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Design Optimization of Storage Terminals through the Application of QRA

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Barcelona, 2013

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Thesis presented to obtain the PhD. Title from the Universitat Politècnica de Catalunya

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ABSTRACT

Design Optimization of Storage Terminals through the Application of QRA

By

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The storage of hazardous materials is a necessary part of the life cycle and operation of any process plant, which intrinsically entails certain hazards and dangers. The results of historical analysis reveal that 17% of major accidents in the process industry occur in storage terminals, and the NFPA of the USA reported that in 2009, 13% percent of the major fire accidents that occurred in that country took place in storage installations, causing $69,980,000 in losses. Therefore, it is clear that a methodology for the optimization of the design of storage terminals from a safety point of view could be very useful. A method that allows doing this, through the combination of Quantitative Risk Assessment, Inherently Safer Design and mathematical optimization, has been developed in this thesis. This methodology has been applied to a real life case study, obtaining results that validate it as a useful tool in the design of storage terminals.

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ACRONYMS

Acronym	Meaning
ALARP	As Low As Reasonably Practicable
ALOHA	Areal Location of Hazardous Atmospheres
ARIA	Analysis, Research and Information on Accidents
BLEVE	Boiling Liquid Expanding Vapor Explosion
CCPS	Center for Chemical Process Safety
CSB	U.S. Chemical Safety Board
EPA	Environmental Protection Agency
FACTS	Failure and Accidents Technical Information System
FPS	Fire Protection System
ISD	Inherently Safer Design
IST	Inherently Safer Technology
LFL	Lower Flammability Level
LNG	Liquefied Natural Gas
LOC	Loss of Containment
LOCs	Loss of Containment Events
LOPA	Layers of Protection Analysis
LPG	Liquefied Petroleum Gas

Acronym	Meaning
LUP	Land Use Planning
MAHB	Major Accident Hazard Bureau
MARS	Major Accident Reporting System
MHIDAS	Major Hazard Incident Data Service
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration
PFD	Probability of Failure on Demand
PHA	Process Hazard Analysis
QRA	Quantitative Risk Assessment
SRD	Standard Reference Databases
VCE	Vapor Cloud Explosion

CHAPTER 1. INTRODUCTION

1.1. Motivation

The storage of hazardous substances is a process that entails significant risks; the results of a historical analysis (Casal and Vílchez, 2010) reveal that 17% of major accidents in the process industry occur in, or involve, storage installations; also, the NFPA (National Fire and Protection Association) of the United States of America reported (Badger, 2010) that in 2009, 13% percent of the major fire accidents that occurred in that country took place in storage installations, causing $69,980,000 in losses. These numbers demonstrates that the hazards associated to storage installations continue to be relevant and that there is work to do in relation to risk analysis, process safety and the storage of hazardous materials.

During the design of a project that includes a storage facility, a vast amount of resources are invested in security measures that are meant to prevent a major accident from occurring in the storage tanks. These measures can make the project significantly more expensive. They include different types of fire protection systems, pressure relief valves, level or explosion detectors and alarms, insulation, etc.

Sometimes these protective measures are not designed or applied correctly, and they are occasionally redundant or ineffective; the problem of obtaining the optimum set of protective measures for a plant has been studied by Caputo et al. (2011). At other times, safety equipment, such as fire protection systems, are not maintained properly and therefore cannot prevent accidents. At the time of a major accident, the wrong design, application or maintenance of safety measures results in double loss of money, as the investment in the devices is worthless if they are ineffective. Even when money is spent on the design, purchase and installation of safety devices, they may not work as expected, and are often damaged or destroyed during accidents. This adds to the losses caused by the event.

Even more important, most of these systems fall in the category of active measures to achieve safety, which means that even though they are effective, useful and necessary, they have an associated failure rate; this makes it necessary to ask if there is a way in which inherent and passive safety measures can be evaluated and included in a systematic way during the design of storage terminals.

One aspect of the process of storing dangerous substances is usually not taken into account during a project's design phase: the consequences of a major accident are directly proportional to the mass of substance involved. Therefore, an accident may have less impact if the mass is divided into more containment units. This aspect can be addressed before the previously mentioned security measures are developed and implemented. In fact, we should be able to determine the optimal number of containment units when a storage terminal is designed; this would mean that an inherently safer design has been found for the installation.

More so, Inherently Safer Design (ISD) principles could and should be applied during the design phase of storage installations, evaluating not only the number of tanks, but the type (technology) of storage units, the state in which the substances will be stored,

the optimal layout or the number of containment dikes and their positions; also, this should be done maintaining a watchful eye on the investment that will have to be made, so that it does not goes over the expected value. The people involved in this thesis believe that this can all be achieved through the use of Quantitative Risk Assessment (QRA) and mathematical optimization (even though QRA is not a technique that has been widely used previously for design).

Therefore, the motivation for this thesis is to improve the way in which storage installations are designed, in order to minimize the risk associated to them, using tools that the researchers involved believe that are ideal for the task, but that have not been widely applied in this field, or in this way, before.

1.2. Thesis Objectives

The main objective of the thesis is to develop a new methodology that allows optimizing the design of facilities in which hazardous materials are stored; this will be done by applying ISD strategies and QRA in order to minimize the risk associated to the installation, while maintaining operability and also optimizing the ratio between safety and investment made in the facility.

A secondary objective is to demonstrate that risk analysis and process safety can be valid approaches at the moment of developing an optimization methodology for industrial installations. Improving the safety of an installation should not be perceived as an economical loss, but rather as an insurance against the multiple possible accidents that could take place at a plant; an insurance which will, in the event of an accident, save a substantial amount of money for the company involved.

Developing the search algorithm to solve the optimization problem that is proposed, or making the final optimization process automatic is not one of the objectives of the thesis, although it is a concern. It has to be clarified that the thesis is centered on

developing the series of steps that have to be followed in order to minimize the risk associated to a storage terminal, not in solving or implementing optimization routines.

1.3. State of the art. Optimization and risk analysis applied to the process industry

The combination of mathematical optimization and risk analysis applied to the improvement of the design of industrial processes is a relatively new field of investigation, in which not many articles have been published, most of them having no relation to one another in the methodologies developed, and in the problems addressed. A short review of some of these articles has been carried out.

The problem of applying mathematical optimization to risk analysis in order to find an optimal value between the potential costs of accidents that can occur and the expenses made in some sort of safety measure, to find the optimal design of an installation, has already been approached by Medina et al. (2009).

In this work the authors studied the problem of optimizing the design of a storage facility to minimize the associated risk by dividing the mass of dangerous substance into more containment units. They proposed a methodology that follows the traditional series of steps necessary to solve an optimization problem, including risk analysis elements in the establishment of the objective function. The first step is the system definition, in which the layout of the plant, or the set of equipment on which calculations are to be based is defined. The next stage is to choose the decision variables, which are those that can have a significant effect on the design of the installation and the hazards associated to it. The third step is to select representative accidents, which due to their consequences could have an impact on the way in which the installation is designed. After this, the effects and consequences of these accidents are estimated, and the calculation of the cost of their consequences over people and equipment is performed; finally, the objective and the constraints of the problem are defined.

The objective function for this methodology is the cost of the consequences of the accidents, depending on the number of units that are used to store the mass and the accident that is studied. The only constraint associated to the optimization in this methodology is associated to a tolerable risk level that must not be exceeded, and that usually depends on the legislation of the country in which the installation will be located. Once the system and decision variables are defined, risk analysis can be performed for different designs, the optimum one being that which minimizes costs of accident while complying with the constraint applied.

The results obtained by these authors, when the methodology proposed was applied to two case studies, validate the hypothesis that the cost of an accident can be minimized by optimizing the design of a storage installation in the initial steps of a project. The methodology developed in the present thesis was initially based on the one established by Medina et al. (2009); in its initial stages, it relied heavily on the ideas and the reasoning behind the method they presented, while incorporating concepts that expanded the original idea, and furthered this line of research. The most significant difference between both contributions is that the methodology presented here is based on the estimation of risk, not of consequences, as was done previously. This means that a new and very important factor will be taken into account: the frequency of the different major accidents that can occur in the installation. This is very important for the optimization from a risk point of view, due to the fact that if an accident has significant consequences but a low frequency of occurrence, it will have less impact on the final solution than another accident with lesser consequences, but a high rate of occurrence; this may turn out to be a key factor as more units are built, and the accidents become more frequent. Another noteworthy variance is the use of more accidents to find the optimum number of units; whereas the previous work was performed studying the consequences of one accident, the present methodology explores the risk associated to the installation for various accidents that can derive from the different types of releases.

Another interesting contribution in this field was presented by Young Lee et al. (2005), involving optimization, risk analysis and the study of the domino effect. The main idea of the paper was that it would be possible to develop an algorithm to optimally allocate explosive facilities when designing a chemical process plant, in order to minimize the possibility of domino effect occurrence in the event of a catastrophic accident; the methodology was developed for a case where the facilities have to be placed in a restricted rectangular surface. The objective was to develop a computer programmed module enabling to determine the optimal positioning of explosive facilities to minimize the possibility of domino effect; it used nonlinear methods and considered that the domino sequence could occur due to thermal radiation, overpressure and missile impact on equipment. It was considered in this work that the thermal and overpressure effects of an accident are proportional to r^{-2} and that the missile impact is proportional to e^{-r}, where r is the distance between the object that suffers the accident and the surface affected; the height of the facilities was not taken into account. The problem was described as having n-explosive facilities of the same type, such as storage tanks, in an arbitrary rectangular space in which they have to be placed; the installations have initially defined placement points and the same explosion probability. An objective function was presented that calculates the probability of domino effect as a function of the distance between the facilities; this function will have to be minimized in order to find the optimal solution to the problem. This was achieved by using the gradient descent method. This paper presented a series of numerical experiments in which different numbers of facilities were placed in a rectangular space, and concluded that the module developed can be used as a part of a decision support system to prevent domino accidents.

A different problem that can be found in the risk analysis optimization landscape is ‘‘the valve location problem’’, which objective is to find the optimal location of shut-off valves in an oil pipeline, to minimize the consequences a spill could have on the environment. Pipelines are fitted whit shut-off valves to control oil spills, so every time that a loss of pressure is registered, the valves will automatically shut the line. This means

that a possible spill is limited to the volume of the pipe section enclosed between two valves; therefore, it is possible to find an optimal distribution of valves that will minimize the environmental consequences of a loss of containment. This problem has been studied by Grigoriev and Grigorieva (2009) and Medina et al. (2012) using different approaches for the quantification of the cost of environment and the way in which the optimization is solved. Both groups of researchers apply their methods to different case studies and find solutions that optimize the number and positions of shut-off valves across oil pipelines.

Another work that deals with risk analysis and optimization is the previously mentioned paper by Caputo et al. (2011), which proposes a methodology to find the optimal combination of safety measures that a unit should be equipped with, taking into account the possible accidents that can occur in it.

Risk analysis can also be used to optimize a process in regards to the land use planning of the zone in which the plant will be located, to define threat and affectation zones of major accidents and comply with the legislation of the country in which the installation will be located.

The optimization of chemical processes and plants from the point of view of risk analysis is a field in which there is many room for improvement, and that can have a direct impact in the way in which process design is currently carried out. It can be used to take the negative impact that an installation could have on different vulnerable elements (human, environmental or material) into account during the basic design stages; this design can then be optimized, so that the impact is minimized, and the investment made in safety measures is performed in an easier and more correct way.

1.4. General description of the proposed optimization methodology

The proposed method is envisioned to be a design tool in which the user introduces a basic set of characteristics of a storage terminal that is being designed, and obtains a number of optimal designs, based on values of risk and investment cost associated to the installation; afterwards, the user can evaluate the different designs and decide which one suits his needs better.

Amongst the characteristic that the user would have to input would be the space available to build the terminal, the substance and quantity to be stored on the installation, the meteorological conditions of the site, the type, number and location of the different vulnerable elements surrounding the installation, an acceptable value for individual risk and an investment roof for the project.

Using this information, an algorithm programmed in a specific platform (MATLAB was used) would juggle different decision variables like number and type of tanks, distances between tanks and their positions, number and size of containment bunds, etc. to propose different designs; afterwards, it would evaluate the different designs using an integrated QRA to assess the risk associated to the installation. Also, the investment costs of the different designs would be roughly estimated through the use of simple equations (CHAPTER 3). Finally, the designs that show an optimal risk/investment relationship would be presented to the user, who would then be able to decide which one suits the needs of the project better.

1.4.1. Development of the thesis

Several stages were proposed and followed in order to complete the methodology. Since there were no available models implemented in MATLAB, new structures had to be developed during each of the phases of the thesis, which was a significant challenge for the authors.

The first task done was to perform a bibliographical research on all the subjects that would be a part of the thesis; the themes explored were: modeling of major accidents (including effects and consequences), domino effect, threshold values for equipment and structure failure, costs of human life, property (houses) and equipment, estimation of the investment made on process plants, strategies to achieve process safety and mathematical optimization methodologies. Of course, this research was complemented in a continuous effort during the remainder of the thesis.

After the initial research was completed, the next thing done was to program the accident models in MATLAB, so that by introducing the mass and some characteristics of the substance, and the meteorological conditions, the effects of the accidents could be estimated.

The next phase was to develop the first approach to the optimization method (CHAPTER 4). In this stage, the only decision variable considered was the number of tanks, since this initial model was heavily based on the research performed by Medina et al. (2009); it was a way of introducing the frequency term on the consequence based model proposed by Medina et al. to estimate the optimal number of tanks to use in an installation. This first approach proved to be successful in demonstrating that a risk based optimization could be performed, and was a great starting point for the development of risk based objective functions. However, this initial method operated in a disjointed manner, estimating optimal numbers of tanks for individual accidents, and later deciding which accident was more significant in order to select the best solution; also, this approach did not explicitly consider the possible occurrence of domino effect after any of the accidents, which, for installations that store pressurized gases or flammable materials, could result in risk being underestimated.

It was clear that the initial model was a good but flawed starting point; therefore, it was decided to tackle a problem that, if solved in the appropriate way, could serve as a base upon which the first method could be expanded, and a complete optimization methodology obtained. This problem was the modeling of accident sequences, or the modeling of the domino effect in storage installations (CHAPTER 5). In this stage, the heavier part of the programming was done, to produce an algorithm that systematically develops accident sequences; these originate from each of the tanks in an installation and from each of a set of possible initial accidents. This required the programming of a basic QRA, which uses a defined set of accidents for each tank, depending on whether the unit is pressurized, atmospheric or mounded.

The domino effect model develops accident sequences using threshold values for equipment failure, and allows estimating the frequency of each of the accidents down the sequence. Since the effects of the accidents vary depending on the distance, the sequences are affected by the distance between tanks. In this way, the domino effect model was programmed to take into account not only the number of tanks, but also their geometry, size and positions (in short, the layout of the plant) to produce the sequences; it also takes the sizes of containment dikes into account in its calculations.

Once a model that allows developing accident sequences and also estimates their frequencies was available, it was possible to produce the final optimization methodology (CHAPTER 6). This final method combines the first approach with the domino effect model by taking accident sequences and estimating the costs associated to them at each point, and combining them with their frequencies in order to calculate the risk. Therefore, the programmed QRA was modified to systematically develop accident sequences and at the same time, calculate their costs and obtain risk values. Once the QRA is completed, the risk associated to a complete installation is found. It is clear that if this process is repeated over different designs, that use different layouts and types of tanks, different risk values can be obtained until a minimum is found for the optimal design.

Certainly, different designs will not only have differing risk values, but also, different investment costs. The final part of the model calculates the investment cost associated to each design and performs a multi-objective optimization to find the designs that have an optimal risk/investment ratio. Naturally, the designs found always have to comply with some constraints, like limited space, having a value of risk that does not exceed the acceptable value or having an investment cost below a certain threshold.

Next chapters show much of the information that was gathered during the thesis and the different models that were proposed in its duration: the initial optimization procedure, the domino effect model and the final methodology, all of them accompanied by case studies.

CHAPTER 2. FOUNDATIONAL CONCEPTS

In this chapter, some concepts and ideas which are fundamental to the thesis and its understanding are presented; initially, basics of risk analysis and process safety are briefly explained, including the definition of risk, major accidents, QRA, ISD and others; after this, in order to draw close to the main process studied in the thesis, the principal types of storages used in the process industry and the failures most commonly associated to them are presented, followed by a recount of some major accidents that have involved storage installations; finally, the definition of mathematical optimization, the stages followed to solve an optimization problem, and the types of problems that can be found are described.

2.1. Basic concepts of risk analysis and process safety

Process safety refers to the prevention of accidents (releases, fires, explosions, etc.) or near misses through the application of several barriers to a process; these are categorized as: inherent, which tries eliminating or reducing hazards by making essential changes in the process or in the materials used; passive, which minimizes hazards with design features which can reduce the frequency or consequences of a certain accident without the activation of a safety device; active, which refers to control and automatic systems that are used for safety in the process; procedural, which reduces hazards through the application of procedures or operational practices.

Once an accident occurs, people, the environment or material property may be affected; this makes it necessary to know the frequency, effects and consequences of the possible accidents, in order to categorize them and evaluate the risk associated to the process and posed on the nearby vulnerable elements. This labor of identifying hazardous situations, estimating their frequencies, effects and consequences, and combining them in order to obtain risk is known as risk analysis.

Risk analysis can be performed on a process or an installation through the application of a wide range of techniques, like Process Hazard Analysis (PHA) studies, Layers of Protection Analysis (LOPA) or QRA among others.

In this section, some basics of process safety and risk analysis are presented, in order to help the reader get acquainted with this field. First, some basic concepts are presented, after which the definition and classification of major accidents are discussed; later, the strategies used to apply ISD and the QRA technique are explained; all of these concepts are important to understand the methodology developed in this thesis.

2.1.1. Risk, frequency and consequences of accidents

Risk analysis is the science of risks, their probabilities and evaluation. Risk is defined as a measure of the damage caused on humans, the environment or material property in terms of the probability of occurrence of an incident and the magnitude of the damage. It can be expressed mathematically as presented in Eq.(2.1).

$$Risk = Frequency \cdot Magnitude\ of\ Consequences \tag{2.1}$$

It can be said that risk is the probability of a potentially hazardous situation unfolding and impacting a vulnerable element. Risk can be classified in the following ways (Casal, 2008):

a) General classification

- **Category A**: unavoidable and acceptable without compensation.
- **Category B**: strictly avoidable, but considered unavoidable in everyday life.
- **Category C**: clearly avoidable, but people expose to them because they can be rewarding.

b) Industrial activities classification

- **Conventional**: related to the activities and equipment normally found in most industries.
- **Specific**: associated to the manipulation of those substances considered to be hazardous due to their nature (highly flammable, toxic, etc.).
- **Major**: related to exceptional accidents and situations which consequences can be especially severe, as great amounts of energy or hazardous materials can be released in short periods of time.

c) According to the number of affected people

- **Individual risk**: affects an individual placed in the vicinity of a hazard. This definition includes the nature of the injury to the individual, the probability of different types of injury occurring and the time in which the injury occurs.
- **Societal risk**: number of fatalities expected per year. It is calculated using demographic data for an area.

From the definition of risk (Eq. (2.1)), it can be gathered that it is a function of the frequency and the consequences of a possible hazardous situation. In terms of industrial risk analysis, a hazardous event can be defined as the release of material or energy that has

the potential to cause harmful effects on plant personnel, nearby communities or the environment; the frequency of such an event is the number of occurrences by unit of time. Once a hazardous situation develops to its final consequences, resulting in serious injuries to personnel, noteworthy damage to property, adverse environmental impact or a major interruption of process operations, it is called an incident or accident.

The sequels produced by an accident, for example, the thermal radiation in case of fire or the overpressure after an explosion are called effects; the measure of the effects on vulnerable elements (number of injured people, cost of damage to property) are the consequences of the incident.

2.1.2. Individual risk

It is the risk to which a person is subjected when in the proximity of a hazardous installation or activity. The risk to an individual may be estimated as (Manaan, 2005):

$$r_{ind} = \frac{1}{n_p}\sum_{i=1}^{n_a} n_k \cdot f_i \qquad \textbf{(2.2)}$$

Where:

r_{ind} (death·year^{-1}) is the individual risk of death.

n_p is the total number of persons at risk.

n_a is the number of types of accidents.

n_k is the number of deaths for accident type *i*.

f_i (year^{-1}) is the frequency of accident type *i*.

All accidents that might have an effect on this individual risk should be taken into account).

Individual risk can also be estimated in a specific location using the following formula (Casal, 2008):

$$r_{ind(x,y)} = \sum_{i=1}^{n_a} r_{ind(x,y,i)} \quad \textbf{(2.3)}$$

Where $r_{ind}(x,y)$ (deaths·year^{-1}) is the individual risk in a geographical (x,y) location and $r_{ind}(x,y,i)$ is the individual risk for an accident i in a specific point.

$$r_{ind(x,y)} = f_i \cdot P_{Fi} \quad \textbf{(2.4)}$$

Where f_i is the frequency of accident i expressed in year^{-1} and P_{Fi} (deaths) is the probability that the accident i results in death in the (x,y) location.

2.1.3. Societal risk

Societal risk from an engineering point of view is often regarded as the relationship between the frequency and number of people suffering a specified level of harm from a particular hazard (Ball and Floyd, 1998). Following this definition, societal risk can be expressed in similar terms as individual risk; it can be estimated using the same parameters as individual risk, with the addition of the distribution of the population that is affected by the hazardous situations derived from the studied installation. Mathematically, it can be expressed as:

$$Societal\ Risk = \int (Individual\ Risk)[Population\ density(x,y)]dxdy \quad \textbf{(2.5)}$$

2.1.4. Risk tolerability

When an industrial activity is developed in an area, it introduces new hazards to the population living on the surroundings and to the environment, but it also has many perks,

mostly from the economic point of view; therefore, since industrial activities may have a positive impact on the lives of the people near them, the risk posed by industry is tolerated. This does not mean that the activities will be allowed to exist without control, but that the society allows them (despite the hazards) up to a point, if it is clear that the activities are carried out in safe conditions. It is then necessary to establish risk tolerability thresholds and ways to measure the risks associated to industrial activities and their impacts on the population and the environment.

An approach that is normally followed to define acceptable risk is to decide that there is a threshold above which risk becomes intolerable; this can be because its impact and frequency are too high or because it may make the activity non-profitable. The concept of risk becoming intolerable at a specific moment gives way to the idea of applying risk reduction to the point in which the risk becomes acceptable, because it may be technically or economically impossible to decrease it any further; this is known as the ALARP (as low as reasonably practicable) principle.

This principle states that above a certain level, risk cannot be justified on any terms. Below the intolerable region, there is an ALARP region, in which risk is accepted because a profit or benefit is expected. In this region risks are accepted if risk reduction is not practicable, whether because it is technically impossible to reduce them or because the costs of doing it are disproportionate compared to the actual risk decrease; the risk is as low as it can possibly be without making the activity non-profitable. Below the ALARP region, is the acceptable region, in which ALARP must not be demonstrated because risks are almost negligible. A graphical representation of the ALARP approach is presented in Figure 2.1 (Marszal, 2001).

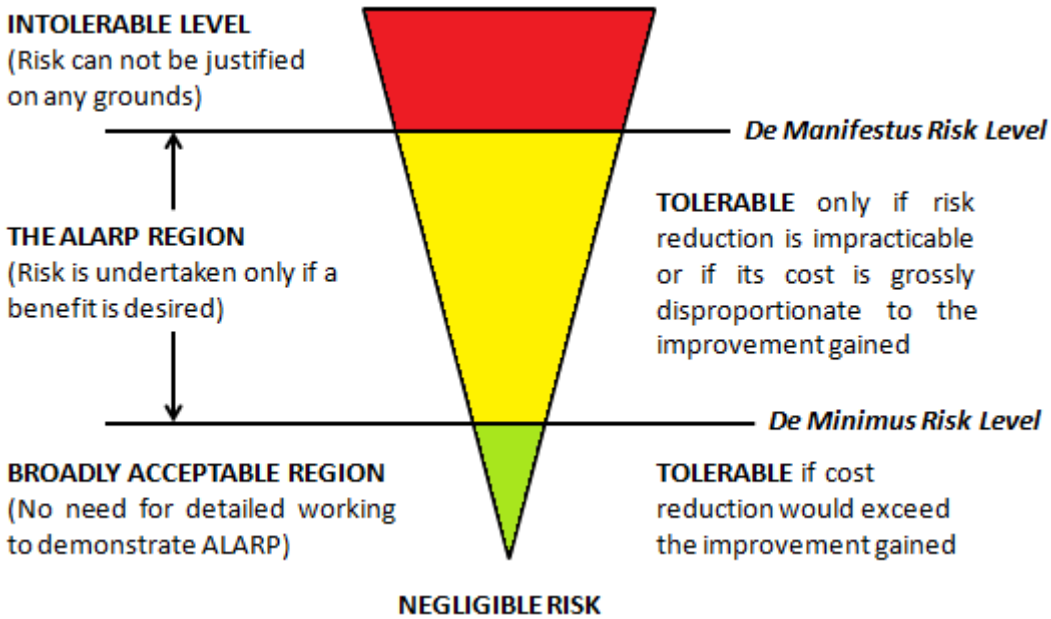


Figure 2.1. The ALARP principle.

It is difficult to decide in which region the risk becomes intolerable and reduction is required; in some countries, like the UK, the Netherlands or Spain (Catalonia), the government develops the acceptable risk criteria, while in others, like the USA, it is the responsibility of the companies that generate risk to decide at which point these become unacceptable. Normally, tolerable risk guidelines developed by governments are to be used for installations placed near populated areas, and rely on the concepts of individual and societal risk. A summary of tolerable risk criteria applied in different countries is presented in Table 2.1 (Marszal, 2001).

It can be seen in Table 2.1 that many countries apply the individual risk as a measure of the tolerable risk; this approach fits perfectly with the proposed methodology, since the results of QRA are normally expressed in individual iso-risk curves, which show areas affected by an individual risk of a specific value. The individual risk and its geographical representation will often be used in this work as the main constraint of the optimization

procedure. The Land Use Planning (LUP) criteria applied in some European countries, and the way in which they could interact with the developed methodology is explored next.

Table 2.1. Government tolerable risk criteria summary.

	UK	Hong Kong	The Netherlands	Australia (New South Wales)
Individual risk de minimus (Worker)	$1x10^{-5}$	Not used	Not used	Not used
Individual risk de minimus (Public)	$1x10^{-6}$	Not used	$1x10^{-8}$	Not used
Individual risk de manifestus (Worker)	$1x10^{-3}$	Not used	Not used	Not used
Individual risk de manifestus (Public)	$1x10^{-4}$	$1x10^{-5}$	$1x10^{-6}$	$1x10^{-6}$
Societal risk anchor	10 persons at $1x10^{-4}$	10 persons at $1x10^{-4}$	10 persons at $1x10^{-5}$	Not used

- **Land Use Planning (LUP) criteria in Europe**

The 96/82/EC or Seveso II Directive requires its Member States to introduce Land Use Planning (LUP) criteria at the moment of designing new, or evaluating existing establishments that fall under the obligations of the Directive. A question that could arise at the moment of applying a methodology as the one proposed in this work is if the different planning criteria applied in various countries could have an effect in the response of the optimization procedure, or if the methodology could have an effect on LUP. Cozzani et al. (2006) have presented a thorough analysis and comparison of the different LUP criteria applied in various European countries, which can be of great help at the moment of ascertaining the relationship that can arise between LUP and a model like the one developed in this work. Cozzani's investigation shows that four principal criteria are used in Europe; these are referred to by the name of the countries that use them, and are: the French, the Dutch, the British and the Italian criteria.

