oct 17, 2024)

To counteract these scenarios, in addition to a well-designed reactor and process, it is essential to develop an immediate detection system. Preventive measures against thermal runaway accidents begin primarily during the chemical process design phase. At this stage, the engineering team must determine the appropriate protection systems, possess a detailed understanding of the chemicals involved, and analyze their chemical, physical, and thermodynamic properties, as well as the kinetics of the primary reaction and any potential secondary reactions. Moreover, it is crucial to account for deviations between theoretical calculations and real-world operational conditions.

The common causes of thermal runaway events can generally be classified into three main categories. The first is the presence of a hot spot within the reactor, often resulting from insufficient mixing of reactants or failures in the agitation system. The second is a cooling system failure, which reduces the reactor's ability to dissipate heat, leading to heat accumulation within the equipment. The third category involves overfeeding, caused by human error or a malfunction in the measurement or injection system.

Regardless of the reactor type in which the thermal runaway occurs, emergency responses and protection methods are centered on relieving overpressure within the reactor, controlling the reaction temperature, and slowing the reaction rate. [5]

<u>Overpressure Relief</u>: Overpressure is caused by the vapor pressure of overheated liquid reactants. In the case of gas-phase reactions, the pressure is directly related to the reaction rate. During a thermal runaway event, the rapid reaction rate and uncontrolled temperature increase accelerate the vaporization of substances. This leads to a pressure rise, as gases occupy significantly more volume than their liquid counterparts. Once this pressure exceeds the maximum resistance of the reactor's casing the mechanical strength of the equipment.

Thus, relieving overpressure is one of the most fundamental emergency operations to ensure the pressure differential between the inside and outside of the equipment remains within safe deformation limits, preserving the integrity of the reactor. However, the released vapor is often highly flammable and/or toxic, necessitating post-treatment such as collection in storage tanks or degradation processes.

One common system for mitigating overpressure is the pressure relief valve or rupture disk, which directs the flow in a controlled manner, allowing the system to depressurize safely. Various factors must be considered when implementing these systems, such as the required flow rate to be relieved, the need for immediate relief, and the direction and location of the vent line outlet. Discharge flows may be directed to a vent stack, cooling tank, liquid-vapor separator, or directly into the atmosphere, depending on the scenario.

<u>Reaction Temperature Control:</u> Temperature increases are the primary drivers of reaction acceleration and pressure buildup within reactors. This variable is managed through heat exchange between the reactor's cooling jacket and the reaction medium. If the cooling capacity is insufficient or the cooling system fails, heat accumulation occurs within the reactor.

Additionally, stable agitation is critical for maintaining uniform composition and temperature throughout the reactants. Inadequate mixing can result in uneven distribution and the formation of hot spots within the reactor, which exacerbate the risk of runaway reactions.

Chemical plants must have secondary cooling systems in place to address potential failures and prevent heat accumulation. Furthermore, staff must be properly trained to identify risky situations and respond effectively to minimize hazards.

<u>Quenching the Uncontrolled Reaction:</u> The aforementioned measures, overpressure relief and reaction temperature control, are classified as passive emergency strategies aimed at minimizing catastrophic consequences. However, it is equally crucial to address the root cause of thermal runaway by stopping the chemical reaction responsible for the risk. This involves inhibiting the progression of the chemical reaction, thereby eliminating the source of heat and extinguishing any flames caused by the runaway reaction.

One potential solution involves injecting inhibitory substances into the reactor. These substances can cool the reactor or halt the chemical reaction altogether. However, this approach is challenging due to the rapid and unpredictable nature of thermal runaway events.

## **2. OBJECTIVES**

The primary objective of this study is to promote a culture of industrial safety through the analysis of real-world cases of significant industrial accidents, demonstrating that the failures leading to these events were avoidable. This work highlights how strict compliance with existing safety standards and the implementation of effective prevention and protection strategies, particularly those proposed in this study, can mitigate risks and prevent catastrophic outcomes. The study seeks to underscore the essential role of industrial safety in protecting human lives, the environment, and the operational integrity of facilities. Additionally, the study presents specific objectives such as:

- Evaluate the application of safety standards: Analyze the effectiveness of key industrial regulations, including the Seveso III Directive, API, ISO, and PED, in preventing major accidents or protecting the environment, people, and industrial facilities by addressing specific risks associated with industrial processes.
- Identify the root causes of accidents: Investigate the causes of major accidents, such as fires and explosions triggered by runaway reactions or overpressure generation, identifying deficiencies in safety systems, regulatory compliance, and process design.
- Propose comprehensive prevention and protection strategies: Present practical and innovative safety measures tailored to specific industrial scenarios, with a focus on overpressure management systems, such as rupture disks, to minimize risks.
- Highlight the role of rupture disks in equipment protection and domino effect prevention: Demonstrate how rupture disks, when properly designed and implemented, can effectively control overpressure, reduce the likelihood of cascading failures (domino effects), and mitigate the severity of industrial accidents.

## 3. METHODOLOGY

The methodology for analyzing real accidents is based on risk zone assessments as defined by the Seveso Directive and analyzed using the ALOHA (Areal Locations of Hazardous Atmospheres) software, as well as the minimum safety distances for process equipment in chemical plants. It also includes techniques for sizing rupture disks to protect against external fires and runaway reactions, ensuring effective risk mitigation and enhanced safety for personnel and equipment.

# 3.1. RISK ZONE ASSESSMENT ACCORDING TO THE SEVESO DIRECTIVE

To assess the potential consequences of the types of accidents outlined, a spatial and temporal consequence analysis is conducted. The objective is to evaluate their potential effects on people, the environment, and property by examining the representative variables of each hazardous phenomenon described. The adopted methodology for assessing effects and consequences focuses on the planning of risk zones (see Table1).

<u>Intervention Zone</u>: This is the area where the consequences of accidents result in a level of damage that necessitates the immediate implementation of protective measures. It represents the highest priority for emergency response efforts to minimize harm to individuals and assets.

<u>Alert Zone:</u> This zone encompasses areas where the consequences of accidents are perceptible to the population but do not justify immediate intervention.

<u>Domino Effect:</u> The domino effect refers to the chain reaction of amplified consequences when hazardous phenomena not only impact external vulnerable elements but also affect other vessels or equipment within the same site or in nearby facilities. This can lead to additional destructive or hazardous events, significantly escalating the severity of the incident. [2]

Table 1: Threshold Values of Representative Variables for Hazardous Phenomena According to the Seveso III Directive for Delimiting Different Risk Zones

Threshold Values According to the Seveso III Directive						
	Intervention Zone Alert Zone		Domino Effect			
Pressure Wave Impulse	150 mbar.sec.	100 mbar.sec.	-			
Local Overpressure from Wave	125 mbar	50 mbar	160 mbar			
Projectile Range Impulse	>10 mbar.sec. in a quantity of 95%	>10 mbar.sec. in a quantity of 99,9%	-			
Thermal Radiation Dose	3 kW/m <sup>2</sup> in 60 sec.	2 kW/m <sup>2</sup> en 45 sec.	8 kW/m <sup>2</sup>			
Toxic Substance Concentration in Air	Concentration in calculated based on		-			

Based on the variables involved in each hazardous phenomenon, such as fire, explosion, or leak, it is possible to calculate values related to the planning of alert zones, intervention zones, and domino effects, as well as important chemical parameters associated with industrial facilities. In this study, risk zones were modelled using ALOHA, a program widely used for planning and understanding chemical emergencies. ALOHA allows for the simulation of scenarios such as toxic gas clouds, flammable gas clouds, BLEVE incidents, jet fires, pool fires, and vapor cloud explosions. To model the accident, the following steps were carried out:

<u>Selection of the chemical substance</u>: The first step was to select the chemical substance involved in the accident, entering or verifying its specific properties in ALOHA to perform the simulations.

<u>Definition of meteorological conditions</u>: General weather conditions were entered, including wind speed and direction, ambient temperature, and humidity. This information was crucial to simulate the dispersion of gases and the behavior of fire or leak scenarios.

<u>Specifications of the storage tank:</u> The type of tank (atmospheric) and its physical characteristics were selected. Key data, such as the liquid level, the tank's total volume, and the properties of the tank material, were entered.

<u>Accident location</u>: The exact coordinates of the storage tank were provided to model the precise spread of hazardous materials and their effects on surrounding areas.

<u>Simulation of the leak scenario</u>: A leak was modeled to analyze the dispersion of hazardous materials into the atmosphere, including parameters such as the size of the opening, the duration of the release, and the amount of hazardous material.

<u>Modeling of fire and explosion scenarios</u>: A pool fire scenario was evaluated, simulating the thermal radiation emitted and its impact on infrastructure and surrounding areas. For the explosion scenario, the program calculated overpressure zones and the potential for secondary accidents due to domino effects.

The results obtained from ALOHA provide a detailed visualization of the risk zones, including areas affected by thermal radiation and the dispersion of hazardous substances. These results enable the assessment of the accident's scope, identification of deficiencies in safety measures, and formulation of strategies to prevent similar events in the future.

Additionally, the directive provides a straightforward and estimative method for calculating the minimum safety distances between potential equipment present in a chemical plant. This model employs a simple and intuitive table (see Figure 4), which facilitates the estimation of safe separations necessary to reduce the risk of cascading accidents or other catastrophic consequences. The calculation process involves identifying the types of equipment involved and referencing their corresponding values in the table. To determine the safety distance, the value at the intersection of the two process equipment types being analyzed must be observed. If the equipment is of the same type, the distance is determined by directly assigning the value specified in the table for that category.

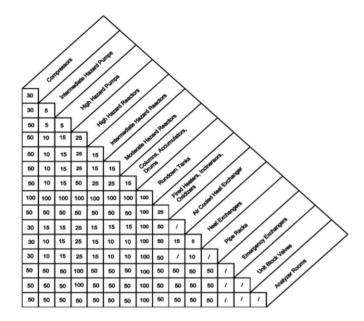


Figure 4: Table for calculating minimum safety distances between equipment in a chemical plant (in ft)

#### 3.2. FIRE PROTECTION: DESIGN OF RUPTURE DISKS

Historical analysis of serious accidents allows us to identify the storage of flammable substances as the most likely cause of fire accidents in the chemical industry. To mitigate the severe consequences associated with this, a robust solution was proposed by designing a pressure relief device: a rupture disk.