The French criterion follows a deterministic/effects based approach that requires the identification of the worst-case scenario for different risks associated to an area, and the determination of damage zones associated to them. The Dutch criterion (also used in

Catalonia, Spain) requires the calculation of the individual and societal risks associated to the area being evaluated, the threshold value for individual risk acceptability being 10^{-6} in residential areas. The British criterion is similar to the Dutch one, but requires the identification of three consultation zones: the inner zone, defined by an individual risk higher than 10^{-5} events/year, the intermediate zone, in which individual risk is higher than 10^{-6} events/year and the outer zone, outlined by an individual risk higher than $3x10^{-7}$ events/year. The Italian criterion is based on the identification of four damage distances for each risk scenario considered during the evaluation, associated to a probability of event occurrence that is ranked between $<10^{-6}$ and $>10^{-3}$ events/year; these damage distances and probability classes are combined using a matrix form, in which each cell represents a specific risk category that can be associated to compatible land-use categories.

The primary goal of the proposed method is to optimize the design, not to comply with LUP criteria in the country in which it is used, but to lower the value of risk associated to the installation during the time in which it will be operational, taking into account the rate of accident occurrence and the consequences of different events. However, the methodology has a direct relationship with LUP, as its application will have a direct impact on individual and societal risk curves used for the Dutch and British criteria, on the worst case scenarios that are applied on the French criterion, and on the damage distances and probability classes used in the Italian approach.

The methodology will be proposed in order to have the capability of being adapted to be used with any of the criteria described above; in this work, the criteria applied in Catalonia has been used, but it could be easily changed for those of the LUP methods used in other countries.

2.1.5. Legal framework

After the occurrence of major industrial accidents like the Flixborough explosion (UK, 1974) and the Seveso disaster (Italy, 1976), a legislation related to the prevention and

emergency response in case of major accidents was developed for its application on the members of the European Community. The 82/501/CEE, known as The Seveso Directive, imposed a set of rules and regulations that industrial facilities which handled a certain amount of hazardous materials had to comply with in order to prevent major accidents, or limit their effects on the population and the environment; its aim was the improvement of the safety of sites containing large quantities of dangerous substances. The Seveso Directive was superseded in 1996 by the 96/82/EC or Seveso II Directive. This second version has been recently modified by the 2012/18/EU, or Seveso III Directive.

The Seveso Directive was transposed to Spanish jurisdiction through the Royal Decree 886/1988, of July, 15, which was later modified by the R.D.952/1990. The 20th of July of 1999, the R.D.1254/1999, which transposed the 96/82/CE (Seveso II), was published.

According to the R.D.1254/1999, all affected establishments must present the following documents and risk analysis to the governments of the regions.

- **Notification**: in which the company that generates the risk is identified, the hazardous substances they handle are specified (for example with safety sheets), the processes performed are explained and a description of the elements placed on the surroundings that can initiate a major accident is presented.

- **Policy of major accidents prevention**: this is, in a broad context, the safety policy of the company that generates the risks.

- **Domino effect**: a document in which the surrounding elements that can initiate a domino effect on the establishment, or that can suffer a major accident due to the activity performed, are identified.

- **Safety report**: a document in which the company that generates the risks demonstrates the following: that a policy for the prevention of major accidents has been instated; that the risks associated to the installation have been identified; that, when necessary, measures have been taken to reduce risks; that the installation has been designed in a reliable way from the safety point of view; that emergency plans have been elaborated for the installation.

- **Emergency plans**: in this document, the company defines the organization and the set of measures that are in place in order to prevent major accidents or mitigate their consequences.

In Catalonia, the 12/2008 law of industrial safety of the Autonomous Government of Catalonia establishes that a QRA is obligatory for companies affected by the Seveso II Directive. This QRA must be evaluated by a credited entity, and must be performed following the methodology described in the CPR18E (2005).

This laws and regulations are important in the frame of the present work and the methodology developed, as the results of this work may have an effect on the way in which QRA is used during the life cycle of a project, and may help companies comply with the regulations in an easier way, from the beginning of the project.

2.1.6. Major accidents

A major accident can be defined as an occurrence (like an emission, fire or explosion) resulting from uncontrolled developments in the course of the operation of an installation, which can pose serious hazards to human health, the environment or material property; these hazards can be immediate or delayed, inside or outside the limits of the installations and involving one or more hazardous substances.

Major accidents, which are always preceded by a loss of containment, involve the instantaneous or continuous release of significant amounts of energy or hazardous materials; this can occur in fixed installations, as well as during temporary operations or transportation.

As has been said before, major accidents can affect people, property or the environment. The consequences on human beings can be physical (death or injury) or psychological, and can affect the employees of the involved installation or the external population; consequences on property are related to the damage or destruction of equipment or buildings, owned or not by the holders of the installation; environmental affectation can be instantaneous or continuous, and includes the emission of hazardous materials to the atmosphere, soil or water. Also, major accidents have related indirect consequences, as the loss of profit or image of the installation involved.

Major accidents can be classified in fires, explosions or toxic dispersions; a historical analysis has been made (Casal, 2008) to deduct the relative frequency with which these accidents occur, obtaining the results shown in Table 2.2.

Table 2.2. Relative frequencies of occurrence of major accidents.

Type of accident	%
Fire	47
Explosion	40
Toxic cloud	13

In this section the different types of major accidents and their variants are described in a general non-detailed way.

2.1.6.1. Fires

Of the various accidents that can occur in the process industry, fires are generally those whose effects are felt on shorter distances, while the effects toxic dispersions and

explosions cover much larger areas; however, the effects of a fire can be severe, as the thermal radiation the emit may affect other equipment, generating a domino effect which may result in more events (releases, explosions) that can increase the scale of the initial accident.

The categories of fires that can occur during the handling, processing, storage or transportation of hazardous substances are presented and described next.

- **Pool fires**: the stationary state combustion of a pool of flammable liquid (usually a hydrocarbon) with a specific size and shape, determined by the presence of a containment dike or bund, or the slope of the ground.

- **Flash fires**: the phenomenon of combustion of a flammable cloud, which has formed after the release of a flammable gas or vapor under certain meteorological conditions like low wind speed; this incident can also occur after the release of a pressurized liquid which suffers vaporization or due to evaporation from a pool. Once the flammable cloud has formed, it will drift according to the direction of the wind until it reaches an ignition source; at this moment, the mass of combustible within the flammability levels will burn quickly and the flames will propagate throughout the cloud. This phenomenon occurs in an extremely low period of time, but the area covered by the cloud is exposed to a tremendous amount of thermal radiation; outside the space enclosed by the cloud, the thermal effects are greatly reduced and considered to be negligible.

- **Jet fires**: **t**his type of fire is caused by the combustion of a flammable gas or vapor that escapes through a hole at a particular velocity. Normally, great amounts of air are mixed with the flames during this phenomenon (due to the turbulence of the flow), which increases the rate of combustion, and results in jet fires having flame temperatures higher than those present in other types of fires; as a consequence of the

form of this accident, a jet which can have a considerable length, and of the high flame temperatures, jet fires are known to lead to domino effects, as they can impact surrounding units or pipes in an installation, causing them serious damages, leading to new releases which are exposed to a direct ignition source.

- **Fireball**: these accidents normally occur after a Boiling Liquid Expanding Vapor Explosion (BLEVE), as a pressurized liquid is violently released from its container and suffers instant depressurization; this will lead to a flash process and the formation of a liquid/vapor biphasic mixture, which, if flammable, will ignite and form a ball of fire, initially at ground level, which will afterwards increase in volume and start ascending, leaving a trail behind.

2.1.6.2. Explosions

An explosion can be defined as a phenomenon which occurs when there is a violent release of energy to the atmosphere due to a rapid increase in the volume of a gas or pressurized liquid, caused by an expansion, the sudden vaporization of a liquid or an uncontrolled chemical reaction. This increase in volume will lead to a quick displacement of air, which may result in an overpressure wave capable of causing damage. When the shock front of the explosion is moving at supersonic speeds, the phenomenon is defined as a detonation, while if it is moving at subsonic speeds, it will be known as a deflagration. Explosions are the second most frequent accident after fires, and before toxic dispersions (Casal, 2008).

Explosions occurring in the process industry can be classified as follows:

- **Vapor Cloud Explosions (VCE)** : this phenomenon may be defined as the ignition of a cloud of flammable vapor, resulting in the formation of an overpressure wave; if there is no shock wave, the phenomenon is referred to as a flash fire. The occurrence of the overpressure has been associated to the presence of obstacles, structures

(congested areas) or semi-confined spaces in the area occupied by the flammable cloud.

- **Mechanical explosions and BLEVES** : these events are related to the burst of vessels; in them, the energy of the explosion derives from the pressure inside the equipment, the higher the pressure, the larger the explosion (Mannan, 2005). One of the most dangerous effects of a vessel explosion is the release of the fragments.

  A Boiling Liquid Expanding Vapor Explosion (BLEVE) is a specific case of mechanical explosion, which normally occurs when a pressurized tank containing a liquefied gas is exposed to, or engulfed by fire, leading to the tank walls loosing properties and ultimately failing, followed by the instantaneous vaporization of the contained liquid.

- **Dust cloud explosions** : when a particulate oxidizable solid, finely divided (such as flour, sugar, aluminum or carbon), suffers a sudden combustion when dispersed on air, a succession of explosions may occur. The characteristics of dust explosion are determined by the size of the dust particle and the concentration of solids on the environment. They normally occur in confined spaces or the interior of equipment (silos, cyclones). Normally, an initial explosion generates a strong turbulence which disperses a great amount of dust that may then ignite, causing a second stronger explosion.

2.1.6.3. Toxic dispersions

The release of a toxic substance can lead to the formation of a toxic cloud. Depending on the relative density of the cloud against air and of the meteorological conditions during the release, the cloud will disperse quickly on the atmosphere, or will evolve closer to the ground and will move at wind velocity. This is the least frequent of the

major accidents, but it is the one which can affect greater zones and have the most grievous consequences.

2.2. Quantitative Risk Assessment (QRA)

Quantitative Risk Assessment (QRA) is one of the backbones of this thesis; in this section, its definition and the steps that have to be followed in order to perform a QRA will be explained.

QRA is a method used to define the risk associated with a plant or industrial site by estimating the consequences and frequencies of a set of possible accidents in a systematic way. Initially, a set of possible Loss of Containment Events (LOCs) is defined for the different equipment in the installation. After this, the accidents that can occur following a specific LOC event, and their frequencies, are defined, for example, by using event trees. The next step is to estimate the effects and consequences of the possible accidents, to finally, estimate the individual and societal risks on the surroundings of the studied industrial site or plant; from this information, curves can be obtained to graphically represent the risk on the affected zone.

QRA is a widely applied and accepted technique, which can have a great impact on the LUP criteria applied on the zone in which the industrial installation is located. Because of this, it can also be very important on the design of a new plant, restricting its location to a zone in which the risk posed by the installation is acceptable; for example, if the risk the installation supposes to a nearby populated area is higher than a certain accepted value, the design of the plant will have to be changed until the risk decreases to permitted levels, or it will have to be relocated to another zone.

2.2.1. Stages of a QRA

A QRA is a systematic procedure that normally follows a set of defined steps or stages. Each one of these is explained in detail in this section.

2.2.1.1. Data recollection

The first stage of a QRA is to gather information regarding the installation that has to be evaluated. It is necessary to know which substances are stored or handled, and in which quantities; also, the size of equipment and the operating conditions of the process are necessary. Knowing if there are containment bunds and drain canalization, and their capacities is also important. Finally, if loading/unloading operations are performed, or if hazardous materials are transported in containers inside the facility, the number and characteristics of these operations will have to be known.

Meteorological conditions on the site of the installation also must be known, as well as the distribution of the vulnerable elements on the surroundings of the plant. It is absolutely necessary to have an integral knowledge of an installation and its background before a QRA is carried out.

2.2.1.2. Identification of accident initiators

In this stage the equipment in which major accidents can occur must be identified; for example, storage tanks, pumps, reactors, main pipes, etc. If different substances are handled in some equipment, a set of representative substances to be used will have to be defined.

After the equipment that will be studied is selected, a set of possible LOCs that occur due to equipment failure has to be defined; for example, a catastrophic rupture of equipment or the continuous release of the product in a specific timeframe.

2.2.1.3. Estimation of the frequency of accident initiators

There are several techniques that can be used to know the frequency of failure of equipment, like historical analysis or fault tree analysis. Data on the frequency of failure of different types of equipment, and the way in which they fail, can be found in the literature (CPR18E, 2005).

2.2.1.4. Determination of the probabilities of occurrence of accidents

After the initial LOCs have been defined, and their frequencies estimated, the sequence of events that can take place after the release must be developed, in order to obtain the possible major accidents that can occur (Figure 2.2).

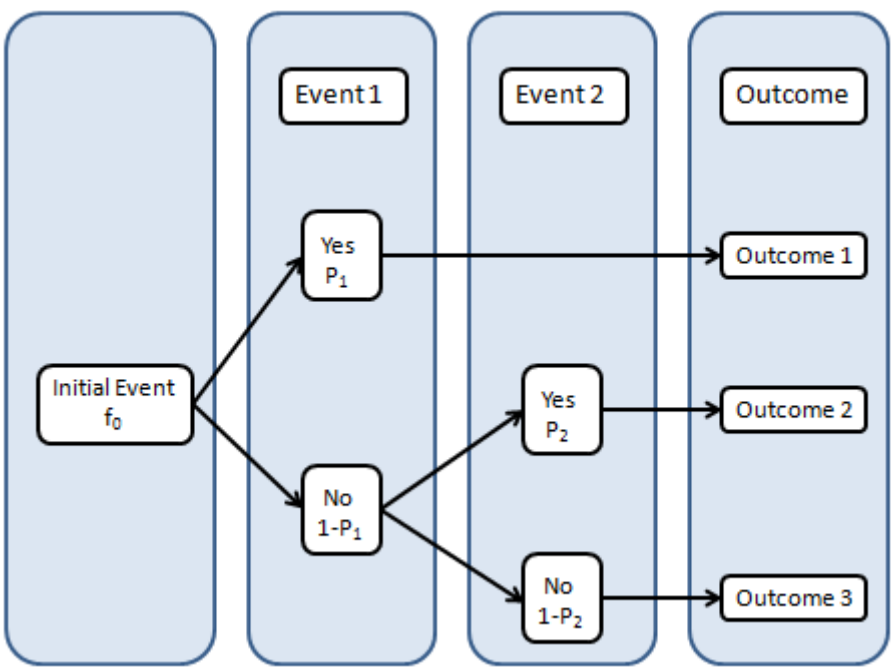


Figure 2.2. Example of an event tree.

This can be done through the use of event tree analysis, which is a technique that aims to find the possible final outcomes of an initial situation, through the development of a sequence of events, each one having a specific probability of occurrence.

If the frequency of the initial event and the probabilities of each of the subsequent occurrences are known, the frequency of the final outcomes can be calculated using the following expression:

$$f_i = \sum_j f_0 (P_1 \cdot P_2 \cdots P_k) \tag{2.6}$$

Where:

f_i is the frequency of outcome i.

f_0 is the frequency of the initial event.

P_k is the probability of occurrence of the intermediate events.

2.2.1.5. Estimation of the effects and consequences of major accidents

Once the possible accidents that can occur in the installation have been defined, and their frequencies estimated, their effects, and the consequences they will have can be estimated as functions of the distance. In this way, the probability of a person suffering an injury or death due to the effects of a specific accident can be known.

2.2.1.6. Estimation of individual risk

If the consequences (as a function of the distance) and frequencies of all the accidents associated to the installation are known, Eq. (2.3) can be used to calculate the individual risk derived from the plant in its surroundings. This result can be presented in individual iso-risk contours (as shown in Section 2.2.2.1).

2.2.1.7. Estimation of global risk population

Finally, if clusters of population result affected by the industrial activity, a distribution of this populace must be estimated and societal risk calculated using Eq. (2.5).

2.2.2. Risk mapping

As has been said before, risk can be represented graphically in different ways; two of the most important and used ways of mapping risk are the individual risk contours and the societal risk (f-N) curves.

2.2.2.1. Individual risk contours

These curves are used to geographically represent the individual risk resulting from an installation or activity. Iso-risk curves connect all those positions in space in which the value of individual risk obtained from a QRA are equal, which means, all the places that have the same lethality probability. This is the most commonly used form of representation of the results of QRA.

In order to produce iso-risk curves it is necessary to take into account the individual contribution of all possible accidents to the overall risk on the evaluated zone, which means that different scenarios and meteorological conditions have to be considered.

Individual risk contours are normally used to know if surrounding clusters of population fall within a region in which the risk for the public is non-tolerable (normally the 10^{-6} curve). Figure 2.3 shows an example of how an individual iso-risk curve, obtained from a QRA, looks like (obtained from CPR18E).

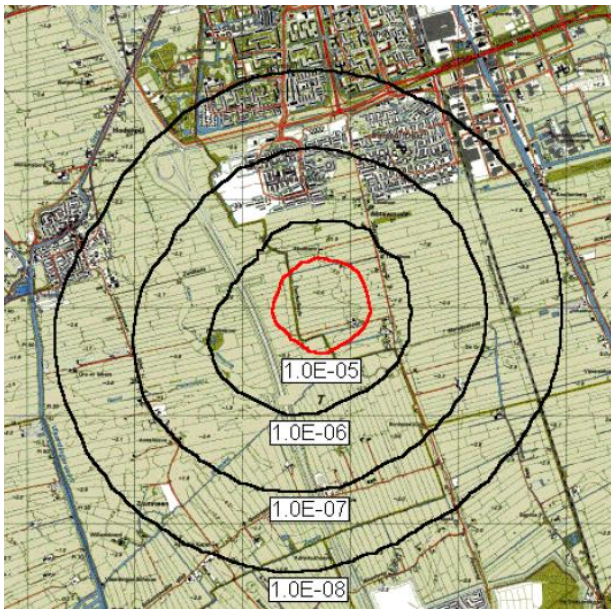


Figure 2.3. Example of an individual iso-risk contour (CPR18E, 2005).

2.2.2.2. Societal risk curves

Societal risk is normally presented in f-N curves, which is a graph of cumulative frequency as a function of the consequences of accidents (commonly expressed as number of deaths). These curves are compared against appropriate societal risk criteria, as seen in Figure 2.4; the graphic shows an example of the results of two projects, one that does not exceed the tolerable limit (Project 1) and another in the opposite situation (Project 2).

2.3. Inherently Safer Design in the process industry

There are intrinsic hazards associated to chemical plants and processes which cannot be completely eliminated; however, as mentioned before, companies are responsible for the control of these hazardous situations, and for making the risk associated to their processes as low as possible and therefore, tolerable.

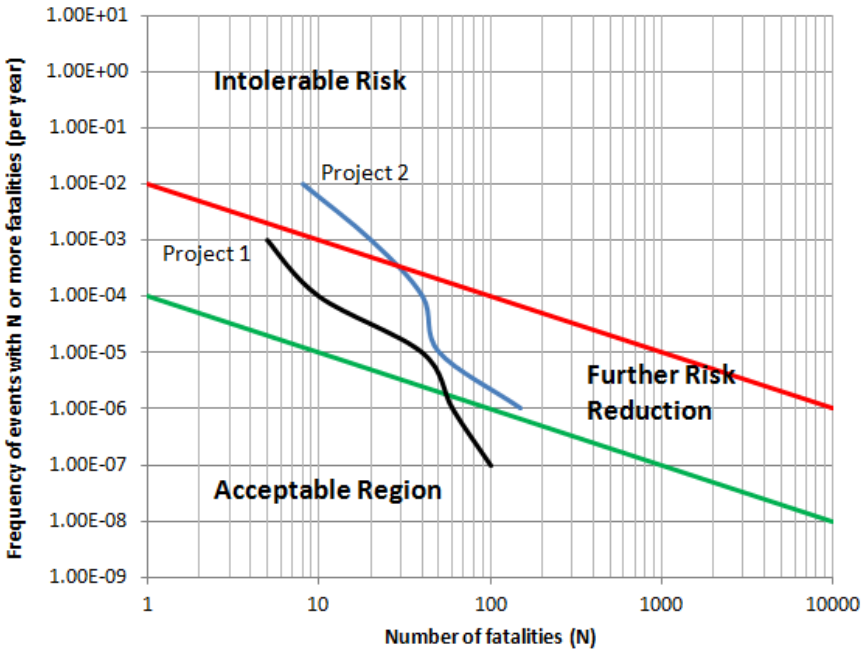


Figure 2.4. Example of a f-N curve.

2.3.1. Chemical process safety strategies

There are four strategies which can be used to achieve safety in chemical processes: inherent, passive, active and procedural (Hendershot, 2006).

- **Inherent**: the inherent approach tries eliminating or reducing hazards by making essential changes in the process or in the materials used. An example would be achieving the liquefaction of a gas through refrigeration, rather than pressurization.

- **Passive**: the passive strategy minimizes hazards with design features which can reduce the frequency or consequences of a certain accident without the activation of a safety device; a clear example is a containment dike surrounding a storage tank, which minimizes hazards after a LOC, but does not require any activation.

- **Active**: active measures refer to control and automatic systems that are used for safety in the process, like safety interlocks or automatic shut-down systems.

- **Procedural** : the procedural strategy is associated with all the administrative measures that are taken in a plant to maintain the safe operation, like operating procedures, emergency plans, training, work permits to perform hazardous operations, etc.

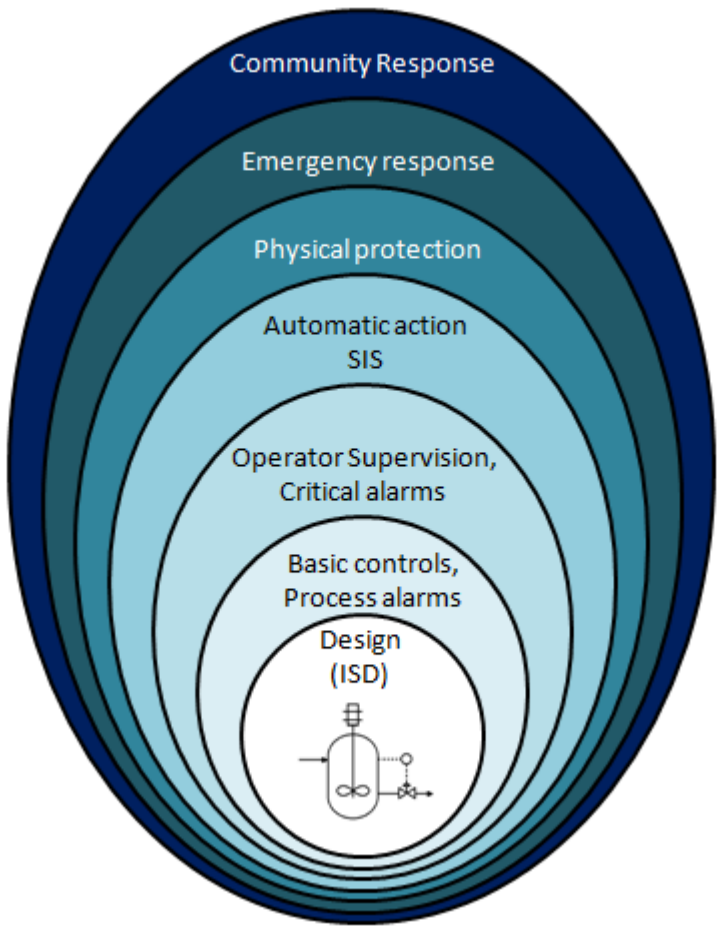


Figure 2.5. Layers of protection in chemical processes.

The application of these strategies is normally presented as "Layers of Protection" (Figure 2.5); these layers range from the basic design of the installation through the

different types of controls in the process (basic control, alarms, safety instrumented systems, etc.) and physical protections (containment dikes), to the emergency plans of the plant, site or community.

Of all these techniques, the inherent approach is the one that brings better results, especially if it is applied at the initial stages of the design of a project. Generally, in order of robustness and reliability, the strategies are ordered as inherent, passive, active and finally, procedural, although there is a necessity for all of them during the life cycle of a process plant (Hendershot, 2006).

This thesis is more concerned with the inherent and passive strategies, as active or procedural risk reducing measures are not considered in any way in the proposed methodology.

2.3.2. Definition of ISD

Inherently Safer Design (ISD) or Inherently Safer Technology (IST) is a concept that, in direct relationship to the process industries, dates from 1974, when, after the Flixborough explosion Trevor Kletz questioned the need for such large quantities of hazardous materials to be stored in process plants, as well as the need for processing at such elevated pressures and temperatures (CCPS, 2010).

The Center for Chemical Process Safety (CCPS) has produced a definition for Inherently Safer Technology (CCPS, 2010):

"Inherently Safer Technology (IST), also known as Inherently Safer Design (ISD), permanently eliminates or reduces hazards to avoid or reduce the consequences of incidents. IST is a philosophy, applied to the design and operation life cycle, including manufacture, transport, storage, use, and disposal. IST is an iterative process that considers such options, including eliminating a hazard, reducing a hazard, substituting a less

hazardous material, using less hazardous process conditions, and designing a process to reduce the potential for, or consequences of, human error, equipment failure, or intentional harm. Overall safe design and operation options cover a spectrum from inherent through passive, active and procedural risk management strategies. There is no clear boundary between IST and other strategies."

One of the most important characteristics of ISD is that it is a relative concept, a certain design or technology may be inherently safer when compared to another, but no design is completely inherently safe; also, a design may be safer from a point of view, while seeming less from others. This means that it will ultimately depend on the people working on the project to decide which design or technology they will use, by assessing the different possible hazards related to the project and deciding the level of acceptable risk for the plant and the economic investment that can be made on safety. It has to be said that an ISD is not necessarily enough to comply with laws and regulations regarding risk, it is an inherent layer of protection that relies on design, but that has to be accompanied by other safety measures in order to decrease the risk as much as possible.

2.3.3. ISD strategies

ISD as proposed by Kletz (1991) is based in five main approaches: intensification, substitution, attenuation, limitation of effects and simplification; however, CCPS divides ISD strategies into four categories (Hendershot, 2012): substitution, minimization, moderation and simplification (Figure 2.6). There is a general consensus to use these four definitive approaches to ISD, as other possible strategies formulated are considered to be sub-sets of those defined by CCPS. These are explained next.

2.3.3.1. Substitute

The substitute strategy is based on the use of less-hazardous materials, chemistry and processes. There are various ways of applying it, for example, changing materials to

reduce fire hazards or make a process more environmentally friendly; another option is substituting a reaction for another one which entails fewer hazards.

2.3.3.2. Minimize

Minimizing refers to the use of small quantities of hazardous materials; reduction of the size of equipment operating under hazardous conditions such as high temperature or pressure.

Through the use of this strategy, the consequences of major accidents (fires, explosions) can be reduced, as the amount of energy present in the process is reduced. Also, applying this strategy can make other safety systems more effective; for example, secondary containment units, dumping, quenching or flaring systems could be designed for lower capacities.

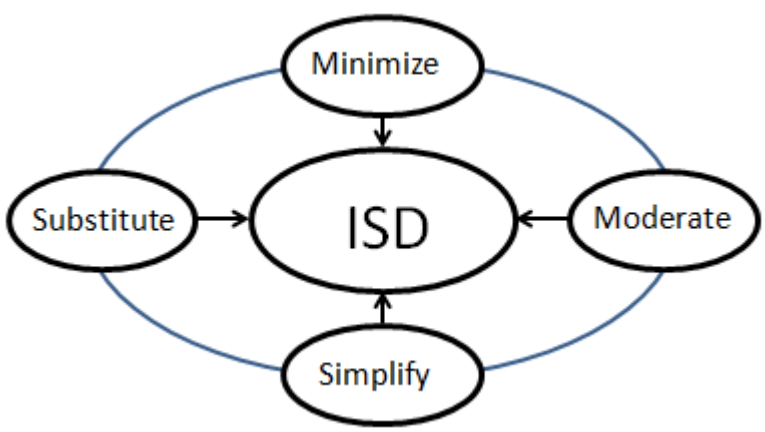


Figure 2.6. ISD strategies.

2.3.3.3. Moderate

This strategy, also known as attenuation, refers to the reduction of hazards by making processes operate at less hazardous conditions. This can be done through the

application of physical means like dilution or refrigeration, or through chemical means, by using reactions which require less hazardous conditions.

2.3.3.4. Simplify

Simplification means eliminating unnecessary complexity in a process; examples of simplification are the removal of alarms that are not critical for the process and that can cause confusion during an emergency situation, or the elimination of pipes that are not normally used in the process. Applying this strategy the probability of accidents occurring due to incorrect operation is reduced.

2.4. Storage of hazardous materials and process safety

This work deals with the problematic of the design of storage installations and how to make them safer; therefore, it becomes necessary to know the types of tanks that are used in the process industry, and the types of failure that they suffer and that ultimately lead to LOCs and major accidents.

2.4.1. Types of storage tanks

Storage tanks can be classified according to different criteria, like shape, material or design parameters. Following, some of the types of storage tanks that are normally used in the process industry are presented; they are classified mainly by their operating pressure and secondarily by shape.

2.4.1.1. Atmospheric tanks

Atmospheric tanks are designed to store liquids at atmospheric pressure. Some types of atmospheric tanks are:

- **Rectangular or square tanks**: used to store innocuous materials like water. They normally have low capacities (< 20 m^3).

- **Horizontal cylindrical tanks**: used to store different types of substances (gasoline, oils, etc.) and having a medium capacity (< 150 m^3). These tanks can be built aboveground or underground (Figure 2.7).

Figure 2.7. Underground and aboveground horizontal cylindrical tanks.

- **Vertical cylindrical tanks**: used to store large quantities (10-20,000 m^3) of hydrocarbons and other types of materials, they are the common type of tank used in oil storage terminals. There are many different types of vertical cylindrical tanks, among which are those with cone roofs or with floating or fixed roofs (Figure 2.8).

2.4.1.2. Pressurized vessels

Pressurized vessels are designed to withstand very high pressures exerted by their contents. They are used to store liquefied or compressed gases. Due to the nature and conditions of the substances that are normally stored in pressurized vessels, when accidents occur in this type of equipment, they are associated to grievous effects, involving

mechanical explosions and fragment projections. Installations using this type of vessel are also more vulnerable to possible domino effects. The types of pressurized storage tanks that will be studied in this thesis are:

Figure 2.8. Floating and conical roof atmospheric tanks.

- **Horizontal cylindrical pressurized vessels**: this type of vessel can be built aboveground or mounded. When mounded, the stored capacity can be increased, and many of the hazards associated to the equipment may be reduced (Figure 2.9).

Figure 2.9. Aboveground and semi-mounded horizontal pressurized vessels.

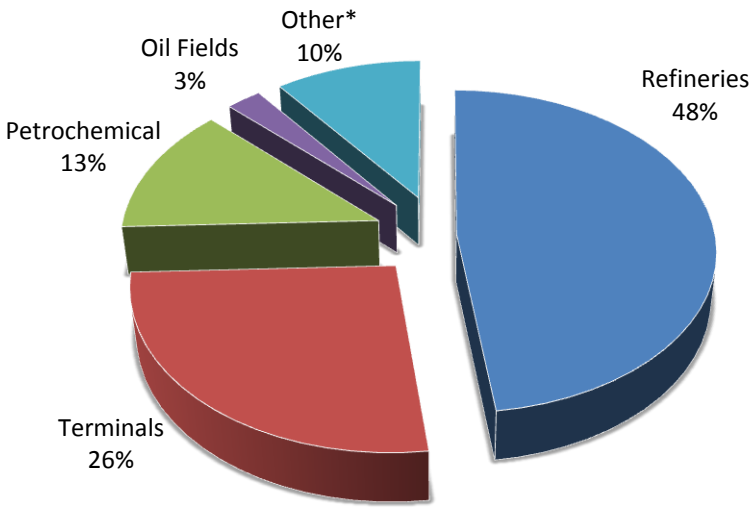
- **Spherical pressurized vessels**: these tanks have a better volume to quantity of material ratio than horizontal tanks, and are used when large quantities of materials need to be stored; however, they are difficult to manufacture and therefore, are more expensive than other vessels (Figure 2.10).

Figure 2.10. Pressurized spherical vessels.

2.4.2. Common causes of failure in storage tanks

There are many ways in which any equipment in a process plant can fail, whether because of a design error, being operated outside safe parameters, poor maintenance, an external event or many other possibilities; a very thorough review of 242 tank accidents that occurred from the ninety-sixties up to the last decade was performed by Chang and Lin (2006), in order to ascertain the causes that led to the failure of the tanks.

From the 242 accidents studied, 47.9% occurred in refineries, 26.4% took place in terminals and pumping stations, 12.8% in petrochemical plants, 2.5% in oil fields and the remaining 10.3% in other types of installations such as power plants, gas plants, fertilizer plants, etc. The type of tank that suffered more accidents was the atmospheric external floating roof tank (55%), followed by the cone top (21%) and pressurized spheres (13%); the remaining accidents were identified on cone with internal floating roof tanks and refrigerated tanks; Figure 2.11 and Figure 2.12 show this data graphically.



*Power, gas, pipeline, fertilizer and planting plants

Figure 2.11. Tank accidents per type of installation (Chang and Lin, 2006).

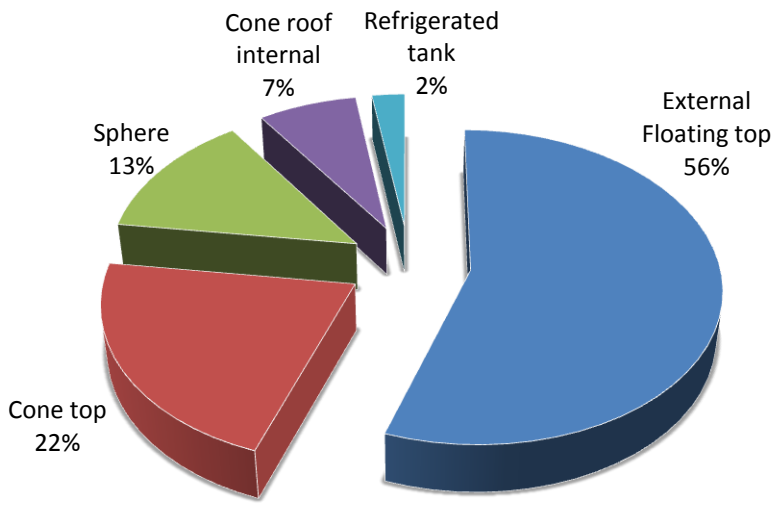


Figure 2.12. Accidents per type of tank (Chang and Lin, 2006).

Many causes of accident were identified during the investigation, of which lightning (an external event) was the more frequent, followed by maintenance error. Other identified

causes of failure were operational error, static electricity, line rupture, etc. The complete list of causes identified is presented in Table 2.3.

Table 2.3. Causes of tank accidents (Chang and Lin, 2006).

Cause	Number of accidents	%
Lightning	80	33.06
Maintenance/Hot work	32	13.22
Operational error	29	11.98
Equipment failure	19	7.85
Sabotage	18	7.44
Crack/rupture	17	7.02
Leaks and line rupture	15	6.20
Static electricity	12	4.96
Open flame	8	3.31
Nature disaster	7	2.89
Runaway reaction	5	2.07
Total	242	100.00

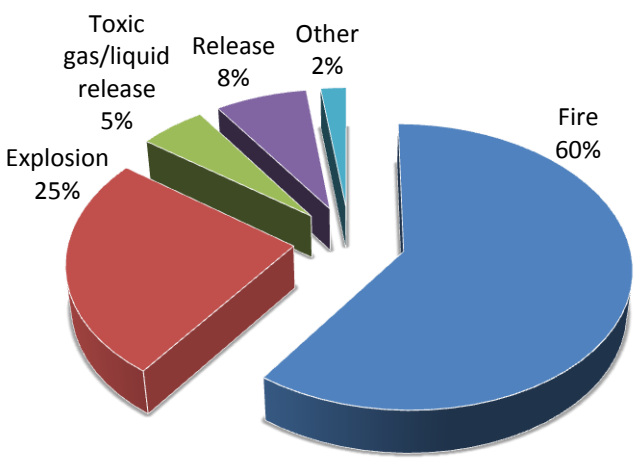


Figure 2.13. Types of accidents in storage tanks.

The causes identified in Table 2.3 were found to lead to major accidents in the following proportion: fire was the most frequent, occurring in 66% of the events; explosions were second with almost 28%; close to 6% of the accidents were related to

toxic gas/liquid dispersions (Figure 2.13). These are the types of accidents that normally occur in storage installations, and that will be evaluated in this work; the mathematical models used to estimate their effects and consequences are presented in CHAPTER 3.

2.4.3. Major storage accidents in the process industry

In order to stress the importance of improving the design of storage installations from a safety point of view, some major accidents that have involved storage installations and that have caused great human or economic losses are presented. The San Juanico disaster (Mexico, 1984) and the Buncefield fire (2005) are not included in this list, since they are studied in detail in case studies presented in CHAPTER 5 and CHAPTER 6. All accident descriptions have been obtained from "Lees Loss Prevention in the Process Industry, Third Edition" (Mannan, 2005) except for the Caribbean Petroleum Corporation oil depot fire in Puerto Rico (2009).

2.4.3.1. Cleveland, Ohio, USA, 1944.

At approximately 2.40 p.m. on 20 October 1944 a cylindrical LNG storage tank at the Liquefaction, Storage and Regasification Plant of the East Ohio Gas Company at Cleveland, Ohio, ruptured and discharged its entire contents over the plant and the nearby urban area. The LNG vapor ignited almost immediately and an intense fire burned at the plant, causing great loss of life and extensive damage. More LNG flowed from the plant as liquid down storm sewers, where it mixed with air and exploded. The final death toll was 128 and the numbers injured were estimated at 200-400. The greatest loss of life occurred within the plant area.

The cause of the rupture is uncertain. The Bureau of Mines investigation concluded that the low carbon steel used in the construction of the vessel may have been unsuitable and that the failure may have occurred due to vibration or seismic shock.

Following the rupture large quantities of liquid topped by burning vapor had flowed considerable distances from the tank. The report discussed the argument that a dike is not useful for a relatively volatile material such as LPG or LNG, concluded that a dike would have reduced the hazard and recommended that storages for liquefied gases should have a dike.

The report also made a number of other recommendations. These included the open siting of storage tanks to permit good ventilation; the use of precautions to eliminate sources of ignition to the standard considered necessary in explosives plants; the provision of remote closure for the bottom off-take valve; the installation of reliable level indicators and alarms; and the conduct of emergency drills.

2.4.3.2. Port Newark, New Jersey, USA, 1951

On 7 July 1951 a fire and BLEVEs devastated a large LPG storage at Port Newark, New Jersey. The storage comprised one section with 70 horizontal bullet tanks, each with a capacity of about 100 m^3, and a further 30 tanks nearby. The tanks were not provided with thermal insulation or fixed water sprays. The initial event was experienced as a slight explosion followed by a fire. Within the next two and half min there were four small explosions near the seat of this fire, followed half a minute later by a large flash, a muffled explosion and a large fireball. Some 10-15 min into the event a BLEVE occurred. The next 100 min were punctuated by tank explosions and BLEVEs every 3-5 min. In all 73 bullet tanks were destroyed (Figure 2.14).

2.4.3.3. Bakersfield, California, USA, 1952.

On 21 July 1952, the Paloma condensate recycling plant in Kern County, near Bakersfield, California, was struck by an earthquake. The earthquake had its epicenter about 12 miles away, measured 7.7 on the Richter scale and had a maximum intensity in the range X-XI. Ground movement was of the order of 0.5 ft vertically and 1 ft

horizontally. It was such as to cause a 60 ft high absorption column to swing at the top in an arc of 3 ft and to stretch its foundation bolts some 1.5 in. Figure 2.15 gives an aerial view of the facility following the earthquake.

Figure 2.14. Port Newark, 1951: tank section part buried in ground (The Bettman Archive).

The plant had five large butane storage spheres which were not designed to earthquake standards. Two spheres collapsed with rupture of the feed lines. Butane escaped and formed a vapor cloud, which ignited some 90 seconds later at a transformer block. The resultant explosion and fire did extensive damage but there were no deaths or serious injuries.

2.4.3.4. Montreal, Canada, 1957.

On 8 January 1957, a series of BLEVEs occurred at a set of storage spheres at Montreal, Quebec. There were three spheres in a common bund: one 800 m^3, one 1,900 m3 and one 2,400 m^3. The 800 m^3 sphere, which held butane, was overfilled due to a faulty level gauge. A vapor cloud formed and found an ignition source, probably at a service station 180 m away, and the flame flashed back to the sphere, where a pool fire started. After some 30 min the 1,900 m^3 sphere, which was less than 20% full, underwent a BLEVE. Some 15 min. later BLEVEs occurred on the other two spheres also.

Figure 2.15. Bakersfield, 1952: recycling plant after the earthquake (The Bettman Archive).

2.4.3.5. Feyzin France, 1966.

On 4 January 1966 at Feyzin refinery in France a leak on a propane storage sphere ignited, caused a fire that burned fiercely around the vessel and led to a BLEVE. The operator had opened two valves in series on the bottom of the sphere in order to drain off an aqueous layer. When this operation was nearly complete, he closed the upper valve and then cracked it open again. There was no flow and he opened the valve further. The blockage, which was presumably hydrate or ice, cleared, and propane gushed out, but the operator was unable to close the upper valve. He did not think at once to close the lower valve and by the time he attempted this, this valve also was frozen open. The alarm was raised and steps were taken to stop traffic on the nearby motorway. A vapor cloud about 1 m deep spread towards the road. It is believed that a car about 160 m distant on the motorway may have been the source of ignition. Flames appeared to flash back from the car to the sphere in a series of jumps.

The sphere was enveloped in a fierce fire (Figure 2.16). Its pressure relief valve lifted and the escaping vapor ignited. The LPG storage installation of which the sphere was a part consisted of four 1,200 m^3 propane and four 2,000 m^3 butane spheres. The fire brigade was not experienced in refinery fires and apparently did not cool the burning sphere, presumably on the assumption that the relief valve would protect it. They concentrated instead on cooling the other spheres. About one and a half hours after the initial leakage the sphere ruptured, killing the men nearby. A wave of liquid propane was flung over the compound wall and flying fragments cut off the legs of the next sphere, which toppled so that its relief valve began to emit liquid.

The accident killed 18 people and injured another 81 and caused the destruction of five of the spheres as well as other damage.

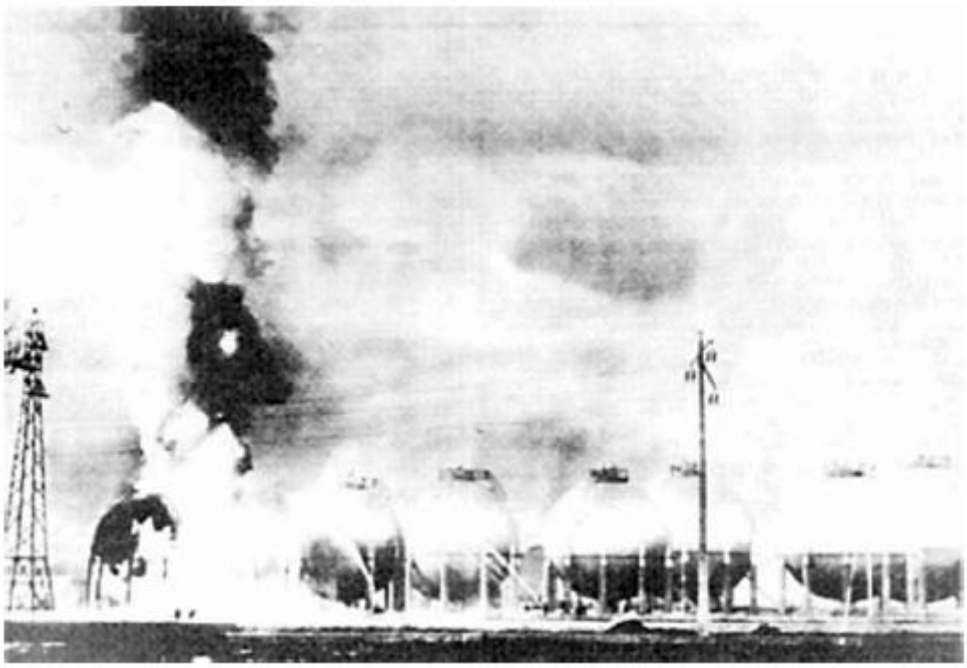


Figure 2.16. Feyzin, 1996: fire at the storage vessels (United Press International).

2.4.3.6. Beaumont, Texas, USA, 1970.

On 17 September 1970 at Beaumont, Texas, a 60 ft - 40 ft oil slops tank was struck by lightning. The tank failed at the shell-floor seam, releasing 11,000 US gal of oil, which burned. The oil spread to involve in the fire another 16 nearby tanks, which did not have containment bunds.

2.4.3.7. Rio de Janeiro, Brasil, 1972.

On 30 March 1972, a BLEVE occurred on an LPG sphere, one of five, at the Duque de Caxais refinery, Rio de Janeiro, Brazil. An operator was engaged in draining water from the bottom of a 1,600 m^3 sphere. He went away, leaving open a 2 in. drain valve. When he returned, he found that he could not reach the valve to turn the flow off, because the jet of liquid, now LPG, had created a crater in the crushed stone under the sphere. A vapor cloud formed, ignited and flashed back to the sphere. Some 15-20 min later the relief valve

opened and the material released ignited. The sphere then suffered a BLEVE. Thirty-seven people were killed and 53 injured. The other four storage spheres survived.

2.4.3.8. Potchefstroom, South Africa, 1973.

At 4:15 p.m. on 13 July 1973, a sudden failure occurred in an anhydrous ammonia storage vessel at the Potchefstroom works of TRIOMF, a company part-owned by African Explosives and Chemical Industries Ltd. The tank was one of four 50 ton horizontal pressure storage bullets. An estimated 30 tons of ammonia escaped from the tank itself and another 8 tons from a tank car. The failure gave rise immediately to a gas cloud some 150 m diameter and 20 m deep. At the time of the accident the air was apparently still, but within a few minutes a slight breeze rose which caused the cloud to move towards a township some 200 m to the north-east. The visible cloud then extended some 450 m downwind and 300 m across.

Deaths occurred both inside and outside the factory fence. At the time there were some 350 persons working in the plant, of whom some 30 were within 70 m of the failed tank. One employee was killed by the blast and eight died while trying to escape from points within a 100 m radius of the tank. Three others died of gassing within a few days. Outside the factory fence four people were killed immediately and two died a few days later. Thus altogether 18 people were killed.

The failures occurred in tank No.3 while it and tank No.4 were being filled simultaneously from a tank car. Actuation of an excess flow valve on the line between the two tanks prevented the release of the contents of tank No. 4 also. The tank car did not have an excess flow valve and did suffer escape of material. The cause of the failure was brittle fracture of the dished end of the tank. Evidence suggested that there had been no overpressure or over-temperature of the tank contents and no other triggering event was determined.

Late in 1971 tank No. 3 was inspected. Two weld faults and a crack were found and were ground out. The tank was hydraulically tested to 347 psig for 30 min. Following repairs to a leaking tank level glass isolation valve, the tank was hydraulically tested to 325 psig for 3-4 h. Metallurgical testing revealed that the metal of the dished end was below its transition temperature under normal conditions. The minimum Charpy impact testing transition temperatures obtained were 20ºC for the fragment and 115ºC for the remaining part of the dished end. Ultrasonic examination of the dished end in No. 4 tank revealed numerous subsurface fissures. Such fissures may have provided the notch from which the brittle fracture in No. 3 tank propagated. After this examination tank No. 4 was withdrawn from service.

Following the inquiry into this accident, the South African authorities laid down that 'All vessels containing dangerous substances shall be given appropriate heat treatment irrespective of the (construction) code requirements.'

2.4.3.9. Puebla, Mexico, 1977.

On 19 June 1977 a leak occurred on one of a group of VCM storage bullets. A fitter had made an error in removing an actuator from a liquid discharge valve on the tank, taking out the wrong bolts so that the valve plug suddenly popped out, allowing an escape through the 3 in. valve body. The release continued for 80 min in calm conditions, the vapor cloud formed being 1,100 ft long, 800 ft wide and 5 ft deep.

Five minutes later the cloud caught fire and flashed back to the tanks. A further 5 min later one tank suffered a BLEVE. Three more tank explosions followed. One person was killed and three injured.

2.4.3.10. Texas City, Texas, USA 1978.

On 30 March 1978, a series of fires and explosions occurred at LPG storage spheres at Texas City, Texas. There were three spheres, each 800 m^3. One of the spheres suffered overpressure while it was being filled, due to failure of a pressure gauge and also of a relief valve. It cracked and leaked LPG. The leak ignited giving a massive fireball.

Accounts differ in their description of the events which followed. According to Selway (1988 SRD R492), after 20 min a second sphere, which was only partially full, suffered a BLEVE. The third sphere, which was virtually empty, failed due to a heat-induced rupture at the top, but remained upright. Thus all three spheres were damaged, but there was only one BLEVE event. Mahoney (1990) states that during the 20 min following the fireball five horizontal bullets and four vertical ones were damaged by missiles, and that the other two spheres were also damaged in this way. The missiles started fires and hit the firewater storage tank and electrical fire pumps, although two diesel fire pumps remained operable.

2.4.3.11. Priolo, Italy, 1985.

On 19 May 1985 a major fire occurred on an ethylene plant at Priola in Italy. A faulty temperature probe initiated isolation of the hydrogenation unit in the cold section, and while the operators were trying to re-establish control, the relief system operated. At the same time fire was observed at the base of the de-ethanizer column. The hydrocarbon released ignited and an intense fire engulfed the adjoining ethylene and propylene distillation columns and spread to the storage area. The water deluge system protecting the storage tanks proved inadequate due to the intensity of the fire. In due course a tall, vertical propane tank exploded, its top section rocketing up some 500 m, and just missing a gasholder. Two propylene tanks fell over, one on a pipe rack and the other against an ethylene tank. In all, five of the eight ethylene and propylene tanks either exploded or collapsed.

2.4.3.12. Thessalonica, Greece, 1986.

On 24 February 1986, an oil terminal at Thessalonica, Greece, experienced a small fire when an oil spillage in a bund was ignited by hot work. The privately owned terminal had 12 fixed and floating roof storage tanks holding crude oil, fuel oil and gasoline. Over the course of seven days, ground fires escalated until they covered 75% of the terminal area and involved 10 of the tanks. The escalation of the initial small fire was due in large part to accumulation of oil from previous spillages; to leaks from flanges exposed to the fire, which then fed it; and to the failure of firefighting efforts in the early stages. By the first day seven tanks were affected.

In the course of the succeeding days, several events occurred which led to major escalations. On Tank 3 overpressure caused the shell-floor seam to burst so that the whole contents flowed out, feeding the fire and involving two more tanks. Tank 8 suffered a boilover with a fireball 300 m high and ejection of burning oil over a wide area, some travelling up to 150 m. The firefighting was hampered, and firemen endangered, by burn-back of flame in areas where the oil fire had already been extinguished by foam.

2.4.3.13. Code Island, Australia, 1991.

On 21 August 1991, an explosion occurred at A Terminal of Terminal Pty. at Coode Island, Mevaporourne, Australia. The site involved had 45 storage tanks, none pressurized, with a vapor recovery system. A 230 tons acrylonitrile tank was lifted off its base and projected over four other tanks into the forecourt. There followed a series of bund and tank fires and tank explosions, at the end of which only 13 tanks were left undamaged. There were no deaths or serious injuries.

2.4.3.14. Dronka, Egypt, 1994.

On 2 November 1994, blazing liquid fuel flowed into the village of Dronka, Egypt. The fuel came from a depot of eight tanks each holding 5,000 tons of aviation or diesel fuel. The release occurred during a rainstorm and was said to have been caused by lightning. Reports put the death toll at more than 410.

2.4.3.15. Savannah, Georgia, USA, 1995.

On April 10, 1995, at approximately 11:30 p.m., explosions and fire occurred at Powell Duffryn Terminals, Inc. (PDTI), a commercial bulk liquid chemical storage and transfer facility, in Savannah, Georgia. Flames and thick black smoke from the fire forced the residents of the adjacent townhouse development to evacuate immediately. It took firefighters almost 3 days to finally put out the fire. The fire was within a concrete walled enclosure area containing six large storage tanks. During the fire, part of the enclosure wall was breached releasing contaminated firewater. The run-off from the fire contaminated an adjacent marsh on the Savannah River resulting in a fish kill.

2.4.3.16. Tolouse, France, 2001

A massive ammonium nitrate explosion occurred on Friday 21 September 2001, at the Azote de France (AZF) fertilizer factory on the outskirts of Toulouse, France. The blast occurred in a storage facility that held 200-300 tons of granular ammonium nitrate.

During the tragedy, 29 people were killed; about 2,500 were injured. One wounded person died later. Ammonium nitrate is primarily used as a fertilizer; however, if it combined with certain additives it can be used as an explosive.

The AZF (Azote de France) started up in 1924 on the left branch of the Garonne River outside of Toulouse. The plant is in an industrial zone, but with urban sprawl the site is surrounded by housing and buildings used by the general public.

The blast crated a crater that was about 50-60 m with a depth of over 7 m. Windows were shattered within a radius of 1-1.5 km and windows were blown out in the city centre 3 km away. The strength was estimated to be equivalent to 30-40 tons of TNT.