Atmospheric storage tanks typically employ rupture disks calibrated to low pressures. These devices consist of a sealed, pre-weakened membrane engineered to rupture instantly upon reaching a predetermined pressure and temperature threshold. Recognized by international standards such as the Pressure Equipment Directive (PED), ISO-4126-7, and API, rupture disks are integral to overpressure protection systems in industrial facilities.

The operating principle of a rupture disk is based on the pressure differential between its two sides: the process side and a reference pressure, often atmospheric or a system with backpressure. Upon exceeding the calibrated set point, the disk responds within milliseconds, achieving instantaneous opening to release the required flow. This rapid pressure relief

prevents equipment failure by maintaining internal pressure below the design limit and avoiding mechanical rupture of the tank.

The design and sizing of rupture disks follow the methodologies established in the API 2000 standard, which defines the requirements for the design, selection, installation, and maintenance of pressure and vacuum relief systems for atmospheric and low-pressure storage tanks. A critical parameter in this calculation is the wetted surface area of the tank, which directly influences the rate of vapor generation under heat exposure. For tanks with wetted surface areas below 260 m<sup>2</sup>, the required airflow rate is determined using the following table from the standard (see Figure 5).

Wetted Area <sup>a</sup> m <sup>2</sup>	Venting Required Nm <sup>3</sup> /h		Wetted Area <sup>a</sup> m <sup>2</sup>	Venting Required Nm <sup>3</sup> /h
2	608	] [	35	8,086
3	913	] [	40	8,721
4	1,217	1 [	45	9,322
5	1,521	1	50	9,895
6	1,825	] [	60	10,971
7	2,130	1	70	11,971
8	2,434	1	80	12,911
9	2,738	] [	90	13,801
11	3,347	1 [	110	15,461
13	3,955	] [	130	15,751
15	4,563	] [	150	16,532
17	5,172	[	175	17,416
19	5,780	[	200	18,220
22	6,217		230	19,102
25	6,684	] [	260	19,910
30	7,411		>260 <sup>b</sup>	_

Figure 5: Emergency venting required for fire exposure vs Wetted surface area (expressed in SI Units). Source: Venting atmospheric and low-pressure storage tanks- API Standard 2000 seventh edition- Table 7, March 2014.

In this specific case, the wetted surface area exceeded 260 m<sup>2</sup>, necessitating the calculation of the airflow required to equilibrate internal tank pressure with atmospheric pressure. This was achieved using the appropriate equation (1) provided in the API 2000 standard:

$$q = 3,091 \cdot \frac{Q \cdot F}{L} \cdot \left(\frac{T}{M}\right)^{0.5} = 3,091 \cdot \frac{43200 \cdot AWTS^{0.82} \cdot F}{L} \cdot \left(\frac{T}{M}\right)^{0.5}$$
(1)

Where Q represents the heat input due to fire exposure, measured in British Thermal Units per hour (BTU/h), and F is the environmental factor, commonly adopted with a value of 1, specifically for non-refrigerated storage tanks and considering the worst-case scenario. [6]

L denotes the latent heat of vaporization of the liquid stored at the relief pressure and temperature, expressed in British Thermal Units per pound (BTU/lb). The absolute temperature at the relief condition is indicated by T, measured in degrees Rankine (°R).

Additionally, M is the molecular weight of the vapor released into the atmosphere, which affects the dynamics of the relief system. A<sub>TWS</sub> refers to the wetted surface area of the tank in square meters (m<sup>2</sup>), which is critical for determining heat transfer during fire exposure.

Once the airflow required to prevent tank rupture is determined, the ISO-4126-7 standard for gas/vapor systems is applied to estimate the necessary relief area. This calculation provides the minimum relief area required, which is then used to determine the appropriate diameter and model of the rupture disk (see equation 2).

$$A_0 = \frac{Q_m}{C \cdot K_b \cdot \alpha \cdot P_0} \cdot \sqrt{\frac{T_0 \cdot Z_0}{M}}$$
(2)

In this expression,  $A_0$  represents the minimum relief area required to vent the flow rate calculated in Equation (1), expressed in square millimeters (mm<sup>2</sup>).  $Q_m$  the mass flow rate in kilograms per hour (kg/h), C is the isentropic exponent function,  $K_b$  is the correction factor for theoretical capacity under subcritical flow conditions,  $\alpha$  is the discharge coefficient, and  $P_0$  is the relief pressure in absolute bars.

Additionally,  $T_0$  denotes the absolute relief temperature,  $Z_0$  is the compressibility factor at the relief pressure and temperature, and M is the molecular weight of the gas in kilograms per kilomole (kg/kmol).

The parameters C and  $K_b$  can be estimated using the following expressions (see equations 3 and 4):

$$C = 3,948 \cdot \sqrt{k \cdot \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}}$$
(3)

$$K_{b} = \sqrt{\frac{\left(\frac{2k}{k-1}\right) \left[ \left(\frac{p_{b}}{P_{0}}\right)^{\frac{2}{k}} - \left(\frac{p_{b}}{P_{0}}\right)^{\frac{k+1}{k}} \right]}{k \left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}}} \quad (4)$$

Where k is the isentropic exponent and  $P_b$  is the backpressure, if present, in absolute bars. These parameters can also be found in the reference materials of the standards.

It is important to note that the calculations were performed assuming a direct discharge to the atmosphere. If the discharge system is routed through piping, it is necessary to account for the pressure losses caused by the length of the pipes, bends, and the instrumentation present in the plant. [7]

## 3.3. EXPLOSION PROTECTION IN RUNAWAY REACTIONS: DESIGN OF RUPTURE DISKS IN GASEOUS SYSTEMS

For systems where runaway reactions may occur, the most effective safety protection measure to prevent explosions is the rupture disk. For a perfect design of them it is necessary to consider several factors. These include the state of the substances at the moment the reaction becomes uncontrolled, the rapid increase in temperature and pressure within seconds, the quantity of product released, and other specifications that make each scenario unique and require individualized treatment.

When protecting reactors from a gas-phase runaway reaction, the primary principle is to install the relief system at the bottom of the reactor. This allows for the maximum possible removal of product from the equipment while simultaneously relieving overpressure. This practice is of critical importance, as an uncontrolled reaction tends to produce explosions whose severity is directly correlated to the mass of material involved in the catastrophic event. Implementing this preventive measure reduces the amount of flammable material in the system by venting through the bottom of the equipment, thereby minimizing the risk and mitigating the consequences of a runaway reaction.

Analysis of historical accidents involving inadequately sized rupture discs offers an opportunity to improve their design. Their documentation on pressure relief systems for runaway reactions outlines various sizing methods tailored to different reaction media and risk scenarios.

In general, in the studies cases of this project, the substance responsible for the thermal runaway was entirely in the gas phase, as it is a salt that decomposes at a specific temperature. The calorimetric analysis conducted by the company investigating the accident was considered, allowing for an estimation of the minimum relief area required using the following expression 5:

$$A = K \cdot \frac{m_0}{m_t} \cdot \frac{\left(\frac{dP}{dt}\right)max}{Pm^{\frac{3}{2}}}$$
(5)

This approach highlights the importance of accurate relief system design, incorporating detailed chemical and thermal analyses to prevent similar incidents and ensure safety in industrial processes. In this calculation, A denotes the minimum required relief area, expressed in square millimeters (mm<sup>2</sup>). The coefficient K is directly related to the type of calorimeter employed; for the Rapid Screening Safety Test (RSST), K has a value of 3×10<sup>-6</sup>. The parameter m<sub>0</sub> represents the mass of material introduced into the reactor, measured in kilograms (kg), while m<sub>t</sub> corresponds to the mass introduced into the calorimeter during testing, also expressed in kilograms (kg). The term (dP/dt) <sub>max</sub> indicates the maximum rate of pressure increase over time, measured in Psig/min, and P<sub>m</sub> refers to the maximum pressure reached in the reactor during the runaway event, expressed in absolute pressure units (Psi). Once the minimum required relief area is determined, a rupture disk must be specified with a size sufficient to meet or exceed this area. This ensures that the disk can effectively handle the relief requirements, mitigating overpressure and maintaining the safety and integrity of the system under the specified conditions.[9]

The sizing process follows the equations (2, 3, and 4) outlined in Section 3.2 of the ISO-4126-7 standard for rupture disk sizing in gas or vapor phase systems. This approach provides a framework to observe how the required disk size changes based on the new estimated flow rate, highlighting the potential inadequacy of the originally installed device and the critical need for accurate re-evaluation when operational parameters change.

## 4. ANALYSIS OF PROTECTION MEASURES IN THREE REFERENCES CASES OF STUDIED

Industrial accidents and incidents have, throughout history, resulted in severe human, economic, social, and environmental consequences. However, they have also served as critical lessons for improving industrial safety and processes across various sectors, as demonstrated by the creation of the Seveso Directive. Each real-world situation, from minor incidents to catastrophic events, provides an opportunity to identify errors, analyze root causes, and develop strategies and operational models that prevent recurrence or mitigate their impact.

Learning from industrial accidents goes beyond investigating immediate causes or addressing obvious problems. It involves understanding underlying factors such as failures in management systems, non-compliance with safety protocols, deficiencies in technical design, communication breakdowns among workers, or inadequate oversight by regulatory authorities. By adopting a multi-faceted perspective, tragedies can be transformed into catalysts for change, fostering a culture of safety awareness in industrial environments.

The first step is recognizing the importance of analyzing and learning from these events with the aim of protecting both workers and the surrounding communities. This approach ensures the pursuit of responsible and risk-conscious industrial development while safeguarding the wellbeing of people and the environment.