2.4.3.17. Puerto Rico, 2009

On October 23, 2009, at 12:23 a.m. an explosion was registered in the Caribbean Petroleum Corporation oil depot in Bayamón, Puerto Rico. The initial explosion destroyed eleven storage tanks in the installation and quickly spread throughout the terminal.

Figure 2.17. Aerial view of the Caribbean Petroleum Refinery fires (CSB, 2013).

The accident was caused due to the malfunction of the monitoring system of a gasoline tank, which led to the undetected overfilling of the unit and the spill of product. After the gasoline was spilled, it dispersed in the atmosphere, forming a flammable cloud which found an ignition source in the north-east section of the facility, causing the initial explosion (Figure 2.17).

The fires burned in the facility for three days (Figure 2.18). There were no fatal victims, but the consequences of the accident included damages to homes and businesses more than a mile away from the installation, and the evacuation of thousands of residents of nearby towns.

Figure 2.18. Multiple fires at the Caribbean Petroleum Corporation oil depot (CSB, 2013).

2.5. Mathematical optimization

The main objective of this thesis is to combine mathematical optimization with QRA; this makes it important that some basic concepts related to the different types of optimization problems and how to solve them, are presented in this work.

2.5.1. Formulation of an optimization problem

Mathematical optimization is the process of finding the values of a set of related variables, that, when evaluated on an objective function, will produce the maximum or minimum values of said function.

The objective function expresses the relation between the variables of a mathematical model; its maximization or minimization is the objective of the optimization procedure. The variables which are manipulated during the optimization process are also called decision variables, design parameters and design variables. For some problems, the variables or the result of the function will have to satisfy a condition, like being positives or integers; these conditions are called restrictions, and are very important at the moment of defining an optimization problem. The universe to which the optimization problem is restricted is called the system. It is completely necessary to define the system and its limits, as well as the decision variables and restrictions in order to propose an accurate objective function and be able to solve an optimization problem satisfactorily.

The general form of an optimization problem is:

$$max/\min f(x) \tag{2.7}$$

Subject to:

$$g(x)\ (\leq, =, \geq)\ z \tag{2.8}$$

Where f is the objective function, x is a vector of decision variables and g is a constraint function.

2.5.2. Stages to solve an optimization problem

There is a series of steps that have to be followed in order to solve an optimization problem (Figure 2.19):

- **System definition:** in this step the problem is delimited, and its scope is defined. The different relations between the variables that form the model are defined.

- **Selection of decision variables:** the variables that will be manipulated during the optimization process are chosen.

- **Definition of the objective function:** a function that relates the decision variables in a way that is as close to reality as possible is found; this function will be maximized or minimized depending on the objective of the problem.

- **Definition of restrictions (if necessary):** in this step, some limitations to the objective function or the variables are defined, for example, that the variables cannot be negative, or that the objective function cannot surpass a certain value.

- **Selection of the optimization method:** once the system, decision variables and objective function have been defined, the optimization method to solve the problem must be chosen. There are many method and programming codes that have been developed to solve different types of problems.

- **Implementation of the optimization process:** the final step to solve the problem is to implement the chosen method, whether as a programmed code or in another manner.

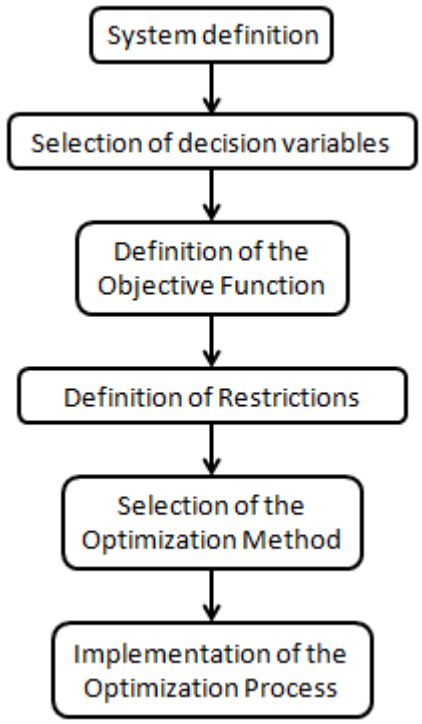


Figure 2.19. Stages to solve an optimization problem.

2.5.3. Types of optimization problems

The field of optimization is wide, and there are hundreds of techniques that can be used to solve different types of problems. However, in practical terms, the main differences between problems consist on whether the objective function and restrictions are linear or not, if the parameters are fixed or include variability and/or uncertainty and if they are integers or continuous. Some of the most common types of optimization problems are presented next.

2.5.3.1. Linear optimization problems

The general form of an objective function in a linear problem can be expressed as:

$$max\ /\ \min f(x_1, x_2, \dots, x_n)\ a_1x_1 + a_2x_2 + \cdots + a_nx_n \qquad \textbf{(2.9)}$$

In which f is the objective function to minimize or maximize, x and a are the decision variables and their coefficients respectively.

The objective function is subjected to restrictions of the form:

$$c_{i1}x_1 + c_{i2}x_2 + \cdots + c_{in}x_n(\leq, =, \geq)b_i \quad \textbf{(2.10)}$$

This is the general form of the linear optimization problem. Any situation which mathematical formulation fits this description is a linear optimization problem.

2.5.3.2. Non-linear optimization problems

The fundamental supposition of linear programming is that all the functions that are part of the problem (objective and restrictions) are linear. Although this condition can be maintained for many practical problems, this is not the case frequently. Therefore, it is necessary to deal directly with nonlinear programming problems, which in their general form can be defined as:

$$max/\min f(x) \quad \textbf{(2.11)}$$

Subject to:

$$g(x) \leq = \geq b \quad \textbf{(2.12)}$$

Where:

$x = (x_1, x_2, \dots, x_n) \in R^n$ is the decision variable.

$f: D \subset R^n \to R^m$ is the objective function and D, its domain.

$g: D \subset R^n \to R^m$ is a vector function $g = (g_1, g_2, \dots, g_m)$ composed by the constraint functions.

$b \in R^m$ is the vector of independent terms. Each expression $g_i(x)(\leq = \geq)b_i$ determines a constraint on the decision variables.

2.5.3.3. Discrete optimization problems

In many practical problems the decision variables only make sense if they take integer values. For example, it is always necessary to assign people, machinery, vehicles, etc. in integer quantities. If the integer requirement is the only way in which a problem differs from a linear programming problem, it is called an integer programming problem.

The mathematical model for integer programming is equal to the linear programming, including a constraint that specifies that variables or results must have integer values. If only some of the variables must be integers, the model is called mixed integer programming. To distinguish the problems, the one that only accepts integers is referred to as pure integer programming.

2.5.3.4. Dynamic optimization problems

Dynamic programming is a mathematical tool useful to make interrelated sequences of decisions. It gives a systematic procedure to determine the combination of optimal decisions.

In contrast to linear programming, there is no standard mathematical formulation of the dynamic programming problem. Instead, dynamic programming can be seen as a general kind of approach to problem solving, and the particular equations used must be developed for each situation.

Dynamic programming provides a way of saving computational operations at the moment of finding the best combination of decisions, especially for large problems, as it avoids the exhaustive enumeration of all the possible choices. For example, if a problem

has ten stages with ten states, and ten possible decisions in each stage, exhaustive enumeration would result in the consideration of up to ten billion combinations, while mathematical programming would not require more than a thousand calculations (ten for each state in each stage).

The main characteristics of a dynamic programming problem are:

- The problem can be divided into stages, with a decision making policy in each stage. A dynamic programming problem requires making a sequence of interrelated decisions, in which each of them corresponds to a stage. Figure 2.20 shows the graphical representation of a dynamic programming problem, in which the stages are symbolized by a group of vertical circles; each circle represents the possible decisions that can be made in each stage and the numbers, the value or cost of the decision.

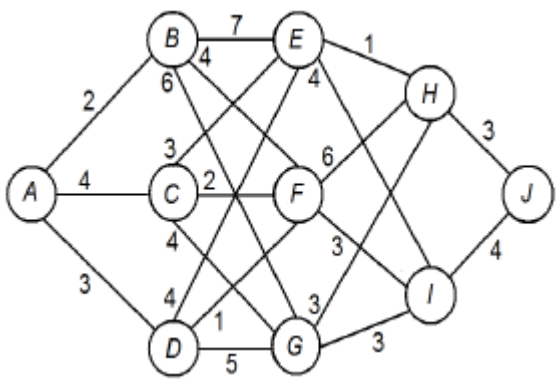


Figure 2.20. Diagram of a dynamic optimization problem.

- Each stage has a number of states associated to its starting point. States are the different possible conditions in which the system can be in a stage of the problem. The number of stages can be finite or infinite.

- The effect of the decision making policy in each stage is to transform the current state to another state associated to the beginning of the next stage (possibly in accordance to a probability distribution). This means that the dynamic programming problems can be interpreted as networks, in which each node corresponds to a state. The network will consist on a number of columns of nodes, each column being a state. The connections between nodes in different columns are the different possible decisions to take. The values assigned to each connection can be interpreted as the immediate contribution to the objective function if that decision was to be made. In most cases, the objective is to find the longest or shortest way through the network.

- The solution procedure is designed to find the optimal chain of decisions for the complete problem, giving information about the optimal decision in each stage.

- Given the current state, an optimal decision for the remaining stages is independent of the decision making policy adopted for previous stages. Therefore, the immediate optimal decision depends only of the current state and not of the way in which it is reached. Generally, for dynamic optimization problems, the knowledge of the current state of the system transmits all of the information about its previous behavior that is necessary to determine the optimal policy to follow. Any problem that does not possess this property cannot be formulated as a dynamic programming problem.

- The solution procedure begins by finding the optimal decision making policy for the last stage. The solution of this stage is normally trivial.

- A recursive relation that identifies the optimal policy for stage n, given the optimal policy for the n+1 stage is available. Using the following notation:

N is the number of stages.

n is the current stage $(n = 1, 2, \ldots, N)$.

S_n is current state for the *nth* stage.

x_n is decision variable for stage n.

x_n^* is optimal value of x_n (given s_n).

$f_n(s_n, x_n)$ = contribution of the stages $n, n+1, \ldots, N$ to the objective function if the system starts in the s_n state in the n stage, the immediate decision is x_n, and the optimal decisions are taken from this point forward $f_n^*(s_n) = f_n(s_n, x_n^*)$.

The recursive relation will always have the following form:

$$f_n^*(s_n) = max_{xn}\{f_n(s_n, x_n)\} \text{ or } f_n^*(s_n) = min_{xn}\{f_n(s_n, x_n)\} \quad \textbf{(2.13)}$$

The recursive relation is maintained as we move backwards stage by stage. When the current number n is decreased by 1, the new function $f_n^*(s_n)$ is derived using the function $f_{n+1}^*(s_{n+1})$, which, in turn, was derived from the previous iteration.

- When the recursive relation is used, the solution procedure starts at the end and moves to the beginning stage by stage, finding the optimal solution in each step until the optimal decision making policy is found for the first stage. This optimal policy immediately produces the optimal solution for the complete problem, which is, x_n^* for each s_n stage.

Dynamic optimization problems can be stochastic or deterministic. This last type can be expressed in diagram form as shown in Figure 2.21.

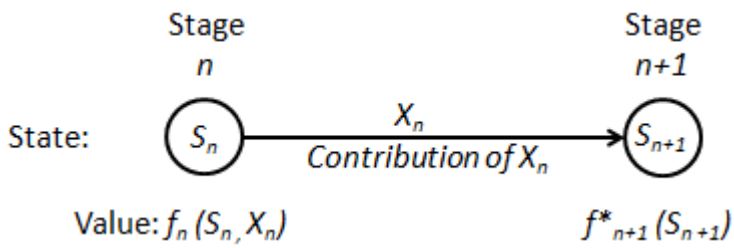


Figure 2.21. Deterministic dynamic problem diagram.

In this way, in stage *n*, the process will be in the sn state. Taking the x_n decision, the process is moved towards the s_{n+1} state in the *n+1* stage. Then, it has been calculated that the contribution to the objective function will be $f^*_{n+1}(s_{n+1})$. The decision taken, x_n, also contributes to the objective function. Combining those two quantities in an appropriate way gives us $f_n(s_n,x_n)$, the contribution to the stages *n* and forward to the objective function. Optimizing against x_n, we obtain $f_n^*(s_n) = f_n(s_n, x_n^*)$. After x_n^* and $f_n^*(s_n)$ have been found for each possible value of s_n, the solution procedure is ready to move one stage backwards.

One way of categorizing deterministic dynamic problems is by the form of their objective function. For example, the objective can be the maximization or minimization of the sum of the contribution of the individual stages. Another categorization can be in terms of the set of states for respective stages. Particularly, sn states can be represented by a discrete or continuous variable.

Probabilistic dynamic problems are different from deterministic ones in that the state of the next stage is not completely determined by the current state and the decision taken in it. Instead of a fixed value, there is a probabilistic distribution for what the next state will be. However, this probability distribution is completely determined by the previous state and the decision taken in it.

The basic structure of a probabilistic dynamic problem is presented in Figure 2.22. In it, *S* denotes the possible number of states in stage *n+1*; the states on the right side will be called *1,2,…,S*. The system will reach the state *i* with a probability of P_i *(i=1,2,…,S)*

given the s_n state and x_n decision in stage n. If the system reaches state i, C_i is the contribution of stage n to the objective function.

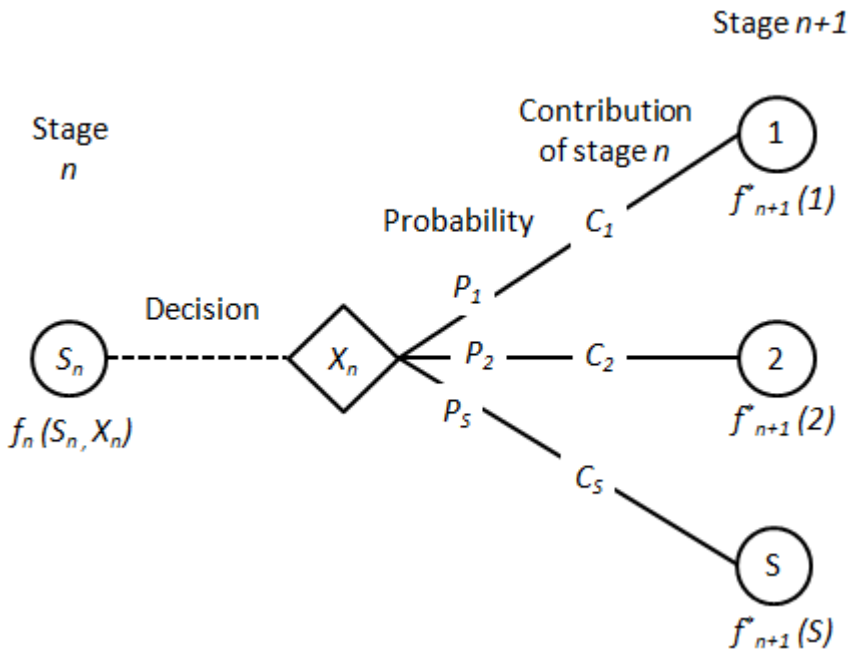


Figure 2.22. Stochastic dynamic problem diagram.

When Figure 2.22 is expanded to include all possible states and decisions in all stages, it is sometimes referred to as a decision tree. If the decision tree is not very long, it gives a useful way of summarizing the different possibilities.

Due to the probabilistic structure, the relation between $f_n(s_n,x_n)$ and $f^*_{n+1}(s_{n+1})$ is necessarily more complicated than for the deterministic problem. The precise way of this relation will depend on the form of the objective function. For example, assuming that the objective is to minimize the sum of contributions of the individual stages, $f_n(s_n,x_n)$ represents the minimal expected sum of stage n and forward, as the state of decision making policy in stage n are s_n and x_n respectively. Therefore:

$$f_n(s_n, x_n) = \sum_{i=1}^{S} P_i \left[C_i + f_{n+1}^*(i)\right] \quad \textbf{(2.14)}$$

With:

$$f_{n+1}^*(i) = min_{x_{n+1}} f_{n+1}(i, x_{n+1}) \quad \textbf{(2.15)}$$

In which the minimization is made over the possible values of x_{n+1}.

2.5.3.5. Multi-objective optimization

Multi-objective or multi-criteria optimization is the process of simultaneously optimizing two or more conflicting objectives that are subjected to different restrictions. Multi-objective optimization problems can be found in various fields of work: design of processes or products, finances, fossil fuel industry, automobiles design or any other situation in which optimal decisions must be made by reaching a compromise between various conflicting objectives. Maximize profit while decreasing cost, or decreasing the weight of a material while maximizing its resistance are examples of multi-objective problems.

If a multi-objective problem is proposed correctly, it should not have a single solution which simultaneously optimizes each objective to the maximum value. In each case, a solution is looked for, so that each objective has been optimized to the point in which if the optimization continues, other objectives would suffer as a result. Finding a solution of this type, and quantifying if it is better or worse when compared to others, is the goal when solving multi-objective optimization problems.

In mathematical terms, the multi-objective problem can be expressed as:

$$min_x [f_1(x), f_2(x), \dots, f_n(x)]^T \quad \textbf{(2.16)}$$

Subject to:

$$g(x) \leq 0$$
$$h(x) = 0 \qquad (2.17)$$
$$x_l \leq x \leq x_u$$

Where f_i are each of the objective functions, g and h are the equality and inequality constraints and x are the decision variables to optimize.

The solution to this problem is a set of Pareto points. Pareto solutions are those for which the improvement of an objective can only occur if, at least, one of the other objectives is affected negatively. Then, instead of having a single solution to the problem, the answer to a multi-objective optimization problem is a set of Pareto points, as has been stated before.

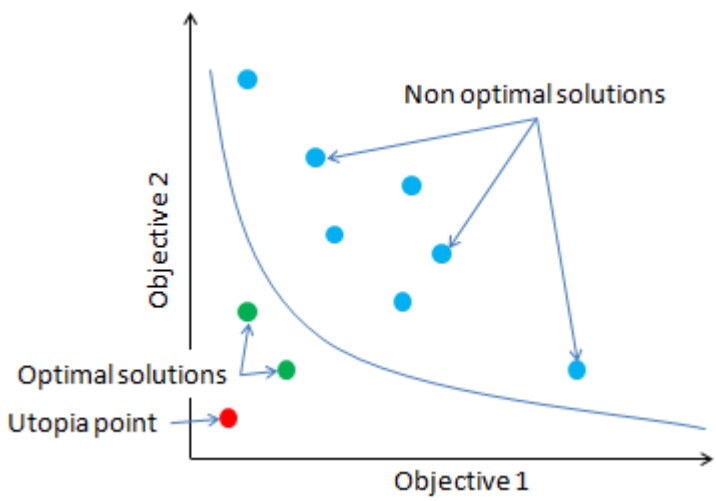


Figure 2.23. Multi-objective optimization diagram.

A point in the objective space f^* is known as a Pareto optimal if there is no other objective, so that $i \leq i^*$ for every $i \in \{1, 2, \dots, n\}$ and $u_j < j^*$ for at least one index of $j \in \{1, 2, \dots, n\}$. However, there exists the idea of the compromise solution, which can be applied to find a single solution point. By minimizing the difference between the potential

optimal and a utopia point, that is the point where all the objectives reach their minimum, the best compromise solution for all the objectives is found (Figure 2.23).

NOMENCLATURE

Symbol	Meaning	Units
B	Vector of independent terms	(-)
C	Contribution of a stage to the objective function	(-)
F	Objective function	(-)
f_0	Frequency of initial event	(-)
f_i	Frequency of event i	($year^{-1}$)
G	Constraint function	(-)
H	Equality constraint function	(-)
N	Current stage	(-)
N	Total number of stages	(-)
n_a	Number of types of accidents	(-)
n_k	Number of deaths	(-)
n_p	Number of people	(-)
P_{Fi}	Probability of an accident resulting in death	(-)
P_k	Probability of occurrence of event k	(-)
r_{ind}	Individual risk	($deaths \cdot year^{-1}$)
S_n	Current state for the nth stage	(-)
x	Vector of decision variables	(-)
x_n	Decision variable for stage n	(-)
x_n^*	Optimal value of x_n	(-)

CHAPTER 3. MODELING CRITERIA

In this chapter, the models and criteria selected during this thesis and used for the proposal of the methodology are presented. First, the LOCs which will be included in the model are presented along the event trees that have been selected from bibliography, which show the final accidents that are systematically studied in the model. After this, the frequency criterion that has been chosen in the thesis for the different LOCs in different types of tanks is presented. Following, the models used for source term, effects and consequences of the accidents are presented; this section also serves to point which effects and consequences are considered in the model. Finally, the values chosen to estimate the costs related to a major accidents and the way to assess the investment made on an installation are presented.

3.1. Selection of LOCs and their frequencies in storage installations

The Loss of Containment events (LOCs) that have been used in this work to perform the QRAs, and apply the designed methodology are those described in the CPR18E "The Purple Book" (2005) and the Reference Manual BEVI Risk Assessments guide (2009) for stationary tanks and vessels, pressurized or atmospheric. In this work, the generic LOCs are defined as those which cover all failure causes not considered explicitly, like corrosion, construction errors, welding failures and blocking of tank vents. Specific LOCs, which are

those specific to the process condition, design, materials or plant layout, will be treated from the point of view of domino effect; the way in which this phenomenon has been modeled is described in CHAPTER 5.

A pressure vessel is defined in the CPR18E as a storage vessel in which the pressure is (substantially) more than 1 bar absolute. The BEVI (2009) defines a mounded pressurized vessel as one which operates at pressures higher than 0.5 bar and is surrounded by inert matter, such as earth, on all sides. The LOCs associated to this equipment and their frequencies, are presented in Table 3.1; each event is defined and the codes by which they will be referred to from this point forward are presented.

Table 3.1. LOCs and their frequencies for pressure vessels.

Code	Definition	Frequency (y^{-1})
G.1	Instantaneous release of the complete inventory	$5x10^{-7}$
G.2	Continuous release of the complete inventory in 10 min at a constant rate of release	$5x10^{-7}$
G.3	Continuous release from a hole with an effective diameter of 10 mm	$1x10^{-5}$

Atmospheric tanks, which are those that operate at pressures near 1 bar absolute, are categorized in The Purple Book in the following manner:

- **Single-containment atmospheric tanks**: consisting of a primary container for the liquid. An outer shell is either present, or not, but when present, primarily intended for the retention and protection of insulation. It is not designed to contain liquid in the event of the primary container's failure.

- **Atmospheric tank with a protective outer shell**: consisting of a primary container for the liquid and a protective outer shell. The outer shell is designed to contain the liquid in the event of failure of the primary container but is not designed to contain any vapor. The outer shell is not designed to withstand all possible loads, e.g. explosion

(static pressure load of 0.3 bar during 300 ms), penetrating fragments and cold (thermal) load.

- **Double-containment atmospheric tank**: consisting of a primary container for the liquid and a secondary container. The secondary container is designed to contain the liquid in the event of the failure of the primary container and to withstand all possible loads, like explosion (static pressure load of 0.3 bar during 300 ms), penetrating fragments and cold (thermal) load. The secondary container is not designed to hold any kind of vapor.

- **Full-containment atmospheric tank**: consisting of a primary container for the liquid and a secondary container. The secondary container is designed to contain both the liquid and vapor in the event of failure of the primary container, and to withstand all possible loads, like explosion (static pressure load of 0.3 bar during 300 ms), penetrating fragments and cold (thermal) load. The outer roof is supported by the secondary containment and designed to withstand loads e.g. explosion.

- **Membrane tank**: consisting of a primary and secondary container. The primary container is formed by a non-self-supporting membrane that holds the liquid and vapor under normal operating conditions. The secondary container is concrete and supports the primary container. The secondary container has the capacity to contain all the liquid and to perform controlled venting of the vapor if the inner tank fails. The outer roof forms an integral part of the secondary containment.

- **In-ground atmosphere tank**: it is a storage tank in which the liquid level is at or below ground level.

- **Mounded atmospheric tank**: a storage tank that is completely covered with a layer of soil and in which the liquid level is above ground level.

The definition and codes for the LOCs events for atmospheric tanks are presented in Table 3.2; their frequencies are shown in Table 3.3. Figure 3.1 shows an example of a G.1 release in an atmospheric tank

Table 3.2. LOCs for atmospheric tanks.

Code	Definition
G.1	Instantaneous release of the complete inventory
	a. Directly to the atmosphere
	b. From the primary container into the unimpaired secondary container or outer shell
G.2	Continuous release of the complete inventory in 10 min at a constant rate of release
	a. Directly to the atmosphere
	b. From the primary container into the unimpaired secondary container or outer shell
G.3	Continuous release from a hole with an effective diameter of 10 mm
	a. Directly to the atmosphere
	b. From the primary container into the unimpaired secondary container or outer shell

Table 3.3. Frequencies of LOCs for atmospheric tanks.

Type of tank	Frequency (y^{-1})					
	G.1a	**G.1b**	**G.2a**	**G.2b**	**G.3a**	**G.3b**
Single-containment	$5x10^{-6}$	-	$5x10^{-6}$	-	$1x10^{-4}$	-
With protective outer shell	$5x10^{-7}$	$5x10^{-7}$	$5x10^{-7}$	$5x10^{-7}$	-	$1x10^{-4}$
Double-containment	$1.25x10^{-8}$	$5x10^{-8}$	$1.25x10^{-8}$	$5x10^{-8}$	-	$1x10^{-4}$
Full-containment	$1x10^{-8}$	-	-	-	-	-
Membrane	-	-	-	-	-	-
In-ground	-	$1x10^{-8}$	-	-	-	-
Mounded	$1x10^{-8}$	-	-	-	-	-

It has to be noted that cryogenic storage tanks are treated as atmospheric tanks of the corresponding type.

Specific LOCs for piping are not included, as this type of equipment is not considered in the method; however, the LOCs presented include not only the tanks and vessels, but also the associated instrumentation pipework.

Figure 3.1. Example of a G.1 release in an atmospheric tank (CSB, 2009).

3.2. Major accidents in storage installations and their probabilities of occurrence

Different possible accidents can occur after a LOC event in a storage tank, depending on the type of equipment and released substance. Event trees can be used in order to know which accidents may take place after a release, and what the probability of occurrence of each one is.

In this work, the case studies have been developed using event trees based in those presented in the BEVI (2009) for different types of releases, tanks and substances, and on the set of rules proposed in The Purple Book to develop event trees. The trees used and the criteria applied to estimate the probabilities of occurrence are presented next.

3.2.1. Instantaneous release of a pressurized liquefied flammable gas in an above-ground tank

When a tank that stores a pressurized liquefied gas suffers an instantaneous release, different accidents can occur depending on whether there is ignition, and the moment it happens (Figure 3.2). In case of a direct ignition, the event tree presented shows that a BLEVE is the next possible path (accompanied by a pool fire); however, if the BLEVE does not take place, an explosion or a flash fire may occur, along with pool fires in each case. If the ignition is delayed long enough for a cloud of flammable material to be formed, an explosion or a flash fire may occur once the material is ignited, a pool fire may also be formed. The final possibility is that, if there is no ignition, the release does not develop into an accident.

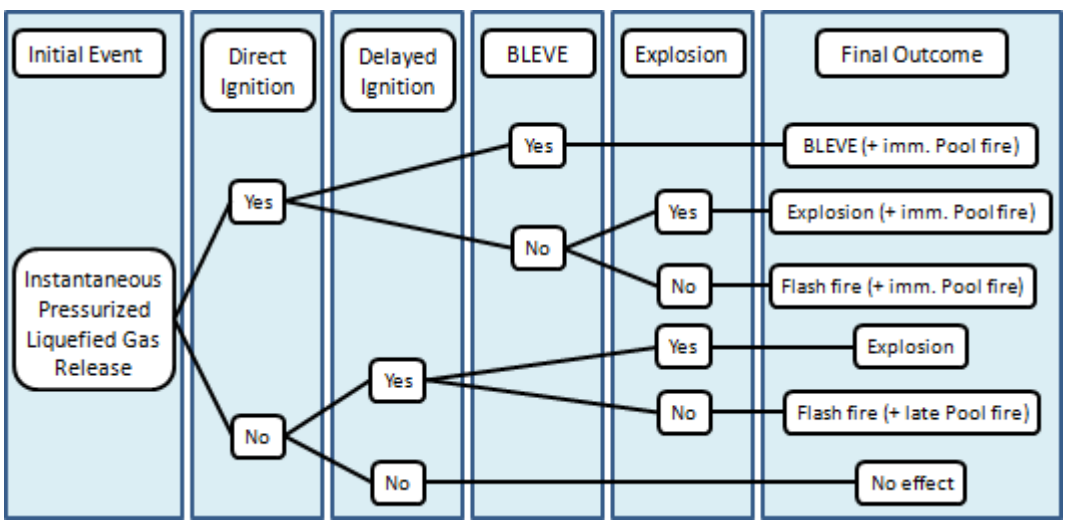


Figure 3.2. Event tree for the instantaneous release of a pressurized liquefied flammable gas in an above-ground tank.

It has to be said that an explosion generated from the ignition of a cloud of flammable material is always associated to a flash fire, but that a flash does not always evolves into an explosion.

3.2.2. Continuous release of a pressurized flammable liquid in an above-ground tank

In the case of the direct ignition of a continuous release of a pressurized liquefied flammable gas, a jet fire and pool fire will occur; if the ignition is delayed, a cloud will form, which may lead to an explosion or a flash fire (Figure 3.3). The release may also lead to no outcome.

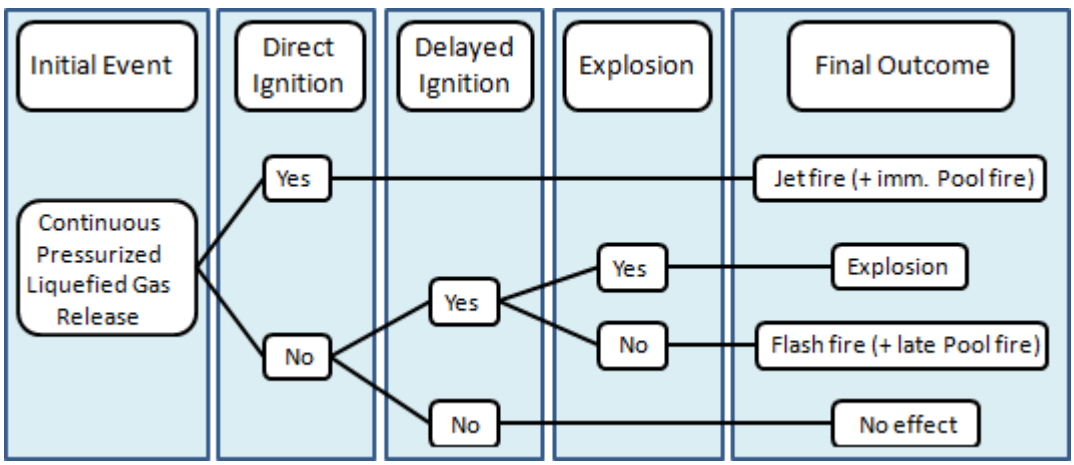


Figure 3.3. Event tree for the continuous release of a pressurized liquefied flammable gas in an aboveground tank.

3.2.3. Instantaneous release of a pressurized liquefied flammable gas in a mounded tank

According to the BEVI (2009), the main difference between releases in a pressurized above ground tank and a pressure mounded tank is that for the second, although there can be a direct ignition, there is no possibility for BLEVE occurrence, which means that this branch of the tree comes to no outcome and may be discarded (Figure 3.4).

3.2.4. Continuous release of a pressurized liquefied flammable gas in a mounded tank

Since the possibility of direct and delayed ignition are maintained, the event tree for the continuous release of a pressurized liquefied flammable gas in a mounded tank is the same as for a release in an aboveground tank of the same characteristics.

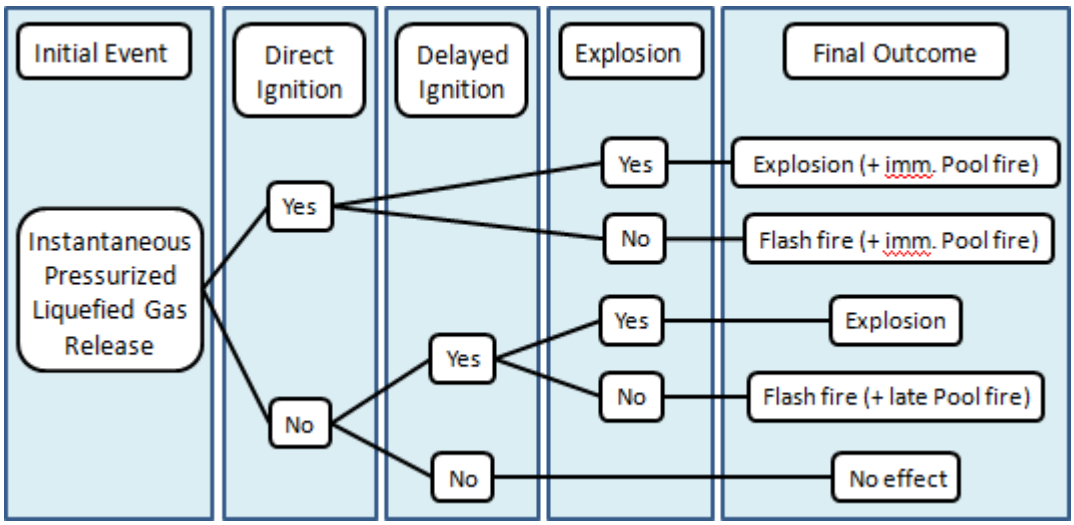


Figure 3.4.Event tree for the instantaneous release of a pressurized liquefied flammable gas in a mounded tank.

3.2.5. Release of a flammable liquid in an above ground tank

If a highly flammable liquid is released from an atmospheric tank, and a direct ignition occurs, the flowing contents will be ignited, forming a pool fire; if the ignition is not direct, a pool of flammable material will form, and eventually, so will a flammable cloud; this cloud may ignite later, leading to flash and pool fires or an explosion. If there is no ignition, there will be no final accident (Figure 3.5).

3.2.6. Release of a toxic gas in an above-ground tank

The release of a toxic gas will result in the formation of a toxic gas cloud, independently of the nature of the release (instantaneous or continuous) (Figure 3.6). If the gas is pressurized and liquefied, it will flash upon release, instantaneously forming a cloud. If it is stored cryogenically and is released, it will form a pool of liquid which will start evaporating and will form a cloud after a longer period of time.

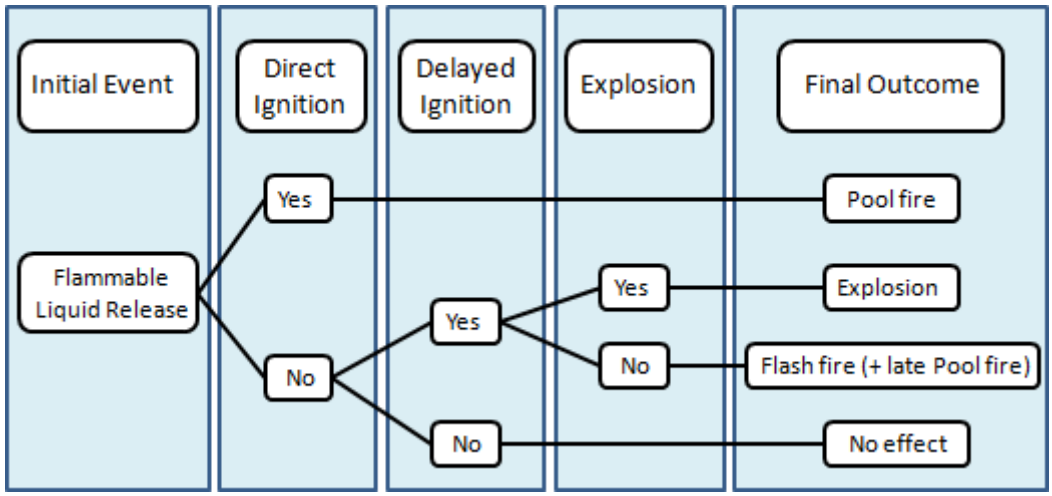


Figure 3.5. Event tree for the release of a flammable liquid in an aboveground tank.

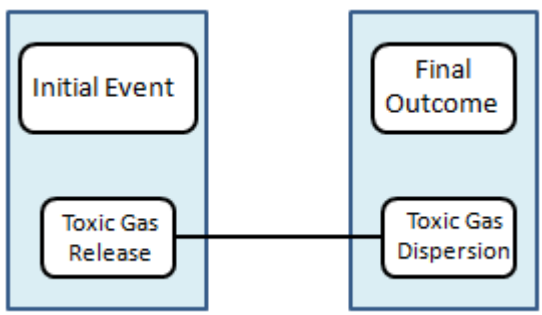


Figure 3.6. Event tree for the release of a toxic gas.

3.2.7. Criteria for the probability of ignition and explosion

In order to calculate the probabilities of occurrence of the different accidents in the event trees, it is necessary to know the probability of some of the events that define the tree. In The Purple Book (2005) and the BEVI (2009) guide, the probability of direct and delayed ignition, BLEVE and explosion are the events that characterize the trees and their probabilities; they depend on the mass and flow of the release, the category of the substance and the characteristics of the installation.

The probabilities of direct ignition for different cases are shown in Table 3.4. The probability of delayed ignition for substances in the categories 0 and 1 is calculated as:

$$P_{delayed\ ignition} = 1 - P_{direct\ ignition} \quad \textbf{(3.1)}$$

The probability of BLEVE once the direct ignition has occurred is of 0.7 for fixed equipment (tanks, vessels, etc.). Following the ignition of a gas cloud, the fraction modeled as an explosion (+ flash fire) is 0.4, which leaves the fraction of pure flash fire as 0.6.

Table 3.4. Probabilities of direct ignition.

Substance category	Source term continuous	Source term instantaneous	Probability of direct ignition
Category 0 Average/high reactivity	< 10 kg/s	< 1,000 kg/s	0.2
	10 – 100 kg/s	1,000 – 10,000 kg/s	0.5
	> 100 kg/s	> 10,000 kg/s	0.7
Category 0 Low reactivity	< 10 kg/s	< 1,000 kg/s	0.02
	10 – 100 kg/s	1,000 – 10,000 kg/s	0.04
	> 100 kg/s	> 10,000 kg/s	0.09
Category 1	All flow rates	All quantities	0.065
Category 2	All flow rates	All quantities	0.01
Category 3, 4	All flow rates	All quantities	0

3.3. Modeling the source term

Once the LOCs and subsequent accidents that may occur in storage installations have been defined, it is necessary to assess how to model the release of product.

In order to estimate the effects of an accident, the amount of material released has to be defined; this depends on the type of substance and storage tank, the atmospheric conditions and the type and time of the release. This last parameter is fixed by the definitions of the LOCs for the G.1 and G.2 releases; for the G.3 type, the duration is set to 30 minutes.

The substances that have been used to develop and test the optimization methodology can be classified as liquefied gases, flammable liquids and heavy gases. The first type of substance will be released as a flashing liquid, the second as a liquid and the third as a heavier than air gas.

3.3.1. Liquid release

In case of an instantaneous release, the complete contents of the tank will escape. In the case of a liquid, this means that the product will form a pool, which diameter will be limited by physical barriers or expand until a maximum value that can be calculated using Eq.(3.13).

For continuous releases, the following equation can be used to estimate the initial mass flow of liquid through a hole in a tank (CPR14E):

$$q_s = C_d \cdot A_h \sqrt{2(P - P_a)\rho_l} \quad \textbf{(3.2)}$$

With:

$$P = P_h + P_{aL} \quad \textbf{(3.3)}$$

And:

$$P_h = \rho_l \cdot g \cdot h_0 \quad \textbf{(3.4)}$$

Where:

q_s (kg·s^{-1}) is the mass flow rate.

C_d is the discharge coefficient (-); a value of 0.62 (sharp orifices) has been used in this work.

A_h (m^2) is the cross sectional area of the hole.

P (Pa) is the total pressure at the opening.

P_a (Pa) is the atmospheric pressure.

ρ_l (kg·m^{-3}) is the density of the stored liquid.

P_h (Pa) is the hydraulic liquid pressure.

P_{aL} (Pa) is the external pressure above the liquid.

g (m·s^{-2}) is the gravitational acceleration.

h_0 (m) is the initial height of liquid in the tank.

In this work a conservative assumption (Casal, 2008) of constant discharge rate during the full length of a release has been assumed in all cases. A procedure for estimating the varying mass flow rate or obtaining an equation to calculate the time at which the tank is emptied can be found in CPR14E.

Upon release a liquefied gas will suffer a sudden flash, becoming a mixture of gas and liquid. A flash fraction will be calculated for this kind of substance to know which part of the total mass is vaporized; depending on the value of this factor, the mass of the cloud will be calculated as the total contents of the tank multiplied by a factor and the flash fraction. The flash fraction is calculated as (Casal, 2008):

$$f = 1 - e^{\frac{-c_p(T_{cont} - T_b)}{\Delta H_v}} \quad \textbf{(3.5)}$$

Where:

f (-) is the flash fraction.

C_p (kJ·kg^{-1}·K^{-1}) is the heat capacity.

T_{cont} (K) is the temperature of the liquid before depressurization.

T_b (K) is the boiling temperature of the liquid.

ΔH_v (kJ·kg^{-1}) is the mean latent heat of vaporization between T_{cont} and T_b.

To calculate the mass that becomes part of the cloud, the following equations (depending on the flash fraction) are used (CPR18E):

$$\begin{aligned} &\text{If } f < 0.1 && m_{cloud} = 2 \cdot f \cdot m \\ &\text{If } 0.1 \leq f < 0.36 && m_{cloud} = \left(\frac{0.8f - 0.028}{0.26}\right) \cdot m \\ &\text{If } f \geq 0.36 && m_{cloud} = m \end{aligned} \tag{3.6}$$

Where m_{cloud} (kg) is the mass of the cloud and m (kg) is the total mass stored.

3.3.2. Heavy gas release

In order to model the release of gases, the ALOHA (Areal Location of Hazardous Atmospheres) modeling program was used (v5.4.1.2). This software, which is developed jointly by the NOAA (National Oceanic and Atmospheric Administration) and the EPA (Environmental Protection Agency), allows modeling the instantaneous or continuous release of toxic products from different sources; it can also be used to estimate how a toxic cloud might disperse after a chemical release and also features fire and explosion scenarios. ALOHA displays its results as threat zones: areas in which a hazard (toxicity, flammability, etc.) has surpassed a user-specified threshold.

3.4. Modeling the effects of major accidents

The following models are used to estimate the effects of the different accidents that can occur due to a LOC event in a storage tank.

3.4.1. Thermal radiation. The solid flame model

The model used in this work to estimate the effects of thermal accidents is the solid flame model, which is based on the idea that fire can be represented as a solid body with simple geometric form which emits radiation through its complete surface. To avoid the underestimation of the flame volume, the geometries of both the fire and the receiving body must be considered, as well as their relative positions; these factors are included in the calculation of the radiation intensity by the introduction of a view factor which depends on the contours of the source, the receiver and the distance between them. In order to estimate the radiation intensity, it is also necessary to know the emissive power, which is the total radiation that abandons the surface of the fire by unit of area and time, and the transmissivity, which evaluates the absorption of radiation by the medium placed between the emitter and the receiver. All the equations presented for the solid flame model were obtained from (Casal, 2008).

The thermal radiation intensity which reaches a certain object is calculated as:

$$I = \tau\, F\, E \tag{3.7}$$

Where:

τ (-) is atmospheric transmissivity.

F (-) is the view factor.

E (kW·m^{-2}) is the emissive power of the flames.

3.4.1.1. View factor

This factor represents the relationship between the thermal radiation emitted by the flame and received by an object which is not in contact with it. The view factor depends on the size and shape of the flame, the distance between the flames and the object and the relation between both surfaces. The maximum view factor, corresponding to the surface localized perpendicularly to the direction of the radiation can be calculated as:

$$F = \sqrt{F_h^2 + F_v^2} \tag{3.8}$$

Where:

F_h (-) is the horizontal view factor.

F_v (-) is the vertical view factor.

3.4.1.2. Emissive power

The emissive power is the radiating heat emitted by unit of flame surface and time ($kW \cdot m^{-2}$) which represents the radiation characteristics of the fire. Actually, radiation emitted from the flames is generated by the totality of the fire, not only by its surface; therefore, emissive power is a bi-dimensional simplification of a complex heat transfer tridimensional problem. Emissive power can be calculated through a simple expression:

$$E = \frac{\eta_{rad}\, m_{comb}\, \Delta H_c}{A} \tag{3.9}$$

Where:

A (m^2) is the solid area of the flame from which radiation comes off.

m_{comb} (kg) is the mass of combustible involved in the fire.

ΔH_c ($kJ \cdot kg^{-1}$) is combustion heat.

η_{rad} (-) is a factor known as radiant heat fraction. A suggested conservative value for this factor is 0.35.

3.4.1.3. Atmospheric transmissivity

This is the parameter which accounts for the radiation that is absorbed by the atmosphere, essentially due to the carbon dioxide and water vapor.

$$\begin{aligned} &\tau = 1.53\ (P_w d)^{-0.6} \text{ for } P_w d\ <\ 10^4\ \ N/m \\ &\tau = 2.02\ (P_w d)^{-0.09} \text{ for } 10^4\ N/m < P_w d < 10^5\ \ N/m \\ &\tau = 2.85\ (P_w d)^{-0.12} \text{ for } P_w d\ >\ 10^5\ \ N/m \end{aligned} \tag{3.10}$$

In which:

P_w (Pa) is the partial pressure of water in the atmosphere.

d (m) is the distance between the flame and the receiver.

P_w can be estimated as:

$$P_w = P_{wa}\frac{HR}{100} \tag{3.11}$$

Where:

P_{wa} (Pa) is the saturated water vapor pressure at atmospheric conditions.

HR (%) is the relative humidity of air.

P_{wa} can be obtained from the atmospheric temperature as:

$$ln(P_{wa}) = \ 23.1896 - \frac{3816.42}{(T - 46.13)} \tag{3.12}$$

With P_{wa} expressed in Pa and T in K.

In order to estimate the effects of a fire using the solid flame model it is necessary to know the size and shape of flames. Next, some equations that can be used to estimate the form of the different types of fire which appear in this thesis are presented.

3.4.1.4. Pool fires

The effects of pool fires depend on the maximum diameter the pool of liquid reaches; if the pool is not bounded, this can be calculated as:

$$D_{max} = 2\left(\frac{V_l^3 g}{m^2}\right)^{1/8} \quad \textbf{(3.13)}$$

Where:

D_{max} (m) is the maximum diameter of the pool.

V_l (m^3) is the volume of spilled liquid.

m ($m \cdot s^{-1}$) is the combustion rate.

Combustion rate can be estimated as:

$$m = m_\infty\left(1 - e^{-kD}\right) \quad \textbf{(3.14)}$$

Where:

D (m) is the diameter of the pool.

m_∞ ($kg \cdot m^{-2} \cdot s^{-1}$) is the combustion rate of a pool of infinite diameter.

k (m^{-1}) is a constant.

Values for m_∞ and k can be found in the literature; for large fires, $m \approx m_\infty$.

The pool fires that appear in this work normally occur inside containment dikes; in this case the maximum diameter must be calculated, and if it is bigger than the enclosed area, then the dimensions of the pool fire will be equal to those of the bund.

Once the diameter of the pool has been estimated, the height of the flames can be calculated as:

$$\frac{H}{D} = 55\left[\frac{m}{\rho_a\sqrt{gD}}\right]^{0.67} \cdot (u^*)^{-0.21} \qquad \textbf{(3.15)}$$

Where:

H (m) is the height of the pool.

ρ_a (kg·m^{-3}) is the density of air.

u^* is a dimensionless wind velocity calculated as:

$$u^* = \frac{u_w}{\left(\frac{g\,m\,D}{\rho_a}\right)^{1/3}} \text{ if } u^* < 1 \text{ it is assumed that } u^* = 1 \qquad \textbf{(3.16)}$$

Where:

u_w (m/s) is the wind velocity.

Wind can have an important effect on the effects of pool fires, as the flames can be tilted. However, this effect is not taken into account in this work, and the equations used to correct the dimensions of pool fires due to wind are not shown; they can be found in Casal (2008).

Finally, knowing the height and diameter of the flames, the surface of the fire can be approximated to that of a cylinder. This area can be used in Eq. (3.9) to estimate the emissive power of the fire.

3.4.1.5. Jet fires

The dimensions required to estimate the area of a jet fire are its length and diameter. In a situation of calm wind, the length of a jet fire can be estimated using the equation proposed by Hawthorne:

$$\frac{L}{d_{or}} = \frac{5.3}{C_{st-vol}}\left[\frac{T_{ad}}{\propto_{st} T_{cont}}\left(C_{st} + (1 - C_{st})\frac{M_a}{M_v}\right)\right]^{1/2} \quad \textbf{(3.17)}$$

Where:

L (m) is the length of the visible flame, from the initial point in which there is flame, up to the tip of the jet.

$C_{st\text{-}vol}$ (-) is the molar fraction of combustible in the stoichiometric combustible-air mixture.

d_{or} (m) is the diameter of the orifice through which the combustible is released.

T_{ad} (K) is the adiabatic flame temperature.

M_a (kg·mol^{-1}) is the molecular weight of air.

M_v (kg·mol^{-1}) is the molecular weight of fuel.

α_{st} (-) is the ratio between the number of reactants and products moles for a stoichiometric combustible-air mixture.

The length of the flameless jet can be calculated as shown in Eq. (3.18).

$$s = \frac{6.4\,\pi\, d_{or}\, u_j}{4\, u_{av}} \quad \textbf{(3.18)}$$

Where:

u_j (m s^{-1}) is the velocity of the jet.

u_{av} (m s^{-1}) is the mean velocity of the jet ($u_{av} \approx 0.4\, u_j$).

If it is assumed that the jet is a cylinder, its diameter can be estimated as a function of its length using the following expression:

$$D_j = 0.29\left[ln\frac{L+s}{x}\right]^{1/2} \quad \textbf{(3.19)}$$

Where:

x (m) is the axial distance from the orifice.

s (m) is the length of the flameless jet.

Like in the case of pool fires wind can have a significant effect on the geometry of jet fires, however, this effect is not taken into account in this thesis.

3.4.1.6. Flash fires

A Flash fire results from the ignition of a flammable cloud, which means that the dimensions of such an accident depend entirely on the way in which the cloud is dispersed in the atmosphere. The models used to simulate flammable (and toxic) dispersions are explained in Section 3.4.3.

3.4.1.7. Fireballs

When a BLEVE involves a flammable substance, it is usually followed by a fireball. This phenomenon is characterized by a strong heat emission from its start; Eq. (3.9) is slightly modified to take the time of the phenomenon into account, therefore, the emissive power for a fireball can be calculated as:

$$E = \frac{\eta_{rad}\, m_{comb}\, \Delta H_c}{\pi\, {D_{FB}}^2\, t_{fb}} \quad \textbf{(3.20)}$$

Where:

η_{rad} (-) is the fraction of radiant heat emitted by the fireball.

m_{comb} (kg) is the mass of combustible involved in the accident.

ΔH_c (kJ·kg^{-1}) is the fuel's heat of combustion.

D_{FB} (m) is the diameter of the fireball.

t_{fb} (s) is the time corresponding to the duration of the fireball.

η_{rad}, which value normally varies between 0.2 and 0.4, and can be estimated as:

$$\eta_{rad} = 0.00325\, P_{cont}^{0.32} \quad \textbf{(3.21)}$$

Where:

P_{cont} (Pa) is the pressure in the container in the moment before the explosion. Typically, this pressure can be supposed to be the relief pressure of the container.

The duration of the fireball and its diameter are calculated as functions of the mass of combustible (kg) involved in the accident. The equations that describe them are:

$$t_{fb} = 0.9 \cdot {m_{comb}}^{0.25} \quad \textbf{(3.22)}$$

$$D_{FB} = 5.8 \cdot {m_{comb}}^{1/3} \quad \textbf{(3.23)}$$

The mean height reached by the fireball will be approximately:

$$H_{FB} = 0.75 \cdot D_{FB} \quad \textbf{(3.24)}$$

3.4.2. Overpressure effects

Accidental explosions are associated to a sudden release of energy which produces large quantities of quickly expanding gas. This expansion produces an overpressure wave that can have significant effects of the area surrounding the accident. The most important value that has to be obtained when estimating the effects of an explosion is the maximum value of the overpressure wave.

The model used to estimate the effects of explosion in this thesis is the TNT-equivalency method, which tries to guess the amount of TNT that would produce the same level of damage as a specific explosion. This method is employed in this work to estimate the overpressure effects of VCEs and BLEVEs. The equations presented were obtained from (Casal, 2008).

For VCEs the equivalent mass of TNT can be calculated as:

$$M_{TNT} = \eta \frac{M\ \Delta H_c}{\Delta H_{TNT}} \tag{3.25}$$

Where:

M_{TNT} (kg) is the mass of combustible in the cloud.

ΔH_c (kJ·kg^{-1}) is the heat of combustion of the fuel.

η (-) is the explosion yield factor. An accepted value for η is 0.03.

ΔH_{TNT} (kJ·kg^{-1}) is the explosive energy of TNT (4,680 kJ·kg^{-1}).

For BLEVEs, the Eq. (3.26) can be used to estimate the equivalent mass of TNT.

$$M_{TNT} = 0.021\beta \left(\frac{P_{cont}\ V}{\gamma - 1}\right)\left(1 - \left(\frac{P_a}{P}\right)^{\frac{\gamma-1}{\gamma}}\right) \tag{3.26}$$

Where:

β (-) is the fraction of the released energy converted into a pressure wave (0.45 is the assumed value in this work).

P_a (bar) is the atmospheric pressure.

P_{cont} (bar) is the pressure in the vessel before the explosion.

V (m^3) is the initial volume of vapor.

γ (-) is the ratio of specific heats of the fuel.