### 4.1. CASE 1: FIRE IN STORAGE TANKS

Table 2: General Data on the Accident at Intercontinental Terminals Company, LCC

Location	Deer Park, Texas, USA		
Date	Sunday, March 17, 2019		
Organization	Intercontinental Terminals Company, LCC		
Industrial sector	Petrochemical Product Storage		
Substances Present	Naphtha enriched with butane		
Hazards	Flammable substances Pressurized Gases		
Number of Fatalities	0		
Number of Injuries	0		

#### Accident Context:

The accident occurred at the storage terminal of Intercontinental Terminals Company, LLC (ITC), located in Deer Park, Texas, USA (see characteristics in Table 2). This company had been operating for over five decades, providing storage and management services for petrochemical products. The facility consisted of 242 fixed tanks with capacities ranging from 1,272,000 to 25,440,000 liters. Specifically, Tank 80-8 contained butane-enriched naphtha, a complex mixture of hydrocarbons in the C4-C10 range. At the time of the incident, the tank was being fed through a truck injection system. [10]

#### Relevance for Analysis:

This case is highly relevant to the study of chemical safety and accident prevention in industry. It highlights the severe consequences of inadequate process safeguards and the lack of fire protection systems for atmospheric storage tanks containing volatile and flammable substances. Additionally, the incident emphasizes the critical importance of maintaining minimum safety distances between equipment within the plant to prevent a fire from triggering a domino effect. In this case, thermal radiation from the fire impacted adjacent tanks,

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exacerbating the severity of the accident. Furthermore, the event underscores the need for robust safety programs, even when not explicitly required by regulations. It also demonstrates the value of having safety experts capable of anticipating potential human errors or mechanical failures, significantly reducing the likelihood of such catastrophic outcomes.

#### Accident Description:

Tank 80-8, with an atmospheric capacity of 12,720,000 liters, was used to store butane-enriched naphtha. The tank was equipped with a truck-operated butane injection system, allowing pressurized butane (using nitrogen) to be directly injected into the tank through an external recirculation loop for naphtha (see Figure 6). This system was designed to maintain the homogeneity of the naphtha-butane mixture.

Before the accident, Tank 80-8 contained approximately 11,177,000 liters of the mixture. The recirculation pump had been running continuously since the previous night, during which two truck deliveries of butane were completed, lasting a total of about three hours. The operating conditions were essentially atmospheric, with the recirculation loop active to ensure the mixture remained uniform.

At approximately 9:30 a.m., a mechanical seal on the recirculation pump failed, leading to the release of butane-enriched naphtha into the atmosphere. Between 9:30 and 10:00 a.m., the tank's volume decreased by more than 28,140 liters due to the uncontrolled leak. At 10:00:46 a.m., the released product ignited, triggering a fire. ITC personnel were unable to contain or isolate the flames immediately, allowing the fire to spread to 14 other tanks within the same containment zone. This escalation created a domino effect that intensified the catastrophe. The fire continued for three days, during which emergency response teams worked tirelessly to extinguish the flames and prevent further damage. [10]

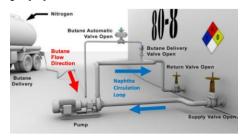


Figure 6: Diagram of the Butane Injection System by Truck at ITC. Source: LCC ACCIDENT

#### Accident causes:

The incident was the result of a combination of human errors, technical failures, and procedural shortcomings that contributed to its escalation.

From a human perspective, the absence of formal mechanical integrity procedures for the recirculation pump and a lack of oversight were significant factors. These deficiencies allowed the failure of the pump's bearing to go unnoticed, which subsequently caused the malfunction of the mechanical seal and led to the release of the flammable mixture. This failure resulted in the continuous release of butane-enriched naphtha into the atmosphere. The situation was further exacerbated by the lack of a gas detection system that could have identified the presence of a hazardous atmosphere.

Procedurally, the plant lacked sufficient safeguards. There were no gas detectors in place to warn of the leak, nor were there fire protection systems for other atmospheric storage tanks in the area. These deficiencies allowed the fire to spread to nearby tanks and equipment, triggering a domino effect.

Additional conditions that facilitated the propagation of the fire included the poor design of the tank area, which impeded the emergency response. The exclusion of Tank 80-8 from the regulatory requirements of the OSHA Process Safety Management (PSM) and the EPA Risk Management Plan (RMP) in the United States meant the tank was subject to fewer safety controls and oversight. Furthermore, minimum safety distances between storage tanks were not maintained, further increasing the risk of fire spreading. These combined factors illustrate critical gaps in safety systems that contributed to the severity of the accident. [10]

#### Consequences:

The accident resulted in significant environmental, material, and economic consequences. From an environmental perspective, the breach of the secondary containment system caused the release of approximately 74,725,000 to 83,151,000 liters of chemical products and contaminated water. This spill reached the Houston Ship Channel, forcing the closure of 11 kilometers of the waterway as well as several coastal parks.

In terms of material damage, fifteen atmospheric storage tanks with a capacity of 12,720,000 liters each, along with their associated infrastructure, were destroyed (see Figure 7).

Fortunately, no human casualties were reported thanks to a well-executed emergency plan, highlighting the critical importance of implementing robust safety measures to protect workers and nearby communities.

Economically, the losses exceeded 145 million €, including the costs of cleanup, temporary operational shutdowns, and potential regulatory fines. This figure underscores the importance of proactive measures to avoid such costly outcomes. [10]

The consequences of this accident emphasize the vital need for comprehensive safety protocols, robust containment systems, and effective emergency management in facilities handling hazardous materials.



Figure 7: Fire and domino effect caused by the butane leak. Source: LCC ACCIDENT

#### Corrective Measures:

As demonstrated in this incident, a series of failures contributed to catastrophic outcomes. These included inadequate maintenance and supervision of the pump feeding the atmospheric storage tank, as well as the absence of alert systems to detect the presence of a potentially hazardous atmosphere. Additionally, analysis of similar industrial accidents reveals that basic failures, such as neglecting routine maintenance and technical supervision of process instruments or equipment, are common in the industry and must be addressed to prevent large-scale losses. However, the primary issue in this incident was the domino effect, whereby the fire spread to 14 additional storage tanks located in the same containment zone as Tank 80-8. Beyond the previously mentioned failures, the lack of external fire protection measures for the tanks was a

key factor in the fire's propagation. Once the butane leak ignited, external fire protection devices on the adjacent tanks could have prevented the domino effect, limited the spread of flammable materials, and mitigated the overall consequences.

For companies handling large volumes of flammable or hazardous substances, it is crucial to implement multiple layers of prevention and mitigation safeguards, ensuring that the failure of a single measure does not result in catastrophic consequences. One essential safeguard is the strategic placement of gas detection systems, which enable the early identification of hazardous atmospheres and significantly reduce the likelihood of ignition.

One corrective measure that could have been implemented is the installation of rupture disks on each of the atmospheric storage tanks. These disks would be pre-dimensioned and calibrated to provide protection against external fires. In the event of a fire that increases the ambient temperature around the tanks, the stored volatile substances would begin to evaporate as their boiling points are exceeded. Since gases occupy significantly more volume than liquids, this evaporation leads to overpressure within the tanks. If the internal pressure exceeds the tank's design pressure, the equipment could rupture, causing massive spills of highly flammable products.

Rupture disks, designed to break at minimal pressure increases, would release the pressure inside the tank by equalizing it with atmospheric pressure. This mechanism prevents the stored products from vaporizing excessively, thus avoiding the large-scale leaks and overpressure that occurred in this incident.

In conclusion, while continuous maintenance and supervision of process instruments and equipment are critical, these failures are challenging to predict. However, rupture disks, as external fire protection devices, could provide an efficient solution, preventing the domino effect and giving emergency teams more time to respond. By containing the fire to a smaller area, the incident would be easier to manage, reducing both the severity of the consequences and the overall risk to the facility.

The selected rupture disk is a flat, direct-acting model pre-calibrated to open at the slightest pressure increase. The sizing calculation for the atmospheric storage tanks was conducted in accordance with the API 2000 and EN 4126-7 standards, focusing on a scenario of protection against external fire as detailed in the methodology outlined in Section 3.2 of this study.

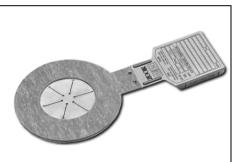
To achieve a realistic estimation, the physical and chemical properties of hexane, a hydrocarbon in the C4-C10 range, were used. Additionally, since the investigation report did not provide the exact tank dimensions, the tank diameter and height were estimated to approximate the real volume. The calculation assumed that the relief flow discharge would be directly to the atmosphere. Details of these estimations can be found in the appendices (see Figures 19 and 20 presented in Appendices 2).

For this scenario, the company would need to purchase 15 rupture disks, one for each of the storage tanks, along with an additional 5 units for potential replacements. As a single-use safety device, rupture disks must be replaced by the maintenance team after activation. Based on the estimation, the recommended rupture disk model has the following specifications (see Table 3):

Table 3: Specification Sheet for the Proposed Rupture Disk for External Fire Protection

#### ARD-L DISK

Composite metal unidirectional disk. Flat direct-acting disk. Direct installation between flanges. Suitable for stable pressures. Appropriate for liquids, gases, and biphasic systems.



Fluid: Hydrocarbons C4-C10. Hexane is considered.

	Nominal size	DN 400 (16")
	Opening Conditions	0.12 bar +/- 0.023 bar at 22°C
		The disk burst between 0.097 and 0.143 bar at 22°C.
5	Material	Disk: Stainless Steel 316
atic		Seal: Teflon (PTFE)
Sific		Gaskets: Compressed fibers
Disk Specification	Recommended Operating	Operating ratio of 50% of the opening pressure:
	Range	From atmospheric pressure to 0.06 bar at 22°C.
Dis	Additional Information	Maximum working temperature: 260°C
		Released air flow rate: 82,603 kg/h
		MNFA: 117,838 mm <sup>2</sup>
	Certifications	CE Marked
		Opening certificate according to ISO EN 4126-2
		Material certificate 3.1

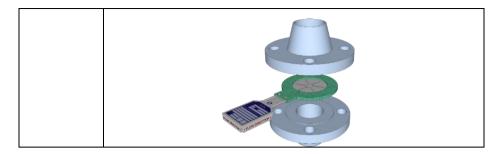


Table 4: Economic Summary for the Quantity of Rupture Disks

Description	Quantity	Unit price
ARD-L DN400 0.12 bar-g +/- 0.023 bar at 22ºC	20	1,938.00€
Total Price	38,760.00€	

The company would have needed to spend  $38,760.00 \in (\text{see Table 4})$  to implement the proposed safety measure, compared to the 145 million  $\in$  incurred in post-accident costs. This represents only 0.03% of the total expenditure. It is important to emphasize that the proposed protective measure would have significantly minimized the consequences of the initial fire by isolating the other tanks in the area and providing the firefighting team with more time to combat the flames effectively.