Once the equivalent mass of TNT has been estimated, a normalized distance has to be calculated:

$$d_n = \frac{d}{M_{TNT}^{1/3}} \tag{3.27}$$

Where:

d_n (m·kg$^{-1/3}$) is the normalized distance.

d (m) is the real distance between the center of the explosion and the point in which the overpressure must be estimated.

M_{TNT} (kg) is the equivalent TNT mass.

The normalized distance can be used to calculate the overpressure peak using Eq. (3.28).

$$\frac{\Delta P}{P_a} = \frac{1}{d_n} + \frac{4}{d_n^2} + \frac{12}{d_n^3} \tag{3.28}$$

Where:

P_a (bar) is the atmospheric pressure.

3.4.3. Flammable and toxic dispersions

The effects of atmospheric dispersions are associated to the evolution of the concentration of the released substance in distance and time; this will depend on the type of substance released and on the atmospheric conditions of the environment.

As explained before, the ALOHA software can be used to model atmospheric dispersions of hazardous gases, and therefore, to estimate their effects. This software has

been used to estimate the concentration of a substance at a specific distance in this work, sometimes in a direct way, and others, producing simple equations from it.

The majority of the case studies presented in this work have been programmed in MATLAB. Therefore, it was necessary to find a way to estimate the effects of toxic dispersions using simple equations that could be introduced in MATLAB; also, it was essential that the repeated use of these expressions would not increase the time required to solve the problem.

To achieve this, expressions were obtained from the ALOHA code; these equations estimate the distance at which a specific concentration (for example lower flammable level) can occur, depending on the mass of the substance that is released. Eq. (3.29) is an example of one of these equations obtained for a propane release; Figure 3.7 shows how, for this equation, the distance to the lower flammable level varies depending on the released mass.

$$D_{LFL} = 0.6618({m_{rel}}^{0,5284}) \quad \textbf{(3.29)}$$

Where:

D_{LFL} (m) is the distance at which the substance reaches its lower flammability level.

m_{rel} (kg) is the mass released.

Of course, equations like Eq. (3.29) had to be developed for different atmospheric conditions, types of releases, directions from the source, and substances released, and are only valid for the specific conditions for which they were obtained.

3.4.4. Fragment projection

Fragment projection has not been considered in this work, as no models that could offer accuracy in the results and be easily introduced in the proposed methodology were

identified. Also, when compared to other effects of the studied accidents (like the thermal radiation from a fireball), which affect large areas, the projection of fragments loses importance, as it will not have generalized effects over a zone.

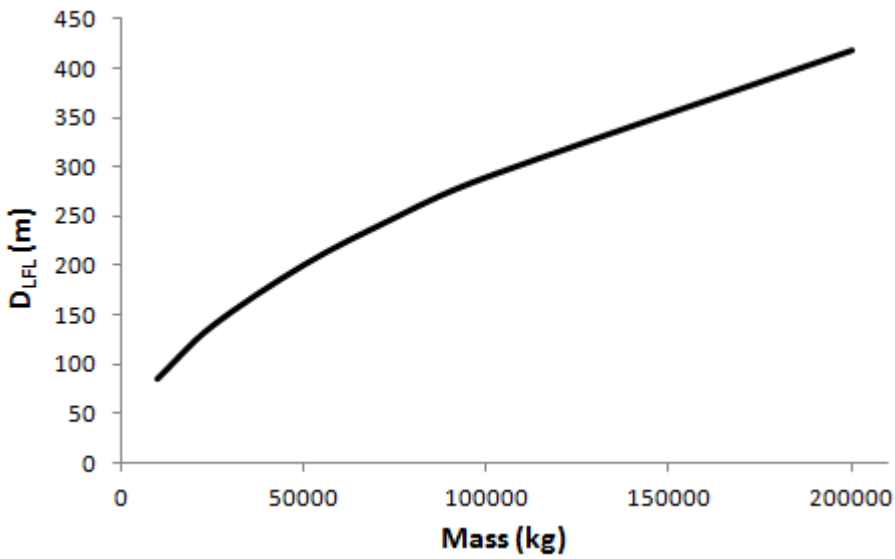


Figure 3.7.Evolution of LFL of propane vs. mass released for Eq. (3.29).

3.5. Modeling the consequences of major accidents

The consequences of a major accident are the measure of its effects on people, the environment or material property. For people the consequences are estimated as the number of persons that are killed or injured due to the accident; for the environment, they are the quantity of a natural vector that is affected; for material property, the consequences are the level of damage caused by the accident.

In this work, consequences on humans have only been considered for fire accidents and toxic dispersions, and are estimated using probit equations for fatalities and simple

equations for number of injuries; damage to material property is only related to overpressure waves, and is estimated through the use of threshold values.

Environmental consequences have not been considered in this work; this has been decided because normally, for storage installations, serious environmental affectation occurs due to the undetected continuous release of product over a long time; this is in contrast to the effects of the accidents studied in this thesis, which have immediate effects on people and property.

3.5.1. Consequences on human beings

Consequences on human beings considered in this work are fatalities and injuries caused by an accident; the only affectation considered for people is due to exposure to thermal radiation or a toxic substance. Evacuation of communities due to accidents has not been taken into account in the thesis (as explained in Section 3.6.1).

3.5.1.1. Estimating the number of fatalities

As has been said, probit analysis is used in this work to relate the effects of accident to the degree of damage it causes on human beings. The probit variable, Y, allows estimating the percentage of a population subjected to an effect (which has a given intensity), that will suffer a certain degree of damage. This variable follows a normal distribution and has a mean value of 5 and a standard deviation of 1. The common expression used to estimate the probit variable, as a function of the intensity is:

$$Y = a + b \cdot \ln(Dose) \tag{3.30}$$

Where a and b are dimensionless constants that are determined empirically from accident data or, in some cases, animal experimentation. Once the value of Y has been calculated, it has to be converted to the percentage of affected individuals, in order to be

able to estimate the real consequences of the accident on the population. This can be done by applying the following expression:

$$\% = 50\left[1 + \frac{Y-5}{|Y-5|} \cdot \mathrm{erf}\left(\frac{|Y-5|}{\sqrt{2}}\right)\right] \quad \textbf{(3.31)}$$

In this work, the following probit expression is used to estimate fatalities related to thermal radiation (Casal, 2008).

$$Y = -36.38 + 2.56 \ln\left(t \cdot I^{4/3}\right) \quad \textbf{(3.32)}$$

Where:

t (s) is exposure time.

I (W·m^{-2}) is thermal radiation intensity.

For fireballs, the time can be calculated using (3.22), while for other fire accidents, a value of 20 seconds has been assumed. For flash fires, it is considered that people within the area of the flammable cloud will suffer death once the accident unfolds.

Toxic substances can come into contact with people through different ways: ingestion, inhalation or dermal absorption. Generally, for major accidents, people are affected by inhalation. The probit equation that is normally used to estimate the number of fatal victims in case of toxic substance inhalation is:

$$Y = a + b \cdot ln \sum_i (c_i^n \, \Delta t_i) \quad \textbf{(3.33)}$$

In which c_i (ppm or mg·m^{-3}) is the average concentration during the Δt_i time (min).

For each substance, *a*, *b* and *n* are specific parameters. There can be multiple *n* values for just one chemical substance, which apply for different types of affectation; for example, *n* to calculate irritation due to ammonia is of 4.6, while to estimate fatal victims, it has a value of 2. Table 3.5 shows *a*, *b* and *n* values to estimate lethality for some substances.

Table 3.5. Constants for the inhalation lethality probit (Casal, 2008).

Substance	a	b	n
Ammonia	-35.9	1.85	2
Chlorine	-8.29	0.92	2
Hydrochloric acid	-16.85	2.0	1
Methyl isocyanate	-5.642	1.637	0.653
Toluene	-6.794	0.408	2.5

3.5.1.2. Estimating the number of injured people

The number of injured people will be estimated based on the number of fatalities calculated, using the equations proposed by Ronza et al. (2006). These are:

- For accidents involving thermal radiation:

$$n_i = 3\, n_k^{0.86} \quad \text{for} \quad 1 < n_k < 100 \tag{3.34}$$

- For accidents involving toxic dispersions:

$$n_i = 34\, n_k^{0.54} \quad \text{for} \quad 1 < n_k < 30 \tag{3.35}$$

In which n_i is the number of injured people and n_k the number of deaths.

3.5.2. Consequences on material property

All types of property suffer damage after a major accident involving overpressure or thermal radiation, however, in this work the property is divided in two categories: industrial equipment (storage tanks) and residential buildings; for equipment, the effects of fire and overpressure are taken into account to estimate its failure, while for buildings, only overpressure is considered. The way in which the level of damage on material property is estimated is through the use of threshold values.

3.5.2.1. Consequences on storage tanks

A review of literature related to the failure of storage tanks was performed in order to know the threshold values of thermal radiation or overpressure that are normally associated to a certain level of damage in storage tanks. The results of the research are presented in Table 3.6, Table 3.7 and Table 3.9, the first two for overpressure and the last for thermal radiation.

In this work, storage tanks have been categorized as pressurized or atmospheric, making no difference between different kinds included in these categories; therefore, it has been necessary to choose threshold values that apply generally to atmospheric or pressurized tanks. Observing the threshold values proposed in the literature, it has been decided to assign overpressure intervals in which the storage equipment will suffer levels of damage comparable to the LOCs presented in The “Purple Book” (2005) and used in this work. It has to be noted that this threshold values could be changed without the overall methodology proposed in this work suffering an alteration. The values are shown in Table 3.8.

For thermal radiation, the same approach as for overpressure was taken, assigning values at which different LOCs will occur depending on the type of tank that is affected. However, for this type of effect, the different types of accident that can cause it have been

taken into account at the moment of assigning the threshold values; for example, a fireball will not be given the same treatment as a flash fire or a pool fire. The table that shows the threshold values for LOCs in storage tank due to thermal radiation, taking the type of accident into account, is presented and explained in Section 5.3.2.

Table 3.6. Blast damage to atmospheric storage tanks.

ΔP (kPa)	Type of damage
5.17	Minor damage cone roof tank (50% - 100% filled)[1]
7.00	Collapse of atmospheric tank roof[1]
7.00	Partial damage to atmospheric tank[1]
10.00	50% damage of atmospheric tank[2]
10.00	Fixed roof tank damage[1]
14.00	Minor damage of atmospheric tank[2]
18.70	Minor damage, floating roof tank (50% filled) [2]
18.70	Catastrophic failure, cone roof tank (50% filled)[2]
20.00	Deformation of atmospheric tank[2]
20.00	100% damage, atmospheric tank[2]
22.00	Failure atmospheric vessel[4]
22.00	Failure atmospheric vessel[5]
24.00	20% of structural damage steel floating roof oil tank[2]
25.00	Atmospheric tank destruction[2]
27.00	Failure of steel vessel[3]
42.51	Minor damage, floating roof tank (100% filled)[1]
42.51	Catastrophic failure, cone roof tank (100% filled)[2]
45.00	Catastrophic failure, floating roof tank[1]
136.00	Structural damage, low pressure vessel[1]
136.05	Catastrophic failure, floating roof tank (50% - 100% filled)[2]
136.10	99% structural damage of floating roof tank[2]
137.00	99% damage (destruction) of floating roof petroleum tank[2]

[1]Mingguang, et al. (2008), [2]Cozzani et al. (2004a), [3]Cozzani et al. (2004b), [4]Antonioni et al. (2009), [5]Cozzani et al. (2005)

Table 3.7. Blast damage to pressurized storage tanks.

ΔP (kPa)	Type of damage
16.00	Failure pressurized vessel[1]
17.00	Failure pressurized vessel[2]
30.00	Failure of pressure vessel[3]
31.00	Elongated pressurized vessel failure[2]
38.00	Partial damage pressure vessel[5]
39.00	Structural damage to pressure vessel[3]
39.12	Minor damage, pressure vessel horizontal[3]
42.00	Pressure vessel deformation[3]
42.51	Minor damage, floating roof tank (100% filled)[4]
52.72	Minor damage, tank sphere[3]
53.00	Pressure vessel failure[3]
53.00	Failure of spherical pressure vessel[3]
61.22	Catastrophic failure, pressure vessel horizontal[3]
70.00	Failure pressurized storage sphere[5]
81.63	Minor damage, pressure vessel vertical[3]
83.00	20% structural damage of vertical cylindrical steel pressure vessel[3]
88.44	Catastrophic failure, pressure vessel vertical[3]
95.30	99% structural damage of vertical steel pressure vessel[3]
97.00	99% damage of vertical cylindrical steel pressure vessel[3]
108.84	Catastrophic failure, tank sphere[3]
108.90	99% structural damage of spherical, pressure steel vessel[3]
136.00	Structural damage, low pressure vessel[4]

[1]Antonioni et al. (2009), [2]Cozzani et al. (2005), [3]Cozzani et al. (2004a), [4]Cozzani et al. (2004b), [5]Mingguang, et al. (2008)

Table 3.8. Threshold values for blast damage associated to LOCs.

Type of tank	ΔP (kPa)	Type of damage
Atmospheric	≥ 25	G.1 release
	20 < ΔP < 25	G.2 release
	14 ≤ ΔP < 20	G.3 release
	< 14	No consequence
Pressurized	≥ 100	G.1 release
	53 < ΔP < 100	G.2 release
	30 ≤ ΔP < 53	G.3 release
	< 30	No consequence

Table 3.9. Thermal radiation thresholds for failure of storage tanks.

Type of tank	Thermal Radiation (kW/m2)	Type of damage	Source
Atmospheric	100	Failure, atmospheric tank	Antonioni et al. (2009)
	> 10, Fire impingement		Antonioni et al. (2009)
	15 $kW \cdot m^{-2}$ for more than 10 min		Cozzani et al. (2005)
Pressurized	> 40, Fire impingement	Failure, pressure vessel	Antonioni et al. (2009)
	50 $kW \cdot m^{-2}$ for more than 10 min		Cozzani et al. (2005)

3.5.2.2. Consequences on buildings

A similar approach as with equipment was followed for buildings, looking for literature data that reflected the level of damage that a structure can suffer when subjected to an overpressure wave, and relating this values to the percentage of structures that suffer total collapse or structural damage after the accident.

Table 3.10. Damage to buildings and structures due to overpressure (Casal, 2008).

ΔP (kPa)	Damage
0.2	No structural damage; occasional shattering of large glass panels
0.3	Occasional damage to glass
0.7	Breaking of small windows
1.0	Typical breaking limit of glass
2.0	Some damage to roofs; 50% of glasses shatter
3.0	Limited minor structural damage
3.5 – 7.0	Windows usually destroyed; occasional damage to frames
5.0	Minor damage to house structures
8.0	Partial demolition of houses
7.0 - 15	Wood panels displaced
10	Metal structures of buildings slightly deformed
15	Partial collapse of walls and roofs of houses
15-20	Walls of non-reinforced concrete destroyed
18	Inferior limit of severe structural damage. 50% of brickwork destroyed
20	Metal structure of buildings deformed and separated from foundations
20 - 28	Non-reinforced steel buildings destroyed.
35	Most buildings destroyed, except for reinforced concrete ones
35-50	Total destruction of houses
50-55	25 – 35 cm thick walls deformed
70	Probable total destruction of buildings

Observing the values presented in Table 3.10, thresholds to relate overpressure to the percentage of buildings affected that suffer collapse or damage have been proposed (Table 3.11).

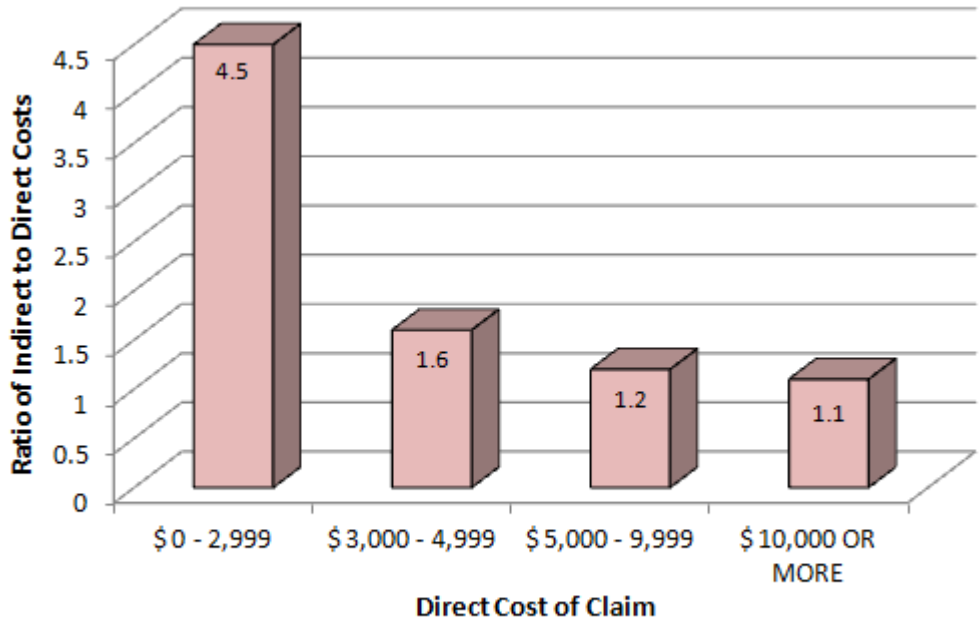
Table 3.11. Damage and collapse effects of overpressure on structures.

ΔP (kPa)	% Damage	% Collapse
$3 < \Delta P \leq 5$	10	0
$5 < \Delta P \leq 8$	25	0
$8 < \Delta P \leq 15$	50	20
$15 < \Delta P \leq 24$	50	50
$24 < \Delta P \leq 35$	25	75
$\Delta P \geq 35$	0	100

3.5.3. Indirect consequences of major accidents

There exists a series of consequences which are very difficult to estimate and cannot be associated to the direct effects of an accident, even though they are directly related to it. These can be the loss of production registered after the event, the damage to the image of the involved company and the costs related to it, the necessity to hire extra personnel for different needs (investigations, reparations, cleaning), etc.

There is no fixed value that can be used to estimate the cost of the indirect consequences of accidents, though many have been proposed; numerous sources suggest a ratio between the indirect and direct consequences (Casal, 2008). The Occupational Safety and Health Administration of the United States of America (OSHA) mentions (OSHA, 2012) studies that show that the ratio of indirect to direct costs can vary greatly, from a high 20:1 to a low 1:1; however, they propose ratios that go from 4.5 to 1.1 depending on the direct costs of the accident, stating that higher direct costs entail lower indirect costs and vice versa, as presented in Figure 3.8. In this work, a 4:1 ratio between direct and indirect costs will be used, when these lasts are taken into consideration.



Source: Bussiness Roundtable, Improving Construction Safety Performance: A Construction Industry Cost Effectiveness Project Report, Report A-3, January, 1982.

Figure 3.8. OSHA's ratio of indirect to direct costs (Reproduced from http://www.osha.gov/SLTC/etools/safetyhealth/mod1_costs.html on 30/01/2013).

3.6. Estimating the costs of major accidents

The cost of major accidents will be calculated using the following expression:

$$C_A = C_H + C_E + C_S + C_{Prod} + C_I \quad \textbf{(3.36)}$$

C_A is the total cost of the accident, C_H is the cost of consequences on human life, C_E is the cost of the equipment involved in the accident, C_S is the cost of the structures collapsed or damaged, C_{Prod} is the cost of the product lost in the accident and C_I are the indirect costs associated to the accident (All expressed in € in this work). The equations used to calculate these parameters are presented next, with the exception of the cost of the product, which depends on the specific substance.

3.6.1. The cost of human life

Human life can be impacted by a major accident in several different ways, depending on the severity of the effect and the localization of the population. After a major accident people may die, be injured or have to be evacuated from their homes, situations which should represent a cost for the company responsible of the event.

Monetization of any aspect of human life is a polemical subject, although it is necessary to do it in order to estimate the economic impact of an accident; it is impossible to estimate the value of the life of one person, or the possible everlasting costs (not only economical) that a major accident will have on a person that has suffered its effects. However, for the methodology that is developed in this work, it is indispensable to assign an economical value to at least some of the possible consequences of major accidents on human life.

Guidi et al. (2001) present a thorough analysis on this subject, showing a series of average values for injuries and loss of life, based on Italian laws. Average values for causing the death or injury of a bystander are set at approximately €1.2 million or €100,000 depending on the level of damage caused. Therefore, the equation used in this work to estimate the cost that derives of human affectation after an accident is:

$$C_H = 1.2x10^6 \cdot n_k + 1x10^5 \cdot n_i \qquad \textbf{(3.37)}$$

The value for the evacuation and displacement of one person during 30 days is estimated to be of € 4,600 (Guidi et al., 2001); using this value, the costs of evacuation would be negligible compared to those of injuries or fatalities in the case studies presented, which has led to evacuation costs not being considered during this work.

It has to be said that in this work people working in the studied installations are not taken into account at the moment of estimating or monetizing the consequences of possible accidents.

3.6.2. Costs of material property

In this section, the value of the material property that is considered to estimate the costs of accidents is discussed. This will include the costs of storage tanks, the cost of the lost product and the cost of the damage on surrounding structures (houses, offices, etc.).

3.6.2.1. Costs of storage tanks

Cost of industrial equipment can be estimated through different means, like using power laws found in literature (Smith, 2005) or using commercial software.

During the initial stages of the thesis, Eq. (3.38) was used to estimate the cost of a pressurized stainless steel tank, of volume V_{Tank} (m^3) (Smith, 2005):

$$C_E = 85{,}165\left(\frac{V_{Tank}}{5}\right)^{0.53} \tag{3.38}$$

As the thesis progressed and the necessity to estimate the costs of different types of equipment appeared, a method different than power laws was used. The process and cost engineering company Matches offers a free service in their web site (http://www.matche.com) that can be used to estimate cost of different types of process equipment, from distillation columns to filters or pressurized equipment. For example, in Matches' site, the weight and construction material of a pressure vessel can be used as input to obtain the cost of the equipment in 2007 US dollars (which can be easily converted to current € values).

Using the information provided by Matches[1] the graph presented in Figure 3.9 was developed; it shows how the cost of carbon steel spheres and horizontal pressure vessels vary in relationship to their weight.

This service was also used at the moment of estimating the economic values of atmospheric vessels.

3.6.2.2. Estimation of costs of storage tanks in accident sequences

A great part of this work is based on the development of accident sequences and the estimation of the risks associated to said events. It has already been showed how the total cost of a storage tank will be calculated; this value can be used to estimate the cost of a catastrophic release on the tank. However, since not all accidents cause the destruction of equipment, it will also be necessary to estimate the cost of the equipment being damaged in less severe ways. This has been done by multiplying the overall cost of the tank by a less than one factor that varies for different possible releases and accidents.

If a tank suffers a G.1 release, it is understood that it is destroyed, and the cost is the total economic value of the tank (the factor is 1); G.2 releases will be assigned a value of half the cost of the tank (a factor of 0.5), while G.3 will have a value of 10% the cost of the tank (a factor of 0.1).

However, if G.2 or G.3 releases develop into jet fires, it is understood that the tank involved will suffer severe damage and become useless; the accident has a cost of the total value of the tank. The same criterion has been applied to pool fires or explosion generating from continuous releases. It is considered that flash fires do not damage the equipment in a significant way, and therefore, a factor of 0 is used for this accident. It is clear that

[1] *http://www.matche.com/EquipCost/Vessel.htm, http://www.matche.com/EquipCost/Tank.htm

accidents occurring after a G.1 release are not associated to a cost in the tank, since it will have already been destroyed.

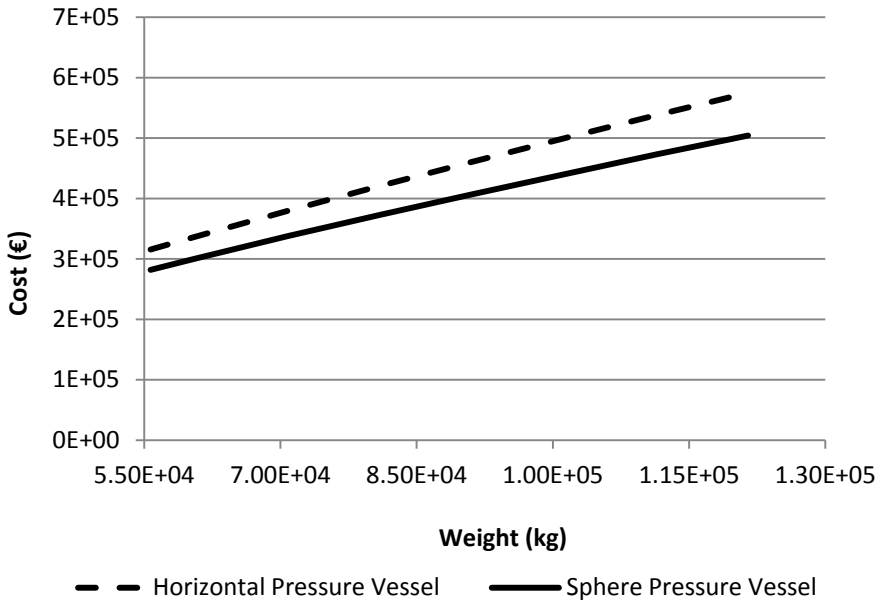


Figure 3.9. Cost vs. weight of carbon steel pressure vessels.

3.6.2.3. Costs of buildings

The economic value of structures will depend on the level of damage they sustain due to an accident, which is determined using the threshold values presented in Section 3.5.2.2, and is divided in two categories, total collapse or damage to the structure; the average cost of a collapsed house will be of approximately 174,000 €/unit and the money loss resulting from damaging a structure will be of 123,000 €/unit (ATASA, 2008). The equation used to calculate the cost of buildings is:

$$C_S = 174{,}000\, n_{col} + 123{,}000\, n_{dam} \quad \textbf{(3.39)}$$

In which n_{col} is the number of collapsed structures and n_{dam} is the number of damaged buildings.

3.6.3. Indirect costs

As explained in Section 3.5.3, when indirect costs are considered in this work, they will be estimated as having a value of 4 times that of the direct costs, which can be mathematically expressed as:

$$C_I = 4 \cdot (C_H + C_E + C_S + C_{Prod}) \quad \textbf{(3.40)}$$

3.7. Estimating the investment made on storage terminals

The estimation of the cost of the installation is necessary in this thesis to optimize the design, not only from the safety point of view, but also taking into account the investment that will have to be made.

Table 3.12. Percentages of installation cost based on the cost of equipment.

Operation	% of equipment cost
Equipment Installation	30-60%
Insulation Costs	8-9%
Instrumentation and Control	6-30%
Piping	60%
Electrical Installation	10-15%
Service Facilities	8-20%
Land	4-8%
Engineering and Supervision	30%
Construction Expense	4-21%
Contractor Fees	1.5-6%
Contingencies	6%
Startup Expense	6%

This cost will be calculated based on the cost of the purchased equipment, adding additional costs for different requirements of the project, like installation, piping, insulation, etc. as percentages of the cost of the equipment; for this, the percentage ranges presented in Peters and Timmerhaus (1991) will be used, varying them depending on the type of installation, tank or substance handled. The percentage ranges are presented in Table 3.12. Finally, the cost of the installation will be the sum of the economic value of the tanks and additional costs.

NOMENCLATURE

Symbol	Meaning	Units
a	Constant for probit calculation	(-)
A	Solid area of the flame	(m^2)
A_h	Cross sectional area of the hole	(m^2)
b	Constant for probit calculation	(-)
C_A	Total cost of an accident	(€)
C_d	Discharge coefficient	(-)
C_E	Total cost of equipment involved in accident	(€)
C_H	Total cost of accident on human life	(€)
c_i	Average concentration	(ppm) ($mg \cdot m^{-3}$)
C_I	Indirect costs related to an accident	(€)
C_p	Heat capacity	($kJ \cdot kg^{-1} \cdot K^{-1}$)
C_{Prod}	Total cost of product loss	(€)
C_S	Total cost of structures involved in an accident	(€)
$C_{st\text{-}vol}$	Molar fraction of combustible in the stoichiometric combustible-air mixture	(-)
d	Distance	(m)
D	Diameter of a pool of liquid	(m)
D_{FB}	Diameter of a fireball	(m)
D_{LFL}	Distance to the lower flammability level	(m)
D_{max}	Maximum diameter of a pool	(m)
d_n	Normalized distance	($m \cdot kg^{-1/3}$)
d_{or}	Orifice diameter	(m)
E	Emissive power	($kW \cdot m^{-2}$)
f	Flash fraction	(-)
F	View factor	(-)

Symbol	Meaning	Units
F_h	Horizontal view factor	(-)
F_v	Vertical view factor	(-)
g	Gravitational acceleration	($m \cdot s\text{-}^2$)
h_0	Initial height of liquid in a tank	(m)
H	Height of a pool fire	(m)
H_{FB}	Height of a fireball	(m)
HR	Relative humidity of air	(-)
I	Thermal radiation intensity	($kW \cdot m^{-2}$)
k	Constant	(-)
L	Length of the visible flame of a jet fire	(m)
m	Combustion rate	($m \cdot s^{-1}$)
M	Total mass stored in a tank	(kg)
M_a	Molecular weight of air	($kg \cdot kmol^{-1}$)
m_{cloud}	Mass of the cloud	(kg)
m_{comb}	Mass of combustible involved in a fire	(kg)
m_{rel}	Mass released in an accident	(kg)
M_{TNT}	Equivalent mass of TNT	(kg)
M_v	Molecular weight of fuel	($kg \cdot kmol^{-1}$)
m_∞	Combustion rate of a pool of infinite diameter	($kg \cdot m^{-2} \cdot s^{-1}$)
n	Constant for probit calculation	(-)
n_{col}	Number of collapsed structures	(-)
n_{dam}	Number of damaged structures	(-)
n_i	Number of injured people	(-)
n_k	Number of fatalities in accident	(-)
P	Total pressure at the opening	(Pa)
P_a	Atmospheric pressure	(Pa) (bar)
P_{al}	External pressure above the liquid	(Pa)
P_{cont}	Pressure inside a container	(Pa) (bar)
$P_{delayed\ ignition}$	Probability of delayed ignition	(-)
$P_{direct\ ignition}$	Probability of direct ignition	(-)
P_h	Hydraulic liquid pressure	(Pa)
P_w	Partial pressure of water in the atmosphere	(Pa)
P_{wa}	Saturated water pressure at atmospheric conditions	(Pa)
q_s	Mass flow rate	($kg \cdot s^{-1}$)
S	Length of the flameless jet	(m)
t	Exposure time	(s)

Symbol	Meaning	Units
T	Atmospheric temperature	(K)
T_{ad}	Adiabatic flame temperature	(K)
T_b	Boiling temperature	(K)
T_{cont}	Temperature of liquid inside tank	(K)
t_{fb}	Duration of a fireball	(s)
u_{av}	Mean velocity of the jet	($m \cdot s^{-1}$)
u_j	Jet fire velocity	($m \cdot s^{-1}$)
u_w	Wind velocity	($m \cdot s^{-1}$)
u^*	Dimensionless wind velocity	(-)
V	Initial volume of vapor	(m^3)
V_{Tank}	Volume of tank	(m^3)
V_l	Volume of spilled liquid	(m^3)
x	Axial distance from the orifice for jet fires	(m)
Y	Probit variable	(-)
α_{st}	Moles of reactant per moles of product in a stoichiometric fuel mixture	(-)
β	Fraction of the released energy converted into a pressure wave	(-)
ΔH_c	Latent heat of combustion	kJ kg^{-1}
ΔH_{TNT}	Explosive energy of TNT	$kJ \cdot kg^{-1}$
ΔH_v	Latent heat of vaporization	kJ kg^{-1}
ΔP	Overpressure peak	Pa
η	Explosion yield factor	(-)
η_{rad}	Radiant heat fraction	(-)
ρ_l	Density of the liquid	(kg/m^3)
τ	Atmospheric transmissivity	(-)
γ	Ratio of the specifics heat of the fuel	(-)

CHAPTER 4. INITIAL APPROACH TO SOLVING THE OPTIMIZATION PROBLEM

In this chapter the initial method for the estimation of risk associated to storage plants developed during the thesis is presented; it is followed by the early series of steps proposed to solve the "design optimization of storage facilities" problem; after this, some case studies solved using this initial approach are shown; finally, some conclusions regarding the first proposition for the method, and the ways in which it could be improved are explained.

4.1. Initial proposal for the estimation of risk related to storage facilities

To calculate the risk associated with a storage facility, it was thought that the definition of risk presented in Eq. (2.1) could be expanded to include the possibility of accidents occurring in any of the tanks existing in an installation, and accidents occurring at the same time in various units.

First, the probability of accident occurrence per storage unit was calculated using basic principles of statistics. If n is the number of units in the facility, and n_f is the number of units that suffer similar accidents at the same time, then the probability of occurrence as independent events will be:

$$P = \left(\frac{1}{n}\right)^{n_f} \tag{4.1}$$

The consequences of possible accidents were estimated using the criteria presented in Section 3.5, taking into account loss of human life, possible injuries and damage to residential structures and process equipment in Eq. (3.36) (in this Chapter, Eq. (3.38) was used to estimate the cost of process equipment).

Finally, to calculate the risk (€·year^{-1}) associated with a storage facility, taking into account the possibility of an accident occurring in any of the equipment, the following equation was proposed:

$$r_{(n)} = \sum_{n_f=1}^{n} \left[C_n^{n_f} \cdot C_{T(n_f)} \cdot f \cdot P\right] \tag{4.2}$$

Where f (y^{-1}) is the frequency of an accident, $C_{T(nf)}$ (€) is the cost of the accident, which depends on the number of tanks that fail, and $C_n^{n_f}$ is the number of accident combinations that can occur when n_f units suffer an occurrence out of n units that are built:

$$C_n^{n_f} = \frac{n!}{n_f!\,(n - n_f)!} \tag{4.3}$$

4.2. The initial optimization methodology

Figure 4.1 shows a diagram of the first proposed optimization procedure, which is based on the series of steps followed to solve any optimization problem, and that uses the definition of risk presented in Eq. (4.2). If this procedure were to be applied at the earliest stages of the design of a storage facility, it could serve as a decision-making tool, offering information about the interactions between the frequencies, the probability of occurrence, the cost of accident consequences and the number of units to use in the project. This series of steps is the forerunner of the methodology that is the final result of the thesis, and much of it can be extrapolated to the work performed afterwards. Next, these steps are explained in detail.

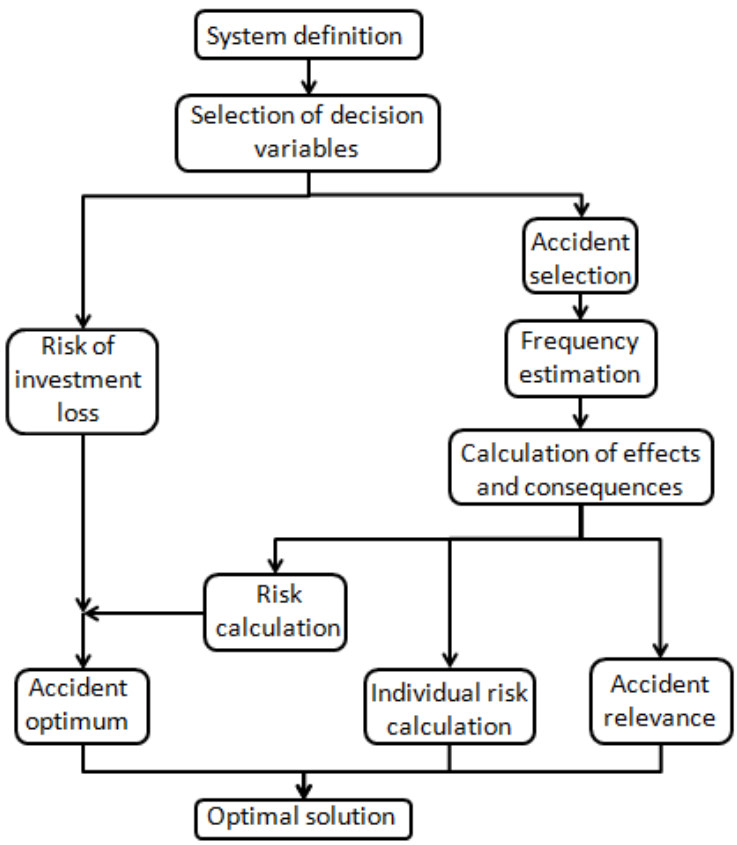


Figure 4.1.Diagram of the initial optimization methodology.

4.2.1. System definition

The system is comprised of the facility and its surroundings, up to the point where they can be affected by any potential accident. It takes into account the people, properties and equipment that are located in this area. In this step, the following must be defined: the substance to be handled, the type of units used to store it and the process conditions, plus the number of people or housing structures that surround the facility.

4.2.2. Decision variables

The design variable at this stage of the thesis was the number of tanks used to store the dangerous substance. This variable allows the mass involved in an accident to be controlled (up to a point) or manipulated. The calculation of risk is designed to be dependent on this variable. For instance, if all the mass is stored in a single tank, the consequences of a catastrophic accident will be the worst possible as all of the mass will escape, ignite or explode. However, if two tanks are used and one of them suffers an accident, the maximum mass involved will be half of the total and the magnitude of the consequences will decrease. This trend is maintained as the number of equipment increases (note that the domino effect was not included at this point of the thesis).

4.2.3. Risk calculation

Risk is calculated using Eq.(4.2) as presented in Section 4.1.

4.2.4. The objective function. Risk of investment loss and accident optimum

The objective function is an expression giving the risk associated to the facility, as a function of the number of tanks. The risk will decrease as this number increases. It can be calculated for each case using Eq. (4.2).

The solution will be the number of tanks for which the risk of an accident reaches a minimum or is lower than the risk of losing the investment made in the facility. This investment risk will be calculated as the frequency of accidents multiplied by the investment made in the plant, which, at this point of the research was estimated as the double of the cost of equipment, accounting for other costs, as control and instrumentation, piping, and installation of equipment (a less refined approach than that shown in Section 3.7):

$$r_{inv} = 2 \cdot n \cdot f \cdot C_E \tag{4.4}$$

4.2.5. Constraints

The only constraint applied to the problem was that the individual risk obtained for the facility has to be lower than a tolerable risk value, which is set by safety regulations for different cases. A value of $1x10^{-6}$ deaths per year has been used during the complete thesis. Individual risk during this stage was calculated as the risk in Eq. (4.2), with the difference that only the number of fatalities was taken into account in the calculations:

$$r_{i(n)} = \sum_{n_f=1}^{n} \left[C_n^{n_f} \cdot n_k \cdot f \cdot P_{(n_f)} \right] \tag{4.5}$$

4.2.6. Performing the optimization for various accidents

The procedure has to be performed for several of the catastrophic accidents that can occur in a storage facility, depending on the type of substance that is being handled.

If the substance is a pressurized flammable, then the event trees for continuous and instantaneous release show that five accidents may result from a loss of containment (reference manual BEVI Risk Assessment, 2009): BLEVE + fireball, vapor cloud explosion, flash fires, pool fires and jet fires. Only the first three were included in this

initial method, as they are potentially dangerous to elements outside the facility, and domino effect was not considered at this moment; jet and pool fires are more directly dangerous to a facility's equipment and employees than to exterior elements. Hence, the optimization would be forced to choose only one tank as the best solution for every case of jet or pool fires.

4.2.7. Final decision making. Accident relevance and optimal solution

The final decision of how many units to use to store the hazardous substance takes into account the results found for each one of the accidents studied. Once the risk is estimated for each accident in a possible design, a weighted average can be calculated for the values of risk for each accident; this will provide a measure of the accident that has the highest risk for every possible decision. This value is referred to as the accident's relevance. For example, in a design, there may be many possible scenarios of flash fire or various possibilities for occurrences of pool fires or other accidents; if the risks (in €/year) related to a specific type of accident (flash fire, pool fire, etc.) are added, and then divided by the sum of the risks (€/year) related to all possible accidents, a measure of which type of accident contributes more to the overall risk is obtained. The accident relevance is calculated as:

$$Relevance_{Accident} = \frac{\sum_{n=1}^{n} r_{Accident}}{\sum r_{Accidents}} \quad \textbf{(4.6)}$$

The final decision is made using the different accidents relevancies, constraint values and accident optimums.

4.3. Case studies

In this section, two case studies, dealing with different types of substances are presented; the first one, a LPG storage facility, and the second one an installation where a large inventory of chlorine is kept.

4.3.1. LPG storage plant

This example case deals with a facility in which LPG is stored and bottled; the inventory is of about 25,000 m^3. We assume that there are 30 people outdoors at 200 m north of the facility and three houses with an average of five persons inside that could be affected by an accident. The storage and atmospheric conditions are shown in Table 4.1 and Figure 4.2 represents a diagram of the facility.

Table 4.1. LPG case study conditions.

Substance	Propane	Butane
Storing conditions		
Mass to store (kg)	48,843	105,123
Volume (m^3)	116	213
Used Volume (m^3)	98	182
Length (m)	15.8	24
Diameter (m)	3.5	3.5
Pressure (bar)	9.51	2.51
Atmospheric conditions		
Temperature (K)	298.15	
Relative humidity	70 %	
Atmospheric stability class (day)	D	
Atmospheric stability class (night)	F	
Wind velocity (m/s) (day)	5	
Wind velocity (m/s) (night)	1.5	
Ground roughness coefficient (cm)	10	

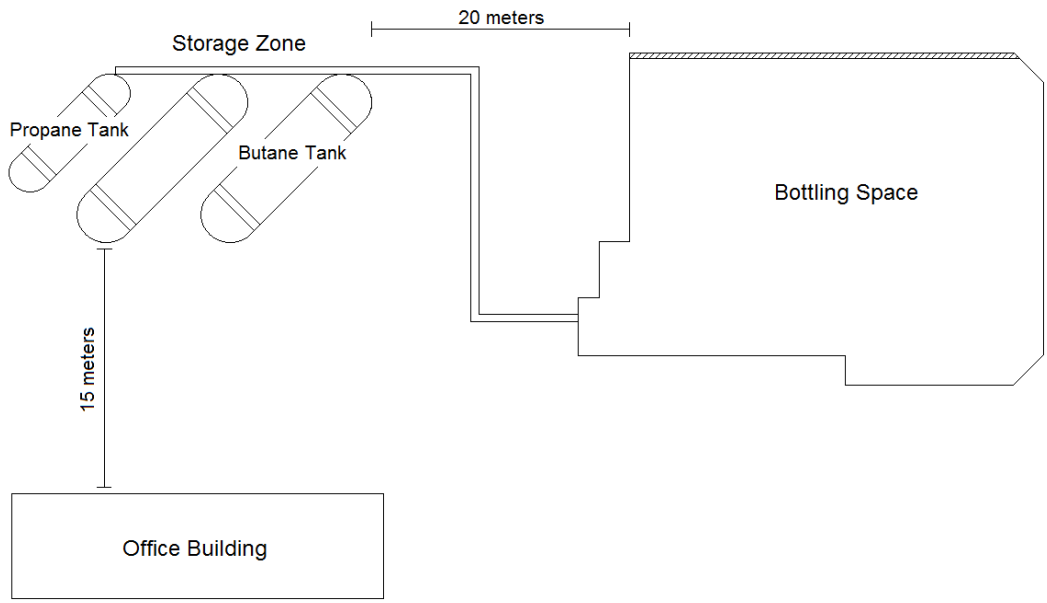


Figure 4.2.Layout of the LPG storage plant.

The objective of the example is to optimize the design of the facility, taking into account the vulnerable elements described. Originally, the facility was designed with two tanks: one to store the entire mass of butane and the other to store the propane.

The problem has to be solved for all the possible catastrophic accidents that can occur at a storage facility of flammable substances in pressurized tanks. The event trees used to decide which accidents have to be studied for instantaneous or continuous release can be found in the reference manual BEVI Risk Assessment (2009). The frequencies used for both scenarios are shown in Table 4.2. For the case of instantaneous release, an extra failure frequency of $1x10^{-6}$ $year^{-1}$ was added to the BLEVE initial frequency, in order to represent an out of the ordinary event caused by the lack of some safety measures. This was based on the criteria presented in The Purple Book (CPR18E, 2005) Section 3.2.1. We have already discussed why pool and jet fires were not considered in this case study (Section 4.2.6).

Table 4.2. Frequencies for the scenarios of instantaneous and continuous release.

Accident	Mass involved (kg)		
	< 1,000	**1,000 – 10,000**	**> 10,000**
Instantaneous release frequencies (year^{-1})			
BLEVE + Fireball	1.07x10-6	1.18x10-6	1.25x10-6
Explosion (VCE)	6.00x10-8	6.00x10-8	6.00x10-8
Flash fire	9.00x10-8	9.00x10-8	9.00x10-8
Continuous release frequencies (year^{-1})			
Explosion (VCE)	4.80x10-8	3.00x10-8	1.80x10-8
Flash fire	7.20x10-8	4.50x10-8	2.70x10-8

4.3.1.1. Propane storage

Figure 4.3 and Figure 4.4 present the risks and individual risks that result when the method is applied to this scenario for the mass of propane to be stored. The first noticeable fact is that flash fire accidents do not pose a threat to the people at 200 m or to the equipment, which is why the risk is always zero for this type of accident. According to the models used to simulate the cloud of propane resulting from the accident, the mass to be stored is not enough for a cloud of propane with dangerous flammability levels to reach the people outdoors. For accidents involving VCE, there is a risk (although very low) for 1–7 tanks, because the overpressure wave can reach the buildings and cause minor damage. This is reason enough to decide that the most relevant accident is the BLEVE–fireball. The high risk of this accident is due to the fact that the fireball associated with the BLEVE will have consequences on the people outdoors. These consequences will decrease as the mass is divided into more tanks. An abrupt climb in investment risk can be appreciated between four and five tanks for the VCE accident (continuous release), as the mass stored per tank becomes less than 10,000 kg, which means that the frequency will be higher for this accident. To decide on the optimum number of units, an individual risk analysis must be performed.

The individual risk analysis presented in Figure 4.4 shows that the only accident that will have a considerable impact on vulnerable human elements is the BLEVE, due to the

high frequency assigned to this accident. Propane should not be stored in one or two tanks, as the individual risk for these designs is above the tolerable value ($1x10^{-6}$ fatalities per year) for the BLEVE scenario.

Table 4.3 summarizes the results for propane storage. The optimal solution would be to store the propane in three tanks of 39 m^3.

Table 4.3. Results for propane storage.

Accident	Optimum tanks	Minimum permitted	Volume (m^3)
BLEVE	3	3	39
Inst. VCE	5	1	24
Inst. Flash fire	1	1	116
Cont. VCE	5	1	24
Cont. flash fire	1	1	116

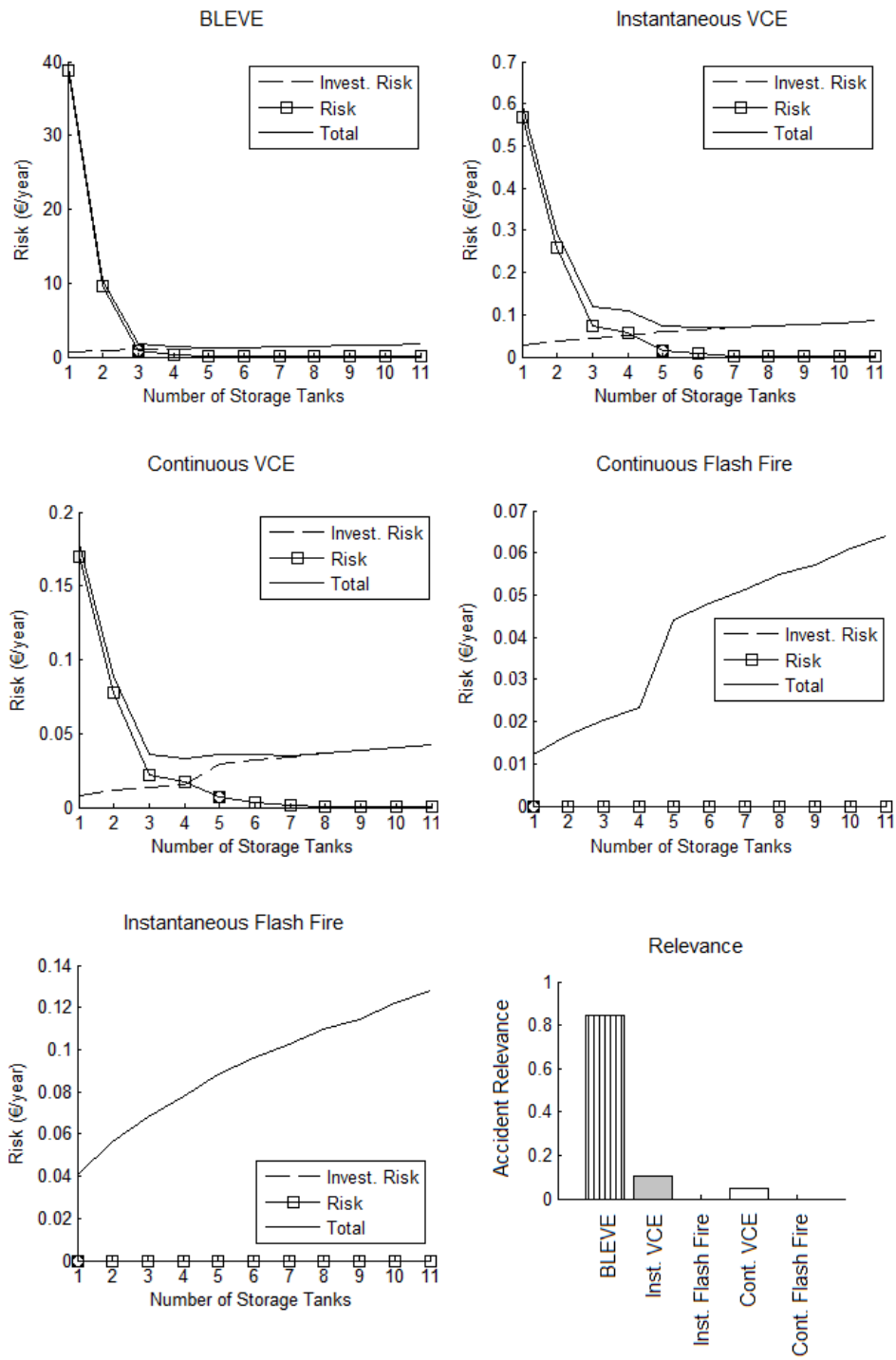


Figure 4.3. Risk results for release in propane tanks.

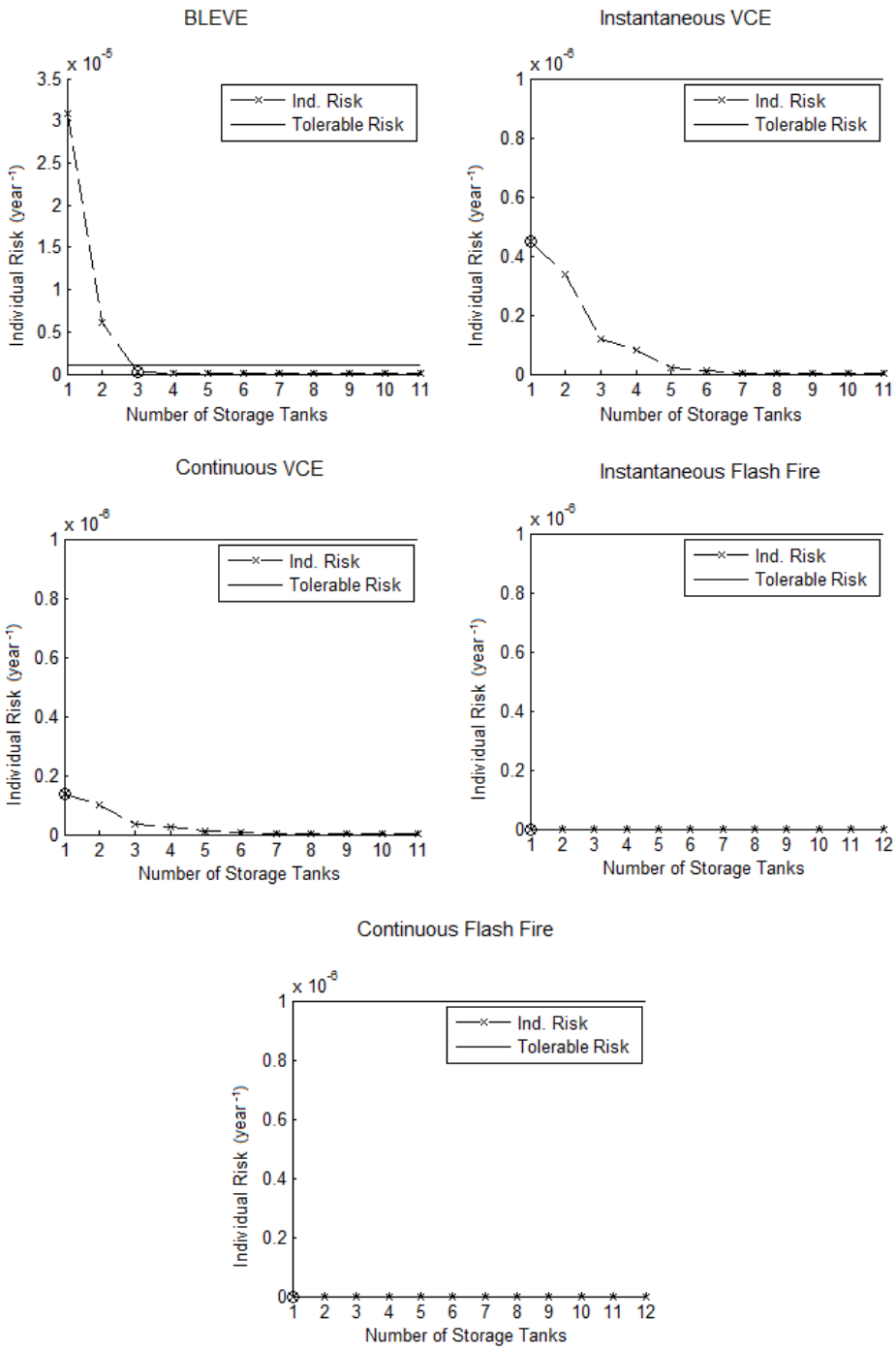


Figure 4.4.Individual risk results for release in propane tanks.