Combining these rupture disk devices with gas detection systems in the areas surrounding the tanks would have been one of the possible strategies to prevent the catastrophic event from escalating to such a scale.

This protective measure applies to various storage tanks of chemical products, aiming to safeguard the tank's contents from potential ignition caused by an external fire. By preventing a larger quantity of flammable products from encountering the flames, it mitigates the risk of more severe consequences and ensures greater safety for industrial facilities.

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Evaluation of Zones Using ALOHA:

A simulation was conducted using the ALOHA program, utilizing data obtained from the accident. The simulation considered the chemical substances involved, specifically butane and naphtha, while applying standard conditions such as wind speed and atmospheric parameters representative of the day of the accident.

The first parameter analyzed was the thermal radiation emitted from the initial ignition source, which stemmed from the leak caused by the failure of the injection pump (see Figure 8). This assessment of thermal radiation provided critical insights into the immediate hazards posed to nearby infrastructure, personnel, and potential ignition sources. From the analysis, it was observed that the thermal radiation emitted by the fire propagated beyond tank 80-8, affecting nearby tanks by heating the equipment and, consequently, the stored substances.

In accordance with the threshold values established in the Seveso III Directive (see Table 1), the thermal radiation at a distance of 10 meters was found to reach 10 kW/m<sup>2</sup>, exceeding the threshold value of 8 kW/m<sup>2</sup>. This highlighted a significant potential for a domino effect, as evidenced during the accident, where thermal radiation contributed to the propagation of the fire to adjacent tanks (see Figure 9).

These findings also supported the definition of an Intervention Zone, which, in conjunction with the emergency plan that was effectively executed, played a vital role in preventing fatalities and injuries.



*Figure 8:* Thermal radiation zones modeled with ALOHA: Red represents areas with radiation exceeding 10 kW/m<sup>2</sup>, orange indicates radiation levels greater than 5 kW/m<sup>2</sup>, and yellow shows zones with radiation above 2 kW/m<sup>2</sup>. Created with: ALOHA

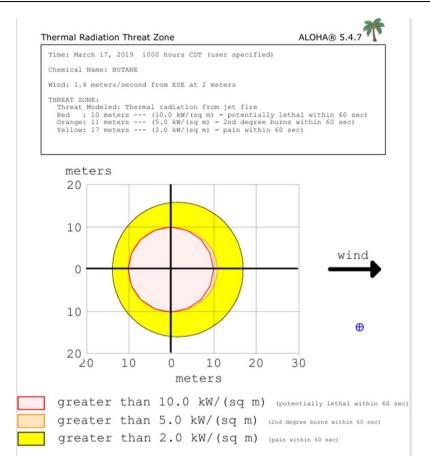


Figure 9: Thermal radiation emitted by the ignition source toward the area where the involved storage tanks are located and potential consequences based on the distance from the origin. Created with: ALOHA

Additionally, according to the calculation model described in section 3.1 of the methodology (see Figure 4), the storage tanks should have been separated by a minimum distance of approximately 30.5 meters. This value is derived from the 100 ft (equivalent to 30.5 m) minimum safety distance specified for rundown tanks. However, in the analyzed area, the tanks were located only about 12 meters apart. This inadequate separation allowed the thermal radiation emitted from the initial ignition point to significantly impact nearby tanks. During the first 60 seconds, the intensity of the radiation ranged between 5-10 kW/m<sup>2</sup> (see Figure 9), sufficient to cause second-degree burns and heat the adjacent equipment.

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These findings underscore the critical importance of adhering to safety guidelines regarding separation distances between tanks to prevent heat transfer and reduce the likelihood of escalation incidents. Proper spacing and compliance with safety regulations are essential to mitigating the risks of domino effects and ensuring the resilience of industrial facilities in the event of a fire or explosion.

On the other hand, using the ALOHA program and modeling the leak of the substances involved in the accident, risk zones were estimated based on the LEL (Lower Explosive Limit), a parameter representing the lowest concentration of gas mixed with air that can ignite and create an explosive atmosphere. In this scenario, it is critically important to implement combustible gas detectors that trigger an alarm before concentrations exceed the threshold defined by the LEL.

According to the investigation conducted by the CSB (Chemical Safety Board), the LEL for naphtha is 1.2%, which corresponds to a concentration of approximately 192 ppm. Setting the concentration of naphtha at 1.2%, the simulation results indicate that from the ignition point to the end of the area encompassing the atmospheric tanks, the concentration of the chemical substance in the air exceeds the LEL threshold (see Figure 10). In other words, the results show that once ignition occurs, the substance's concentration surpasses the LEL within a radius of approximately 177 meters from the source (see Figure 11).

This creates a potentially explosive atmosphere with highly flammable substances, representing a significant risk of explosion within the affected zone.



Figure 10: Risk zones based on the LEL of naphtha: Yellow represents areas with concentrations exceeding 192 ppm (1.2%), orange indicates concentrations above 400 ppm, and red shows zones with concentrations higher than 800 ppm. Created with: ALOHA

ALOHA® 5.4.7

#### Flammable Threat Zone

```
Time: March 17, 2019 1000 hours CDT (user specified)

Chemical Name: NAPHTE

Wind: 1.4 meters/second from ESE at 2 meters

THREAT ZONE:

Threat Modeled: Flammable Area of Vapor Cloud

Model Run: Heavy Gas

Red : 69 meters --- (800 ppm)

Orange: 109 meters --- (400 ppm)

Yellow: 177 meters --- (192 ppm)
```

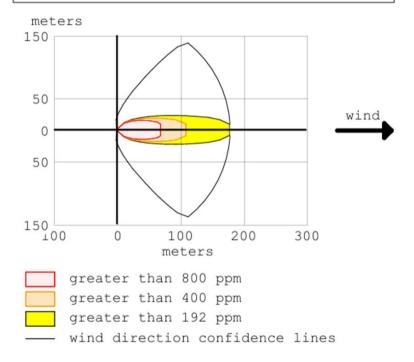


Figure 11: Flammable Threat Zone based on naphtha concentrations and their corresponding distances: Yellow represents concentrations above 192 ppm (1.2%) within 177 meters, orange indicates concentrations exceeding 400 ppm within 109 meters, and red shows concentrations greater than 800 ppm within 69 meters.

## 4.2. CASE 2: UNCONTROLED CHEMICAL REACTION: RUNAWAY EVENT

Table 5: General Data on the Accident at Corden Pharma Limited

Location	Cork, Ireland	
Date	Monday, April 28, 2008	
Organization	Corden Pharma Limited	
Industrial sector	Chemical Manufacturing	
Substances Present	Picoline-N-oxide and Diethyl carbamoyl Chloride.	
Hazards		
	Irritant Irritant via respiratory tract Toxic by inhalation	
Number of Fatalities	1	
Number of Injuries	1	

#### Accident Context:

Corden Pharma Limited (see characteristics in Table 5) produced 2-cyano-3-methylpyridine (CMP) through a two-step chemical process. The first stage involved the reaction of picoline-N-oxide (PNO) with diethyl carbamoyl chloride (DECC) in acetone, carried out in a specialized reactor. The resulting intermediate, an acyloxy pyridinium salt, was then reacted in a second reactor with an aqueous solution of sodium cyanide (NaCN) to produce the final product, CMP (see Figure 12).

The reactor was constructed from carbon steel and lined with glass, equipped with a cooling jacket and an agitation system. It had an operational volume of 2.5 m<sup>3</sup> and a design pressure of 6 bars.

The reactor's safety features included a bolted hatch on the top for maintenance access, a rupture disk, and a relief valve installed in series. Both the disk and the valve were calibrated to activate at 6 bars with a nominal diameter of 50 mm. Additionally, the reactor was connected to a parallel discharge line leading to a tank, which was equipped with another rupture disk. This disk was set to activate at 7 bars and had a nominal diameter of 100 mm. [11]

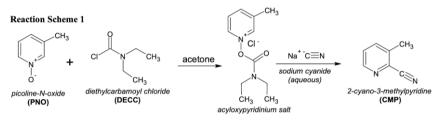


Figure 12: Reaction medium for obtaining the product of interest (CMP)

#### Relevance for Analysis:

This accident underscores the critical importance of understanding and effectively managing the risks associated with hazardous chemical processes. Deviations from critical procedures, such as skipping essential steps, can lead to severe accidents that endanger lives, damage infrastructure, and result in significant economic losses.

Additionally, this case provides an opportunity to study the integration of pressure relief systems in both series and parallel configurations. It highlights the importance of correctly sizing and selecting these devices in compliance with current regulations and adapting them to systems where uncontrolled reactions may occur. Properly designed and calibrated relief systems are essential to mitigate the risks of overpressure and ensure the safety of operations.

Raising awareness of these risks through case studies like this enables companies to improve their safety management systems, strengthen operational controls, and ensure adherence to best practices. Such efforts are key to preventing similar accidents and promoting a culture of safety in the chemical industry. Study of Protection Strategies Against Explosions and Runaway Reactions in Compliance with Directive 2012/18/EU and Industrial Standards

#### Accident Description:

The reactor involved in the pre-reaction to the main chemical process required a series of logical steps that needed to be strictly followed, primarily for safety reasons. Initially, the reactor was inerted with nitrogen in two vacuum cycles and flushed with 100 liters of\_acetone. Following this, 566 kg of picoline-N-oxide (PNO) was loaded, and the reactor was re-inerted with nitrogen before introducing approximately 1,020 liters of acetone. The mixture was then cooled to a temperature range of 15–25°C to prepare for the addition of 702 kg of diethyl carbamoyl chloride (DECC) under vacuum. The DECC was fed into the reactor slowly, over 45–60 minutes, while maintaining the reactor temperature below 40°C using the cooling jacket.

According to thermodynamic data, PNO has a high decomposition onset temperature of 181.7°C, which decreases to 161.7°C when a safety margin of 20°C is considered. However, the intermediate acyloxy pyridinium salt is highly thermally unstable, with a decomposition onset temperature of approximately 71.5°C. The reaction itself is exothermic, with an adiabatic temperature rise of 41°C, but under normal conditions, it would not exceed the identified safety thresholds.

The critical error in this accident was the omission of the acetone charge, which was essential for dissipating the heat generated by the exothermic reaction between PNO and DECC. Without the acetone, the reaction became uncontrolled, leading to a significant temperature increase and, consequently, overpressure within the reactor. The resulting pressure deformed the reactor, rupturing its pressure relief systems and dislodging the seal on the reactor's bolted hatch. This created a breach approximately 10 mm wide, through which hazardous reactants were dispersed. Additionally, the solid feed hopper sustained severe damage, including the violent ejection of its cover and butterfly valve. [11]

#### Accident causes:

The reactor accident was the result of a combination of factors that ultimately led to a catastrophic event. The primary cause was the omission of acetone in the process, a critical step for dissipating the heat generated by the exothermic reaction. This oversight highlighted deficiencies in the HAZOP (Hazard and Operability) analysis of the process. The HAZOP study, based on a systematic analysis of process variable deviations using guide words, is designed to identify and

evaluate deviations that may cause operational or safety issues. This method enables a comprehensive assessment of potential causes and consequences of deviations from normal operating parameters, facilitating detailed evaluations during both design and operational stages. [12]

An investigation conducted by the CSB revealed that, although the violent decomposition potential of the intermediate salt was recognized, the omission of acetone was not identified as a critical deviation. This failure underscored an inadequate evaluation of the risks associated with this scenario, reflecting significant gaps in the process safety analysis.

Moreover, operator training for handling emergency situations was notably insufficient. Upon realizing the absence of acetone and observing the temperature rise in the reaction system, operators attempted to isolate the reactor from the rest of the equipment. This decision tragically resulted in a fatality. Proper training would have instructed operators to evacuate or remain in the control room, as prior calorimetric analysis had indicated that the omission of acetone created an irreparable and highly dangerous condition.

The reactor's emergency relief systems were also critically inadequate to manage the overpressure generated by the uncontrolled reaction. Significant flaws were identified in the design of the pressure relief systems, including improper sizing and calibration of rupture disks and safety valves. These devices failed to vent the required flow rate to prevent reactor failure. Additionally, changes in the diameters of the lines connected to these safety devices created bottlenecks, which severely compromised the effective relief area they could provide. These shortcomings in both safety system design and operational training amplified the severity of the incident, emphasizing the need for robust process safety measures. [11]

#### Consequences:

The accident had severe consequences for human, structural, and operational levels. The loss of containment of reactants impacted the second and third floors of the building, resulting in serious injuries to two operators who were present at the time. Tragically, one of the operators succumbed to their injuries due to the severity of the exposure. These unfortunate outcomes underscore the significant risks associated with direct exposure to hazardous materials and extreme conditions during an industrial emergency.

In addition to the human toll, structural damage occurred to the building, affecting the infrastructure and process equipment located on these levels (see Figure 13). This damage forced the company to suspend operations for approximately three months, leading to substantial financial losses.

Lastly, the company faced sanctions and scrutiny for its failures in safety procedures and risk management. These deficiencies not only contributed to the accident but also damaged the organization's credibility within the industrial sector, highlighting the critical importance of adhering to robust safety and risk mitigation protocols.



Figure 13: The north side of Production Building No. 2 (PB2) after the incident. Source: Runaway chemical reaction at Corden Pharmachem, Cork

#### Corrective Measures:

The accident at Corden Pharma Limited highlights the critical importance of managing all variables and phases in a chemical process effectively. It underscores the necessity for robust risk and operability analysis to ensure that critical processes are conducted safely and efficiently. One key takeaway from this accident is the need to enhance HAZOP analysis. Skilled professionals should conduct thorough evaluations to identify and mitigate risks in critical processes. In this case, the omission of acetone, a crucial step for dissipating heat and preventing the decomposition of the intermediate salt, was a significant oversight. To prevent similar errors, a level controller could have been implemented to monitor and compare the reactor's operating volume before and after acetone injection, ensuring this step was not skipped.

The accident also revealed deficiencies in emergency response protocols. Operators must be trained to prioritize their safety by evacuating immediately during irreversible situations rather than

attempting to physically intervene in hazardous conditions. Such training should include regular drills and a deep understanding of the chemical reactions and their potential consequences. This would enable operators to make informed decisions under pressure, reducing the risk to human life.

In addition to procedural improvements, the accident exposed design flaws in the emergency relief systems. Non-compliance with standards for pressure relief devices was a critical issue. The rupture disk installed in the parallel relief line was incorrectly set to 7 bars, exceeding the limits specified by international standards. According to ASME (American Society of Mechanical Engineers) regulations, when using two overpressure relief lines, the higher-pressure setting must not exceed 16% above the equipment's design pressure, including tolerance. For this reactor, the disk should have been set at a maximum of 6.66 bars, assuming a +/- 5% tolerance. Under EN-ISO 4126-3, this requirement is even stricter, limiting the pressure setting to 10% above the design pressure. In this case, the disk should have been set at a maximum of 6.28 bars, including tolerance. These standards inform:

<u>ASME Standard</u>: The space between the rupture disk device and the pressure relief valve must be equipped with a pressure gauge, test valve, free vent, or another suitable indicator to detect the rupture of the disk or leaks. This arrangement allows for the detection of disk rupture or leakage. For devices under Section VIII, Division 3 (Designation UD3), instead of one of the aforementioned indicators, a series combination with a second rupture disk device in parallel may be provided, with a rupture pressure set at 116% of the vessel's design pressure. [13]

<u>EN-ISO 4126-3</u>: The maximum rupture pressure limit of the safety device with a rupture disk must not exceed 110% of the set pressure of the safety valve, or a gauge pressure of 0.1 bar, whichever is greater. [14]

In cases involving runaway reactions, a combination of pressure relief systems is often employed, as exemplified in the reactor (see Figure 14). The series installation of these devices ensures a fully sealed system where the rupture disk acts as an initial barrier, preventing any sudden and unwanted pressure increases. This setup not only safeguards the reactor but also protects the safety valve from potential issues such as corrosion and polymerization, thereby extending its operational lifespan and ensuring reliable performance. Additionally, a rupture disk is installed in parallel as part of a comprehensive safety strategy, designed to address exceptional events such as fires or uncontrolled reactions. This dual protection system provides an integrated safeguard for the process equipment, ensuring effective protection when properly sized and calibrated. The application of this methodology enhances the overall reliability of the pressure relief system, offering robust protection against potential hazards during critical operations. [15]

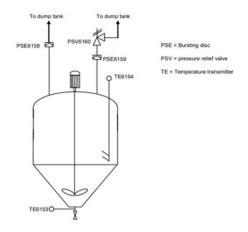


Figure 14: PI&D of the Reactor. Source: Runaway chemical reaction at Corden Pharmachem, Cork

Additionally, given that this reaction involves reactants in the gaseous phase, it is highly recommended that the pressure relief system be installed at the bottom of the reactor. This configuration allows for the maximum evacuation of the product into a containment vessel, which should also be equipped with reaction inhibitors capable of effectively reducing the temperature of the contents. Implementing this practice would significantly reduce the risk of hazardous chemical reactants dispersing throughout the plant at elevated temperatures.

In relation to the rupture disks installed in the reactor, the implemented relief system, consisting of two rupture disks and a relief valve, is estimated to provide a minimum relief area of approximately 11,462.50 mm<sup>2</sup> and a discharge flow rate of 50,074.5 kg/h, assuming a direct discharge to the atmosphere. Although these values are used for analysis, it is important to note that they are not entirely accurate due to the presence of components before and after the relief

devices, which cause pressure losses that directly affect both the relief area and the mass flow discharge rate.

Using the calculation methodology and equation (5) described in Section 3.3, which addresses the protection of equipment during runaway reactions in gaseous systems, the estimated minimum required relief area for this reaction is approximately 108,138 mm<sup>2</sup>. The calculations were based on the following parameters:  $K = 3 \cdot 10^{-6}$ ,  $m_0 = 1268$  kg, mt = 0.1 kg, (dP/dt) max = 24,522 Psi/min, and  $P_m = 420.61$  Psia.

For the relief area calculation, all data provided by the accident investigation were utilized. However, an estimated mass introduced during the calorimetric tests was assumed to be relatively high (100 g) to demonstrate that the existing relief system was insufficient to dissipate the required mass flow rate in the event of a runaway reaction. This analysis indicates that the current system is not designed to handle the mass and pressure requirements during such critical events, highlighting the need for a more robust and precisely sized relief system to adequately mitigate the risks associated with runaway reactions in chemical processes.

Based on the calculated minimum relief area, the following rupture disk is proposed, whose sizing can be seen in Appendices 2 (see Figures 21 and 22), with the specifications outlined in Table 6:

Table 6: Specification Sheet for the Proposed Rupture Disk for Protection Against Runaway Reactions

#### SFAZ DISK

Forward-acting metal disk Suitable for cyclical processes. Suitable for liquids, gases, and biphasic systems. Supports absolute vacuum conditions without the need for a vacuum support. Installation in UHZ disk holder.

Fluid: Acyloxypyridinium salt

tion	Nominal size	DN 300 (12") DN 250 (10")
Disk ecification	Opening Conditions	5.7 bar +/- 5% at 80°C The disk burst between 5.41 and 5.99 bar- at 80°C.
Spe	Material	Disk: Stainless Steel 316

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Standards

Recommended Operating Range	Operating ratio of 90% of the opening pressure: From full vacuum (-1 bar) to 4.87 bar at 80°C
Additional	Maximum working temperature: 482°C
Information	Released air flow rate: 469,863 kg/h
	MNFA DN300: 72967 mm <sup>2</sup>
	MNFA DN250: 50,870 mm <sup>2</sup>
Certifications	CE Marked
	Opening certificate according to ISO EN 4126-2 Material certificate 3.1

	Holder	UHZ Holder DN300
	model	UHZ Holder DN250
	Flange	DN300 EN 1092-1 TYPE 01 PN16
	rating	DN400 EN 1092-1 TYPE 01 PN16
	Material	Stainless Steel 316 on the process side and the atmospheric
		side.
Installation		

The company should purchase two rupture disks of each nominal diameter, one for use and one as a potential replacement, as well as two disk holders for the installation of the device. The investment details can be seen in Table 7:

Description	Quantity	Unit price
SFAZ DN300 5.7 bar +/- 5% at 80°C	2	5,420.00€
SFAZ DN250 5.7 bar +/- 5% at 80°C	2	4,678.00€
UHZ Holder DN300	1	13,814.00€
UHZ Holder DN250	1	11,083.00€
Total Price	45,0	93.00€

Table 7: Economic Summary for the Quantity of Rupture Disks

The combination of two rupture disks connected in parallel, while maintaining the original configuration used in the reactor, results in a relief area of 123,837 mm<sup>2</sup> and facilitates the discharge of a mass flow rate of approximately 469,863 kg/h (see Figures 19 and 20 presented in Appendices 3). This configuration ensures the maximum possible evacuation of the product, balancing the process pressure with atmospheric pressure and mitigating the explosive potential of the runaway reaction.

In conclusion, a comprehensive approach involving a proper HAZOP analysis, accurate application of relevant standards in the specification of relief devices, and the involvement of expert and qualified personnel for the correct sizing of pressure relief systems in highly hazardous scenarios such as runaway reactions, would have provided an effective strategy to safeguard the reactor. This approach could have prevented the fatal accident at the Corden Pharma Limited industrial plant, highlighting the importance of a systematic, scientifically grounded method in addressing safety concerns and mitigating risks in complex chemical processes.

# 4.3. CASE 3: RUNAWAY REACTION: FATAL CONSEQUENCES OF PRODUCTION INCREASE

Table 8: General Data on the Accident at T2 Laboratories

Location	Jacksonville, Florida, USA	
Date	Wednesday, December 19, 2007	
Organization	T2 Laboratories	
Industrial sector	Manufacturing of chemical solvents and fuel additives	
Substances Present	MCMT- Methylcyclopentadienyl manganese tricarbonyl	
Hazards	Hazardous to the environment <ul> <li>Hazardous to the environment</li> <li>Irritant via respiratory tract</li> <li>Toxic by inhalation</li> </ul>	
Number of Fatalities	4	
Number of Injuries	32	

#### Accident Context:

The accident at T2 Laboratories (see characteristics in Table 8) occurred during the production of methylcyclopentadienyl manganese tricarbonyl (MCMT), a highly reactive chemical used as an additive to enhance the octane rating of gasoline. MCMT is synthesized through a three-step process, involving the use of a high-pressure reactor with a capacity of approximately 9,275 liters and a mechanical strength of 600 Psig. The reactor was equipped with both heating and cooling systems to control the temperature, a 4-inch vent line incorporating two 90° bends connected to a 4-inch rupture disk calibrated to 400 Psig, and a 1-inch pressure control valve to manage overpressure. [16]

The production process began with the metalation stage, where a mixture of methylcyclopentadiene (MCPD) dimers and ethylene glycol dimethyl ether was introduced into the reactor. Following this, blocks of metallic sodium were added to the mixture. As the sodium melted, it split the MCPD dimers into individual molecules, forming sodium methylcyclopentadiene, hydrogen gas, and releasing a significant amount of heat. During this step, the temperature increased to 182.2°C, while the pressure was maintained at 50 Psig, triggering the cooling system to stabilize the reactor conditions.

After completing the metalation stage, manganese chloride was added to form dimethyl cyclopentadiene manganese, an intermediate compound. The final stage involved the carbonylation process, during which carbon monoxide was introduced to the reactor to synthesize the target compound, MCMT.

This process required precise control of both temperature and pressure to ensure safe operation. The highly reactive nature of the chemicals and the risk of runaway reactions emphasized the importance of robust safety systems, accurate reactor design, and stringent operational protocols in preventing catastrophic events. [16]

#### Relevance for Analysis:

The T2 Laboratories accident highlights the critical importance of conducting thorough hazard and operability (HAZOP) studies, particularly for chemical reactions with a potential for thermal runaway. This case underscores the need for a comprehensive understanding of process variables and their interactions, emphasizing that no process can be considered effective unless it is also safe.

One of the key lessons from this incident is the failure to adapt and recalibrate safety systems when scaling up production. Despite the increased demands and risks associated with higher production volumes, no significant adjustments were made to the safety instruments or pressure relief systems to account for the changes in process conditions. This oversight ultimately contributed to the escalation of the event into a catastrophic explosion.

Furthermore, the accident illustrates the necessity of addressing all aspects of process design, including redundancies in cooling systems, the adequacy of pressure relief devices, and the implementation of robust risk management strategies. By neglecting to account for these variables, even minor deviations in the process can lead to uncontrollable outcomes.

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Accident Description:

On December 19, 2007, at 1:33 p.m., a catastrophic explosion and fire occurred at T2 Laboratories, involving a 9,275-liter batch chemical reactor. Production of Batch 175 began on the morning of December 19, adhering to standard operating procedures. Raw materials were loaded using an automated process control system, and metallic sodium blocks were manually added by the external operator before sealing the reactor.

At approximately 11:00 a.m., the process operator initiated the heating phase to melt the sodium and begin the chemical reaction. The operator monitored the reactor's temperature and pressure via the control system. When the sodium melted at around 98.9°C, the agitator was engaged, which increased the reaction rate and generated additional heat. Although the operator deactivated the heating system when the temperature reached 148.9°C, the exothermic nature of the reaction caused the temperature to continue rising. Cooling was applied as the temperature approached 182.2°C, following standard procedures. However, a failure in the cooling system prevented effective temperature control, allowing the reaction to escalate.

At 1:23 p.m., in response to the cooling system's failure, the operator and one of the plant owners inspected the reactor and observed signs of potential fire hazards. Despite these observations, the situation deteriorated rapidly. At 1:33 p.m., the reactor was unable to withstand the rapidly increasing temperature and pressure caused by the uncontrolled reaction, resulting in a violent rupture and a subsequent explosion. [16]

#### Accident causes:

The explosion at T2 Laboratories, resulting from an uncontrolled chemical reaction (runaway), was caused by a combination of factors that accumulated due to inadequate risk management. A critical issue was the lack of thorough investigation during the development phase. T2 relied primarily on patents from the late 1950s and early 1960s, which outlined chemistry but failed to address the associated hazards. The process owner conducted tests in a 1-liter laboratory reactor without exploring the reaction at higher temperatures, which prevented the identification of potential extreme exothermic behavior.

When scaling the process to commercial production, T2 underestimated the cooling and overpressure requirements. A formal risk assessment, such as a Hazard and Operability Study

(HAZOP), was never completed. Such an analysis would have highlighted the need for more robust cooling mechanisms and properly sized pressure relief devices to handle emergency scenarios.

Furthermore, the company failed to implement clear emergency procedures to address cooling system failures and lacked a contingency plan for situations where the primary cooling system might fail.

In summary, the absence of a comprehensive risk analysis, insufficient understanding of the reaction's exothermic potential, inadequate safety and cooling systems, and the underestimation of early warning signs all contributed to the explosion. [16]

#### Consequences:

The explosion at T2 Laboratories had devastating consequences for human, material, and economic levels. The powerful detonation, equivalent to approximately 635 kg of TNT, destroyed the chemical company's facilities in Jacksonville, Florida. The impact was so significant that it was felt and heard up to 24 km away.

The human cost was substantial. Four T2 employees, including one of the co-owners, lost their lives, and 32 people were injured, including plant personnel and workers from nearby businesses. The shockwave caused extensive damage within a 500-meter radius of the plant. Debris from the reactor and metallic fragments were projected as far as 1.6 km, endangering nearby infrastructure. Several surrounding buildings sustained significant damage, and the city of Jacksonville condemned four structures as unsafe (see Figure 15). Furthermore, three neighboring businesses temporarily relocated their operations for repairs, while a transport company located adjacent to T2 permanently shut down due to a loss of clients following the accident.

The explosion also posed serious environmental risks. T2 stored large quantities of toxic and reactive substances, including MCMT and metallic sodium. For hours after the blast, firefighters battled a blaze fueled by these solvents and reactants (see Figure 16). Soil and groundwater contamination required extensive remediation and monitoring by environmental agencies. [16]

This accident underscores the critical importance of proactive safety measures, comprehensive risk management, and robust emergency response protocols in preventing such catastrophic outcomes.



Figure 15: Chemical plant of T2 Laboratories after the accident caused by the uncontrolled reaction on December 20, 2007. Source: T2 Laboratories Inc. Reactive Chemical Explosion



Figure 16:Fire caused by the explosion moments after the accident. Source: T2 Laboratories Inc. Reactive Chemical Explosion

#### Corrective Measures:

The accident at T2 Laboratories underscores the critical importance of robust risk management practices and safety protocols in chemical plants dealing with reactive processes. This incident highlights the necessity of conducting a comprehensive process risk analysis during the early stages of research and development. Such analyses should not only focus on normal operations

but also, on identifying and evaluating emergency scenarios, such as total cooling loss or uncontrolled reactions. Additionally, the implementation of Hazard and Operability Studies (HAZOP) is essential for detecting operational deviations, equipment malfunctions, and procedural errors that could lead to severe accidents.

The failure at T2 also demonstrates the importance of investing in redundant cooling systems and appropriately sized pressure relief devices to handle worst-case scenarios. According to the Chemical Safety Board (CSB), the method used by T2 involved two potential exothermic reactions: the desired reaction between sodium and MCPD, occurring at approximately 176.6°C, and a secondary, more energetic reaction between sodium and the solvent diglyme, which occurred when the temperature exceeded 198.8°C. This secondary reaction resulted in a rapid pressure increase of approximately 32,000 Psig per minute and a temperature rise of 1300°C per minute, exceeding the reactor's design limits and triggering the explosion. Once the second reaction began, preventing reactor failure became virtually impossible.

To improve safety, a preventive approach should have focused on relieving the system at a pressure lower than the 400 Psig rupture disk setting. By venting the system during the first exothermic reaction, it would have been possible to release heat and balance pressures, thus preventing the more energetic secondary reaction. Adjusting the rupture disk to a pressure slightly above the working pressure (50 Psig), with an appropriate safety margin, could have likely avoided the catastrophic event. [16]

Another significant issue was the incorrect specification of the emergency venting system. The company failed to adjust the system when production batches were increased by onethird, neglecting to resize the rupture disk or enhance the cooling system's capacity or contact area. For the runaway reaction scenario, incomplete accident data made it\_challenging to accurately determine the nominal diameter required for the venting system. Instead, an estimation method was employed, which involved multiplying the mass flow rate of a standard DN 100 rupture disk by 1.33 to reflect the 33% production increase. This estimated mass flow rate (28,410.13 kg/h) was then used to calculate the minimum relief area necessary to dissipate the flow. However, the actual system introduced additional pressure losses due to the presence of installation elements such as pipe lengths and elbows, while the calculations Study of Protection Strategies Against Explosions and Runaway Reactions in Compliance with Directive 2012/18/EU and Industrial Standards

assumed a direct discharge to the atmosphere (see Figures 23 and 24 presented in Appendices 2).

To prevent highly exothermic reactions like the secondary runaway at T2, the proposed solution involves implementing a correctly dimensioned relief system with the following specifications (see

Table 9):

Table 9: Specification Sheet for the Proposed Rupture Disk for Protection Against Runaway Reactions

#### SFAZ DISK

Forward-acting metal disk Suitable for cyclical processes. Suitable for liquids, gases, and biphasic systems. Supports absolute vacuum conditions without the need for a vacuum support. Installation in UHZ disk holder.



Fluid: MCPD

	Nominal size	DN 150 (6")
	Opening Conditions	60.9 Psig +/- 5% at 180°C
		The disk burst between 57.85 and 63.95 Psig at 180°C.
Specification	Material	Disk: Stainless Steel 316
ifica	Recommended	Operating ratio of 90% of the opening pressure:
Sec	Operating Range	From full vacuum (-1 bar-g) to 52.07 Psig at 180°C
s)	Additional	Maximum working temperature: 482°C
Disk	Information	Released air flow rate: 47,551 kg/h
		MNFA: 18,638 mm <sup>2</sup>
	Certifications	CE Marked
		Opening certificate according to ISO EN 4126-2
		Material certificate 3.1

	Holder model	UHZ Holder DN150
	Flange rating	DN150 EN 1092-1 TYPE 01 PN16
	Material	Stainless Steel 316 on the process side and the atmospheric side.
Installation		

The company should purchase two rupture disks, one for use and one as a potential replacement, as well as a disk holder for the installation of the device. The investment details can be seen in Table 10:

Description	Quantity	Unit price
SFAZ DN150 60.9 Psig +/- 5% at 180°C	2	2,258.00€
UHZ Holder DN150	1	5,450.00 €
Total Price	9,966.00 €	

Table 10: Economic Summary for the Quantity of Rupture Disks

The prescribed pressure relief device highlights a critical oversight following the increase in the production batch size at the T2 reactor: the rupture disk in use was inadequately designed to manage the resulting overpressure scenarios. Although the estimation employed in this analysis is linear and not entirely precise, it represents the minimum adjustment that safety personnel should have implemented. This emphasizes the essential role of employing qualified professionals and the need to scrutinize all systems involved in the production of potentially hazardous chemical substances.

The accident further underscores the urgent need for clear and effective emergency procedures. Operators must be thoroughly trained to recognize early indicators of an unstable reaction and, in the event of a failure in the primary cooling system, be equipped with precise protocols to activate backup systems or execute a plant evacuation. This training must extend to all personnel involved in the operation, ensuring a comprehensive understanding of the potential energy and destruction that could result from an explosion or chemical fire. Effective preparation not only mitigates immediate risks but also builds a culture of readiness and safety awareness across the workforce.

In conclusion, the corrective actions arising from this accident advocate for a comprehensive and proactive approach to risk management. Key measures include optimizing cooling and pressure relief systems, rigorously planning for emergency scenarios, continuously reviewing and improving operational procedures, and cultivating a robust safety culture. Study of Protection Strategies Against Explosions and Runaway Reactions in Compliance with Directive 2012/18/EU and Industrial Standards

## 5. CONCLUSIONS

This study underscores the critical importance of fostering a strong industrial safety culture through the strict adherence to and proper implementation of safety standards, such as the Seveso III Directive, API, ISO, EN, and PED. These frameworks provide essential guidelines for preventing accidents and mitigating their consequences, ensuring the protection of human lives, the environment, and industrial infrastructure.

The industrial accidents analyzed in this study were largely preventable, or their consequences could have been significantly minimized. Most of these accidents resulted from insufficient preliminary studies on the nature of the process, particularly the lack of comprehensive HAZOP analyses, as well as human errors, procedural deficiencies, and the absence of robust safety measures. Raising awareness and providing adequate training are indispensable elements for building a strong safety culture where personnel at all levels prioritize proactive risk identification and mitigation.

Regarding the cases analyzed, it can be concluded that:

<u>Case 1:</u> The catastrophic fire at a petrochemical storage facility demonstrated the severe consequences of failing to maintain proper safety distances between tanks. Thermal radiation exceeded critical thresholds, triggering a domino effect that spread to adjacent tanks. Corrective measures include adhering to specified minimum separation distances and equipping atmospheric storage tanks with external fire protection systems to contain fires and mitigate their spread.

<u>Case 2:</u> The omission of acetone in the process led to a runaway reaction that could have been prevented with greater compliance with safety regulations and process analysis. Properly specified and dimensioned pressure relief systems, such as rupture disks, would have effectively controlled overpressure and minimized the escalation of the reaction. This case highlights the critical need to consider all process variables during design and to ensure that safety devices are adequately sized and maintained.

<u>Case 3:</u> The reactor failure following a production scale-up revealed the consequences of inadequate prior studies and poor adaptation of safety systems. The lack of a properly resized and calibrated rupture disk allowed catastrophic pressure increases during the reaction, resulting in severe consequences. A detailed study of the production scale-up and adjustments to critical safety components could have prevented the reactor explosion and reduced the risk of further damage.

Throughout the study, rupture disks were identified as a key element in protecting industrial process equipment and facilities from potential explosions or external fire scenarios. When properly designed and implemented, rupture disks provide immediate overpressure relief and effectively contain the propagation of hazardous events. These devices offer a reliable and cost-effective alternative for processes involving pressurized systems, significantly enhancing the overall safety of industrial operations.

The findings of this study emphasize the necessity of integrating technical expertise, regulatory compliance, and a commitment to safety in industrial operations. Promoting a culture of safety requires continuous investment in personnel training, the application of advanced engineering solutions, and strict enforcement of regulations. This study demonstrates that such an approach not only prevents accidents but also ensures safer, more sustainable, and resilient industrial operations. By learning from past failures and implementing the lessons derived from this work, industries can create safer environments for workers, communities, and ecosystems.

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# **APPENDICES**

## APPENDIX 1: TYPE OF ESTABLISHMENTS ACCORDING TO THE SEVESO III DIRECTIVE

Categorías de sustancias peligrosas

La presente parte comprende todas las sustancias peligrosas incluidas en las categorías de peligro enumeradas en la columna 1:

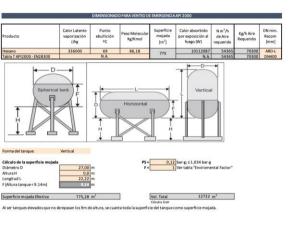
Columna 1	Columna 2	Columna 3
Categorías de peligro de conformidad con el Reglamento (CE) n.º 1272/2008, del Parlamento Europeo y del Consejo, de 16 de diciembre de 2008.	Cantidades umbral (en toneladas) de las sustancias peligrosas a que se hace referencia en el artículo 3, apartado 10, a efectos de aplicación de los	
	Requisitos de nivel inferior	Requisitos de nivel superior
Sección «H» – PELIGROS PARA LA SALUD		
11 TOXICIDAD AGUDA – Categoría 1, todas las vías de exposición.	5	20
12 TOXICIDAD AGUDA Categoría 2, todas las vias de exposición Categoría 3, via de exposición por inhalación (véase la nota 7).	50	200
13 TOXICIDAD ESPECÍFICA EN DETERMINADOS ÓRGANOS (STOT) – EXPOSICIÓN ÚNICA STOT SE Categoría 1.	50	200
Sección «P» – PELIGROS FÍSICOS		
P1a EXPLOSIVOS (véase la nota 8) Explosivos inestables o Explosivos de las divisiones 1.1, 1.2, 1.3, 1.5 o 1.6, o Sustancias o mezclas que tengan propiedades explosivas de acuerdo con el método A.14 del Reglamento (CE) n.º 440/2008, del Parlamento Europeo y del Consejo, de 16 de diciembre de 2008, (véase la nota 9) y no pertenezcan a las clases de peligro «peróxidos orgánicos» o «sustancias o mezclas que reaccionan espontáneamente».		50
P1b EXPLOSIVOS (véase la nota 8) Explosivos de la división 1.4 (véase la nota 10).	50	200
22 GASES INFLAMABLES Sases inflamables de las categorías 1 ó 2.	10	50
23a AEROSOLES INFLAMABLES Aerosoles «inflamables» de las categorías 1 ó 2, que contengan gases inflamables de las categorías 1 ó 2 o líquidos inflamables de la categoría 1.	150 (neto)	500 (neto)
23b AEROSOLES INFLAMABLES terosoles «inflamables» de las categorías 1 ó 2, que no contengan gases inflamables de las categorías 1 d 2 o líquidos inflamables de la categoría 1.	5.000 (neto)	50.000 (neto)

Figure 17: Classification of Establishments: Criteria for Lower-Tier and Upper-Tier under the Seveso III Directive (Part 1). Source: SEVESO III DIRECTIVE

Columna 1	Columna 2	Columna 3
Categorías de peligro de conformidad con el Reglamento (CE) n.º 1272/2008, del Parlamento Europeo y del Consejo, de 16 de diciembre de 2008.	(en ton de las sustan a que se ha en el artículo a efectos de a	es umbral leladas) cias peligrosas ce referencia 3, apartado 10, plicación de los
	Requisitos de nivel inferior	Requisitos de nivel superior
P4 GASES COMBURENTES Gases comburentes de la categoria 1.	50	200
P5a LÍQUIDOS INFLAMABLES Líquidos inflamables de la categoría 1, o Líquidos inflamables de las categorías 2 ó 3 mantenidos a una temperatura superior a su punto de ebullición, u Otros líquidos con un punto de inflamación ≤ 60 °C, mantenidos a una temperatura superior a su punto de ebullición (véase la nota 11).		50
P5b LÍQUIDOS INFLAMABLES Líquidos inflamables de las categorias 2 ó 3 cuando las condiciones particulares de proceso, por ejemplo presión o temperatura elevadas, puedan crear peligros de accidentes graves, o Otros líquidos con un punto de inflamación s 60 °C cuando las condiciones particulares de proceso, por ejemplo presión o temperatura elevadas, puedan crear peligros de accidentes graves (véase la nota 11).	50	200
P5c LÍQUIDOS INFLAMABLES Líquidos inflamables de las categorías 2 ó 3 no comprendidos en P5a y P5b.	5.000	50.000
P6a SUSTANCIAS Y MEZCLAS QUE REACCIONAN ESPONTÁNEAMENTE y PERÓXIDOS ORGÁNICOS Sustancias y mezclas que reaccionan espontáneamente de los tipos A ó B o peróxidos orgánicos de los tipos A ó B.		50
P6b SUSTANCIAS Y MEZCLAS QUE REACCIONAN ESPONTÁNEAMENTE y PERÓXIDOS ORGÁNICOS Sustancias y mezclas que reaccionan espontáneamente de los tipos C, D, E ó F o peróxidos orgánicos de los tipos C, D, E, ó F.		200
P7 LÍQUIDOS Y SÓLIDOS PIROFÓRICOS Líquidos pirotóricos de la categoría 1 Súldos pirotóricos de la categoría 1.	50	200
P8 LÍQUIDOS Y SÓLIDOS COMBURENTES Líquidos comburentes de las categorías 1, 2 ó 3, o Sólidos comburentes de las categorías 1, 2 ó 3.	50	200
Sección «E» – PELIGROS PARA EL MEDIOAMBIENTE		
E1 Peligroso para el medio ambiente acuático en las categorías aguda 1 o crónica 1.	100	200
E2 Peligroso para el medio ambiente acuático en la categoría crónica 2.	200	500
Sección «O» – OTROS PELIGROS		
D1 Sustancias o mezclas con indicación de peligro EUH014.	100	500
D2 Sustancias y mezclas que, en contacto con el agua, desprenden gases inflamables de categoría 1.	100	500
D3 Sustancias o mezclas con indicación de peligro EUH029.	50	200

*Figure 18*: Classification of Establishments: Criteria for Lower-Tier and Upper-Tier under the Seveso III Directive (Part 2). Source: SEVESO III DIRECTIVE

## **APPENDIX 2: SIZING OF A RUPTURE DISK**



Wetted Surface Area, ATWS m <sup>2</sup>	Design Pressure kPa (gauge)	Heat Input, Q
<18.6	≤103.4	63,150.4 <sub>TWS</sub>
≥18.6 and <93	≤103.4	224.200 × (3785 <sup>0.666</sup> )
≥93 and <260	≤103.4	630.400 × (4705 <sup>0.330</sup> )
≥260	>7 and ≤103.4	43,200 × (ATWS <sup>0.82</sup> )
>260	\$7	4,129,700

Calculate the required flow capacity q, expressed in USC units of standard cubic feet per hour of air, for tanks subject to fire exposure as given by Equation (15).

```
q = 3.091 \cdot \frac{Q \cdot F}{L} \cdot \left(\frac{T}{M}\right)^{0.5} where
```

 $\varrho_{-}$  is the heat input from fine exposure as given by Table 4, expressed in British thermal units per hour;

(15)

- is the environmental factor from Table 9 (credit may be taken for only one environmental factor
- is the latent heat of vaporization of the stored liquid at the relieving pressure and temperature expressed in British thermal units per pound:
- T is the absolute temperature of the relieving vapor, expressed in degrees Rankine;
- NOTE It is normally assumed that the temperature of the relieving vapor corresponds to the bubble point one stored fluid at the relieving conditions in the tank.
- M is the relative molecular mass of the vapo

Tank Design/Configuration	Insulation Conductance		Insulation Thickness			
	Wim <sup>2</sup> K	8tu/(h.m2.*F)	cm	in.	/-factor 1	
Bare metal tank	-	-	0	0	1.0	
Insulated tank *	22.7	4.0	2.5	1	0.3 *	
	11.4	2.0	5.1	2	0.15 <sup>b</sup>	
	5.7	1.0	10.2	4	0.075 1	
	3.8	0.67	15.2	6	0.05 b	
	2.8	0.5	20.3	8	0.0375	
	2.3	0.4	25.4	10	0.03 b	
	1.9	0.33	30.5	12	0.025 5	
Concrete tank or fireproofing			-	-	£	
Water-application facilities d	20				1.0	
Depressuring and emptying facilities *					1.0	
Underground storage			-	10.00	0	
Earth-covered storage above grade	-A.V				-	0.03
Impoundment away from tank 1	1 A 1			2	0.5	

Figure 19: Sizing for emergency venting according to API2000 for the LCC Incident



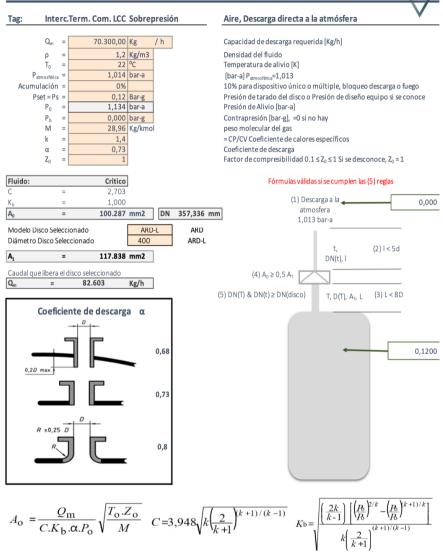


Figure 20: Sizing for emergency venting according to ISO-4126-7 for the LCC Incident

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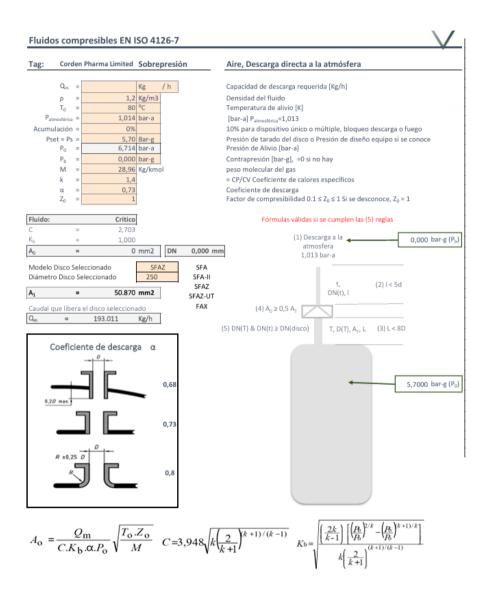


Figure 21: Sizing for runaway systems according to ISO-4126-7 for the Corden Pharma Limited

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#### Fluidos compresibles EN ISO 4126-7

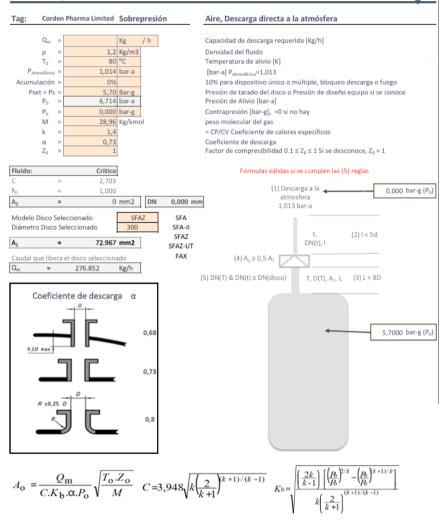


Figure 22: Sizing for runaway systems according to ISO-4126-7 for the Corden Pharma Limited

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#### Fluidos compresibles EN ISO 4126-7

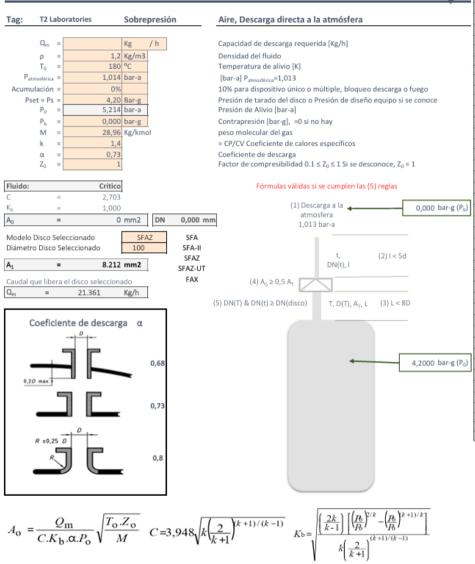
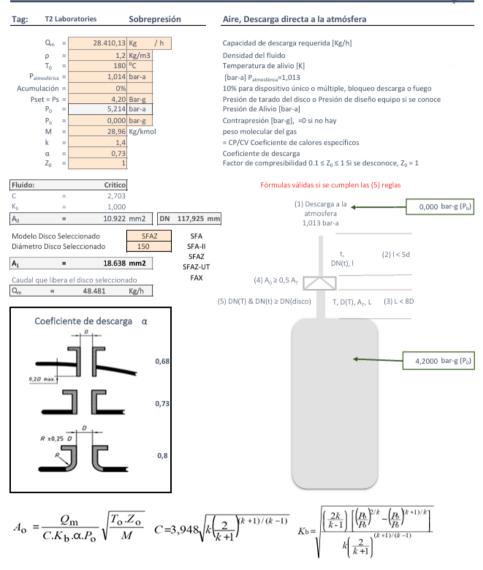


Figure 23: Sizing of the rupture disk used by T2 Laboratories for runaway reaction systems. The flow rate that the rupture disk was capable of dissipating can be observed. This flow rate will be multiplied by 1.33 to obtain the minimum change that should be implemented.

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### Fluidos compresibles EN ISO 4126-7



## F by T2 Laboratories, considering a linear relationship.

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