4.3.1.2. Butane storage

Figure 4.5 and Figure 4.6 show the risk and individual risk resulting from the application of the method to this scenario for the mass of butane to be stored.

In almost every accident the risk diminishes as more units are built, because the affected elements are further from the facility. The risk also drops as the mass of dangerous substance involved in the accidents decreases, as do the consequences for the people and structures that are part of the study. However, for continuous accidents, there is an increase in risk between 10 and 11 tanks. This is due to a rise in frequency when less than 10,000 kg are stored in a unit. The frequency surge between 10 and 11 tanks can only be appreciated in the investment risk and total curves, as the risk for this number of units is so low that the increase in the curve cannot be appreciated.

The risk curves do not reach a minimum for this scenario. Therefore, the chosen optimum will be the value at which the risk is lower than the investment risk. This means that the sum of the probability of occurrence multiplied by the cost of the consequences for every possible accident is lower than the frequency of the accident multiplied by the investment made in the facility.

The most relevant accident is the BLEVE–fireball, followed by the instantaneous flash fire, the VCE and then the other continuous events. This is due to the high frequency of the BLEVE accident. The tolerable individual risk values enable a decision to be made on the fewest units that can be built. For this example, no less than five tanks should be used to store the butane, as can be seen in the BLEVE accident in Figure 4.6.

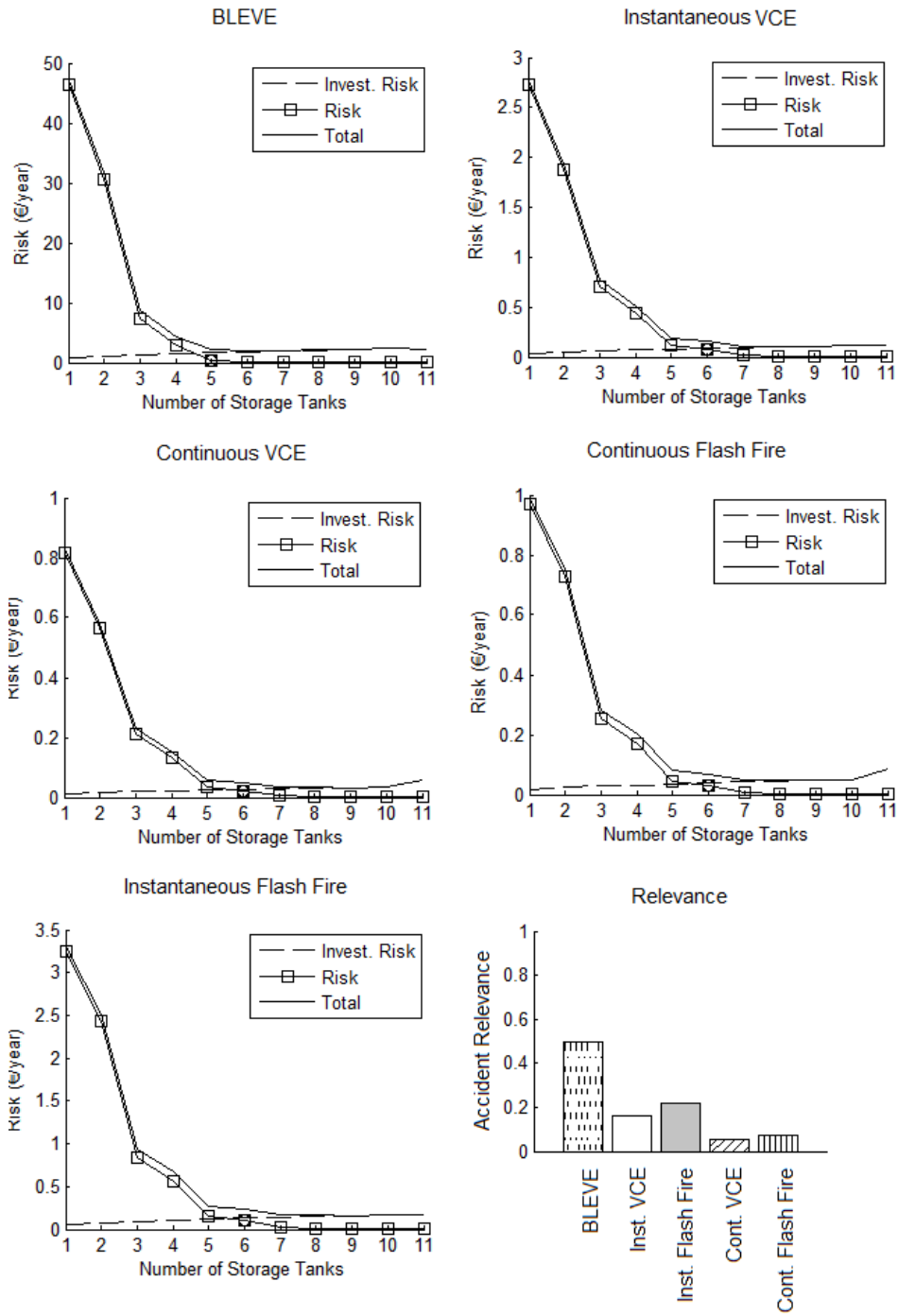


Figure 4.5. Risk results for release in butane tanks.

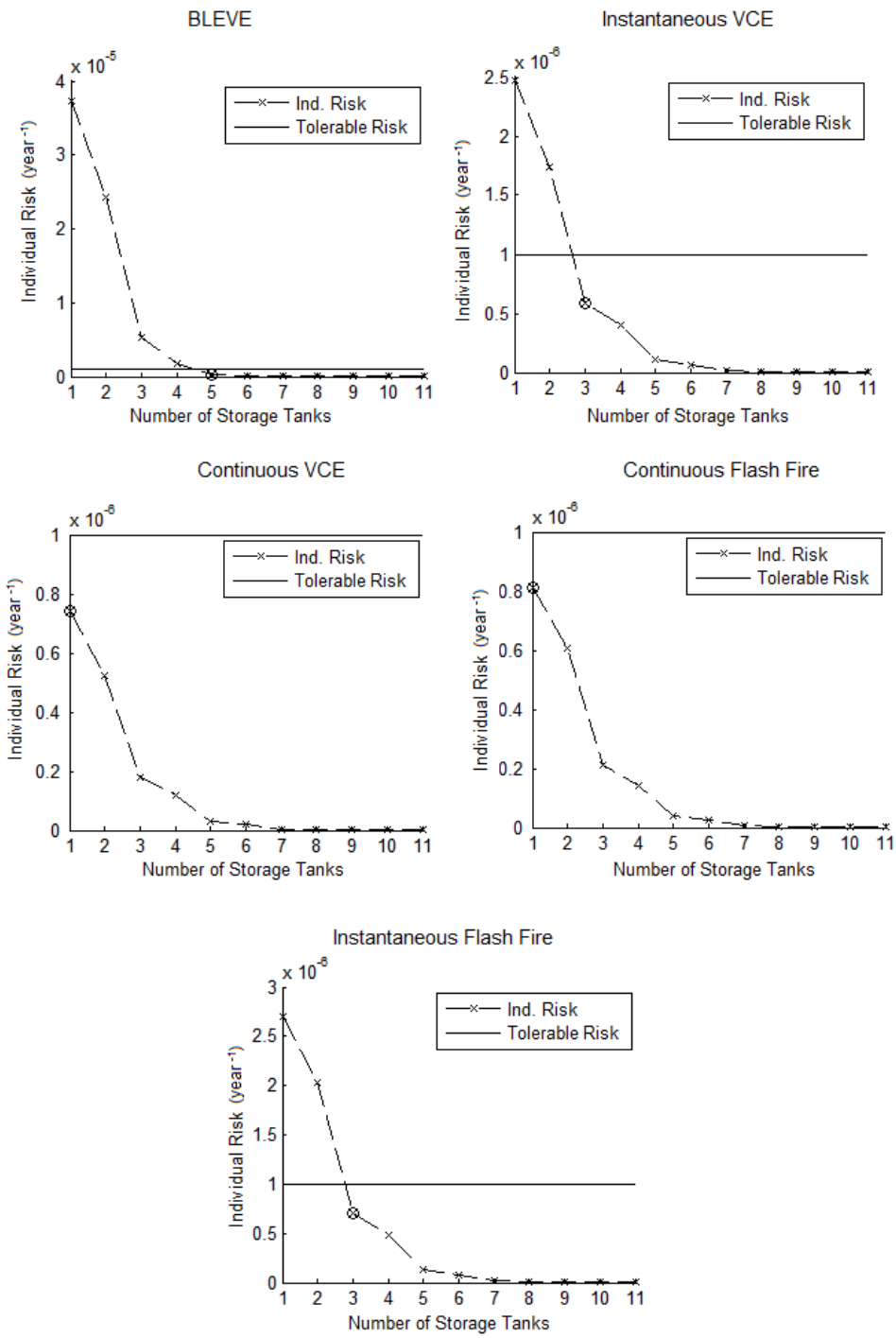


Figure 4.6.Individual risk results for release in butane tanks.

Table 4.4 shows the results for butane storage. The final decision in this case should be to use five tanks of approximately 44 m^3 to store the butane.

Table 4.4. Results for butane storage.

Accident	Optimum tanks	Minimum permitted	Volume (m3)
BLEVE	5	5	44
Inst. VCE	6	3	36
Inst. Flash fire	6	3	36
Cont. VCE	6	1	36
Cont. flash fire	6	1	36

4.3.1.3. Validation through the use of Effects 8.1 and Riskcurves 8.6

To validate the proposed methodology, the results obtained in the case study (three tanks to store the propane and five for the butane) will be compared with the original design of the facility (one tank for each substance). Effects 8.1 will be used to calculate the effects and consequences of some of the accidents that can occur in the plant, and Riskcurves 7.6 will be used to draw the iso-risk curves associated with the project.

Effects 8.1 is a computer program that calculates the physical effects and consequences of the escape of hazardous materials, based on CPR14E (1998) and CPR16E (2008). Riskcurves 7.6 is software that is used to calculate risk by estimating the physical effects, consequences and frequencies of the escape of hazardous materials, based on CPR18E (2005).

The three scenarios that are commonly used for tanks in risk analysis, and the main accidents that can occur were studied using Effects for both the original and optimized design of the tanks. These scenarios are: the instantaneous loss of the entire inventory in one of the tanks, the continuous loss of the entire inventory during a 10 min release, and the continuous release of hazardous materials through a 10 mm hole up to a maximum time of half an hour. All the accidents were evaluated for wind velocities of 5 and 1.5 m/s and

atmospheric stability classes D and F respectively. The results of the simulations are shown in Table 4.5 and Table 4.6. Afterwards, the iso-risk contours are produced using these results and the relative frequencies of the possible accidents for the different environmental conditions.

Table 4.5. Effects results for propane storage.

	Instantaneous release		**10 min release**		**10 mm release**	
	Original	**Optimal**	**Original**	**Optimal**	**Original**	**Optimal**
Number of tanks	1	3	1	3	1	1
m (kg)	48,843	16,281	48,843	16,281	48,843	16,281
BLEVE						
LC1 (m)	422	248	BLEVE does not occur for these releases			
LC50 (m)	267	146				
LC100 (m)	201	129				
Pool fire						
LC1 (m)	85	41	63	39	1	1
LC50 (m)	64	30	47	29	1	1
LC100 (m)	42	18	30	17	1	1
Flash fire						
Length of cloud (D/5)[a]	332	217	157	88	5	5
Width of cloud (D/5)	285	183	81	34	5	5
Length of cloud (F/1.5)[b]	536	336	425	198	28	28
Width of cloud (F/1.5)	518	331	638	309	45	45
VCE						
LC100 Reach D/5	281	189	130	-	-	-
LC100 Reach F/1.5	367	236	302	153	-	-

[a] D/5 Refers to the use of atmospheric stability class D and wind velocity 5 m/s for the calculations
[b] F/1.5 Refers to the use of atmospheric stability class F and wind velocity 1.5 m/s for the calculations

The analysis of the iso-risk curves shows that risk decreases significantly when using the optimal design found via the proposed method (Figure 4.7). Using the original design, the vulnerable elements would be inside the 10^{-6} year-1 risk curve, which means that the plant would have to be redesigned to comply with security standards used in some European countries (e.g. the Netherlands and Spain).

When the curves are plotted for the optimal design, the vulnerable elements fall outside the 10^{-6} year^{-1} curve, which means that use of this proposal would result in a safer facility.

Table 4.6. Effects results for butane storage.

	Instantaneous release		10 min release		10 mm release	
	Original	**Optimal**	**Original**	**Optimal**	**Original**	**Optimal**
Number of tanks	1	5	1	5	1	5
m (kg)	105,960	21,025	105,960	21,025	105,960	21,025
BLEVE						
LC1 (m)	611	283	BLEVE does not occur for these releases			
LC50 (m)	400	168				
LC100 (m)	272	144				
Pool fire						
LC1 (m)	76	76	76	76	1	1
LC50 (m)	58	58	58	58	1	1
LC100 (m)	39	39	39	39	1	1
Flash fire						
Length of cloud (D/5)a	244	129	96	52	10	10
Width of cloud (D/5)	208	108	48	21	1	1
Length of cloud (F/1.5)b	384	195	346	132	9	9
Width of cloud (F/1.5)	375	195	499	223	21	20
VCE						
LC100 Reach D/5	211	118	-	-	-	-
LC100 Reach F/1.5	269	142	244	106	-	-

The same notes made in Table 4.5 apply

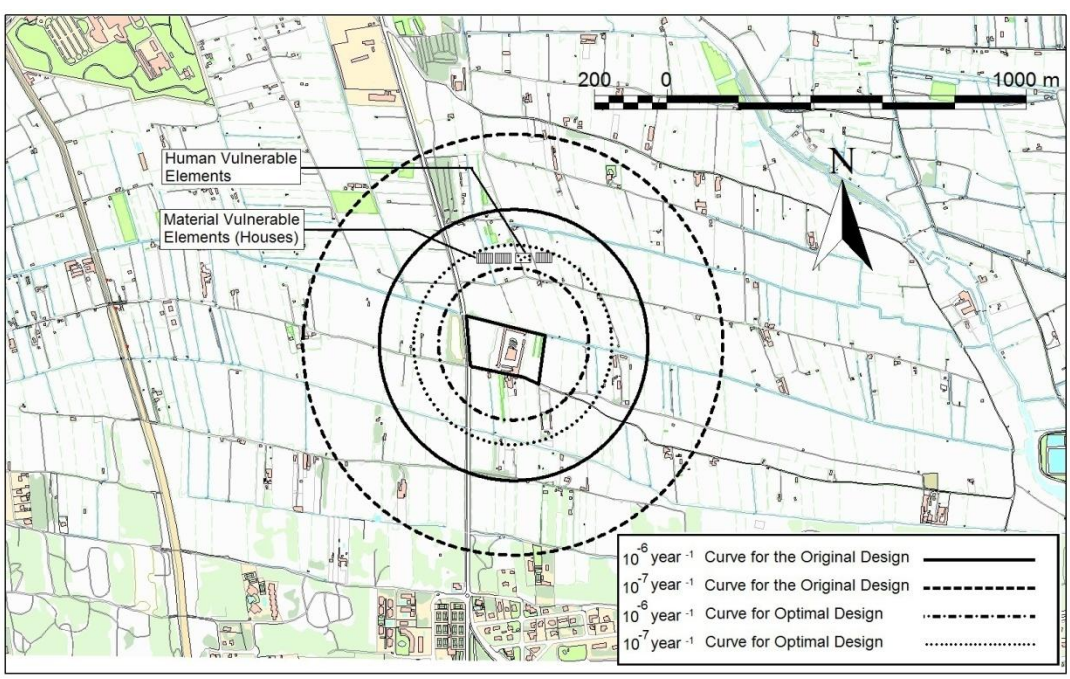


Figure 4.7.Iso-risk curves for LPG storage case.

4.3.2. Chlorine storage plant

An installation where chlorine is stored and distributed is studied. Two pressurized vertical cylindrical tanks are used to keep the chlorine; there are bays at certain distances, in which road tankers load and unload chlorine to be stored or transported, a diagram of the installation is shown in Figure 4.8. Each tank can store up to 80,000 kg; however, this capacity is not necessary, and the plant operates storing 80,000 kg in one tank, and 40,000 kg in the other one.

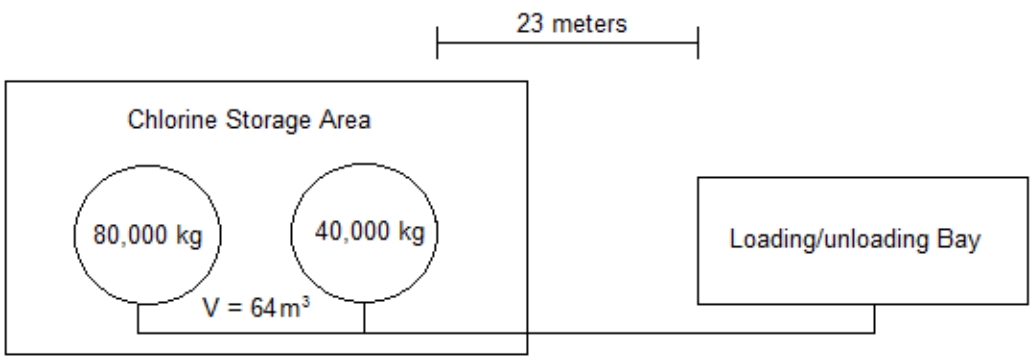


Figure 4.8.Chlorine plant diagram.

The objective of the case study will be to find the optimum number of tanks to use to store 120,000 kg of chlorine, and compare this design to the original one, using risk analysis software, taking into account that there is a group of houses where 20 people live, at 400 m west of the facility. The problem will be solved for the instantaneous release of the whole contents of tanks, the continuous release of the totality of the inventory during 10 min and the continuous release through a 10 mm hole during a maximum time of 30 min. Table 4.7 shows the conditions for which the case was solved.

Table 4.7. Chlorine case study conditions.

Substance	Chlorine
Storage conditions	
Mass (kg)	120,000
Pressure (bar)	5.9
Atmospheric conditions	
Temperature (K)	288.15
Relative humidity (%)	50
Atmospheric Stability class (day)	D
Atmospheric Stability class (night)	F
Wind velocity (m/s) (day)	4.5
Wind velocity (m/s) (night)	2.4
Ground roughness coefficient (cm)	10

From Figure 4.9, Figure 4.10 and Table 4.8, it can be seen that the optimal solution in the case of an instantaneous release would be to use five tanks of 20 m^3 to store the mass, while in the case of a 10 min continuous release of the whole contents of the tanks, the optimal number of units would be of 2, each one with a volume of 48 m^3. The results for the continuous release through a 10 mm hole are not shown, as the effects of this dispersion did not reach the vulnerable elements, prompting that the result be one tank; however, this release is included when the validation through the use of Effects and Riskcurves is performed.

The minimum permitted number of units would be 3 for the instantaneous release, and 1 for the continuous one. The individual risk for the instantaneous release restricts the solution to be of at least three tanks and since this accident presents higher values of risk than the continuous release, a compromise solution between the optimum for this case and the restricted value will be used; taking this into account, it is decided that the optimal solution will be to use four tanks of 24 m3 to store the chlorine.

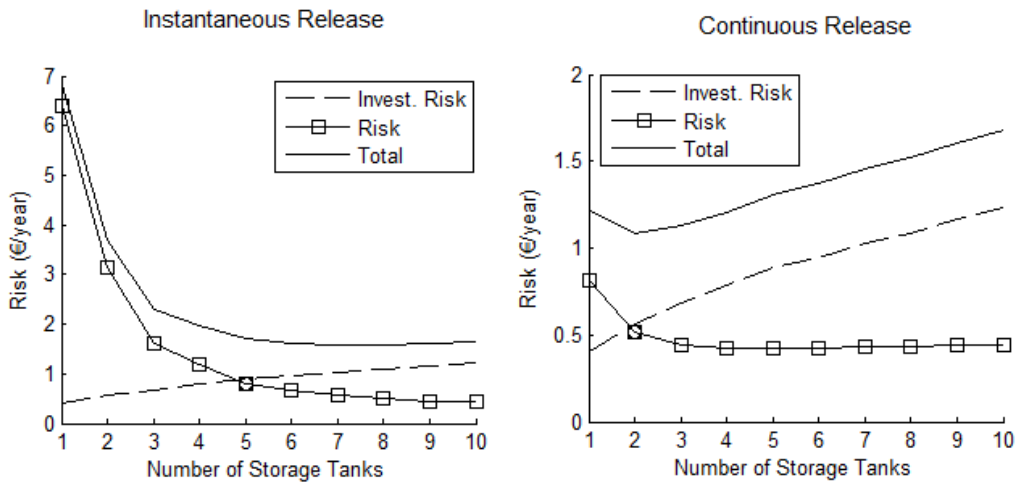


Figure 4.9.Risk results for release in chlorine tanks.

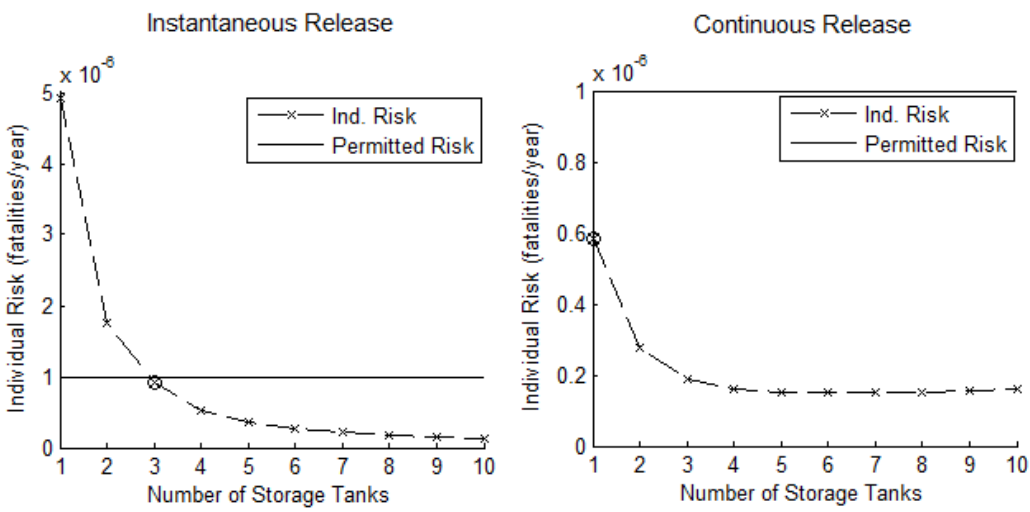


Figure 4.10. Individual risk results for release in chlorine ranks.

Table 4.8. Results for chlorine case study.

Accident	Optimum tanks	Minimum permitted	Volume (m^3)
Instantaneous	5	3	20
Continuous	2	1	48

In the real facility, one of the tanks is always used at half capacity; in other installations, one tank is always kept out of service, in order to have some extra inventory space, or to use it in case repairing is needed in any of the other units. For this factor to be taken into account in the methodology proposed, more mass of substance would have to be introduced, even though the storage space for the extra amount will not be used during the normal operation of the facility. This would produce a solution that would take into account the possibility of more mass being stored in the installation.

4.3.2.1. Validation through the use of Effects 8.1 and Riskcurves 8.6

The optimal and original designs of the case study will be compared using risk analysis software as was done for the LPG storage facility case.

Table 4.9. Effects results for chlorine storage (Optimal design).

Met. Cond.	LC1		LC10		LC50		LC100	
	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)
Optimal design (4 tanks, mass per tank = 30,000 kg)								
Instantaneous release								
4.5 D	2,400	1,100	1,800	940	1,200	760	591	456
2.4 F	3,000	2,680	2,300	2,300	1,600	1,740	758	880
Continuous release (10 min)								
4.5 D	2,400	420	1,500	340	806	240	285	152
2.4 F	3,400	1,260	2,400	1,080	1,500	860	635	570
Continuous release (ϕ = 10 mm)								
4.5 D	584	90	353	68	189	54	63	34
2.4 F	857	240	534	154	306	106	119	104

The results of length and width of cloud for the different affectation levels (LC1 – lethal concentration for 1% of deaths to LC100 – lethal concentration for 100% of deaths) are shown in Table 4.9 and Table 4.10; the results are presented for the optimal case, using four tanks to store the mass, and for the configuration used currently, two tanks, one with 80,000 kg and another one with 40,000 kg; in every case, the calculations were carried out

for two sets of atmospheric conditions, one with a wind velocity of 4.5 m/s and stability class D, and the other with 2.4 m/s and stability class F.

Table 4.10. Effects results for chlorine storage (Original design).

Met. Cond.	LC1		LC10		LC50		LC100	
	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)	Length (m)	Width (m)
Original design (tank – 80,000 kg)								
Instantaneous release								
4.5 D	3,300	1,240	2,900	1,080	1,700	900	857	600
2.4 F	4,100	3,280	3,100	2,800	2,200	2,340	1,100	1,520
Continuous release (10 min)								
4.5 D	3,800	740	2,400	600	1,300	442	481	282
2.4 F	5,200	2,240	33,800	1,920	2,500	1,600	1,100	1,100
Continuous release (ϕ = 10 mm)								
4.5 D	750	102	490	80	264	68	89	34
2.4 F	1,200	260	735	200	420	164	160	106
Original design (tank – 40,000 kg)								
Instantaneous release								
4.5 D	2,600	1,190	2,000	1,010	1,300	830	634	490
2.4 F	3,100	2,770	2,400	2,400	1,650	1,800	851	1,120
Continuous release (10 min)								
4.5 D	2,700	500	1,700	400	930	300	332	186
2.4 F	3,900	1,480	2,700	1,280	1,700	1,040	740	680
Continuous release (ϕ = 10 mm)								
4.5 D	620	95	380	71	204	55	68	34
2.4 F	925	245	572	163	330	118	127	104

The data shown in Table 4.9 and Table 4.10, along with the frequency of accident as discussed in the methodology, were introduced in Riskcurves 7.6 to obtain the iso-risk curves for each design; these results are shown in Figure 4.11. It is clear when observing the 10^{-6} year^{-1} curves that the optimized design presents a significant improvement risk-wise when compared to the original design; the 10^{-7} year-1 curves are not shown in the figure, as they cover a greater area, and in presenting them a scale problem would arise.

The improvement is really noteworthy for this case, as the changes in design would only require using two more tanks, all of them smaller and cheaper than the originals, but would signify that the installation can be placed in this area without any problem, as it would not affect the vulnerable elements, which it does when using the original design. This case study proves that the methodology can be applied to the storage of substances of diverse types, producing a solution that optimizes the design of the installation by reducing the loss of money that can be generated by major accidents.

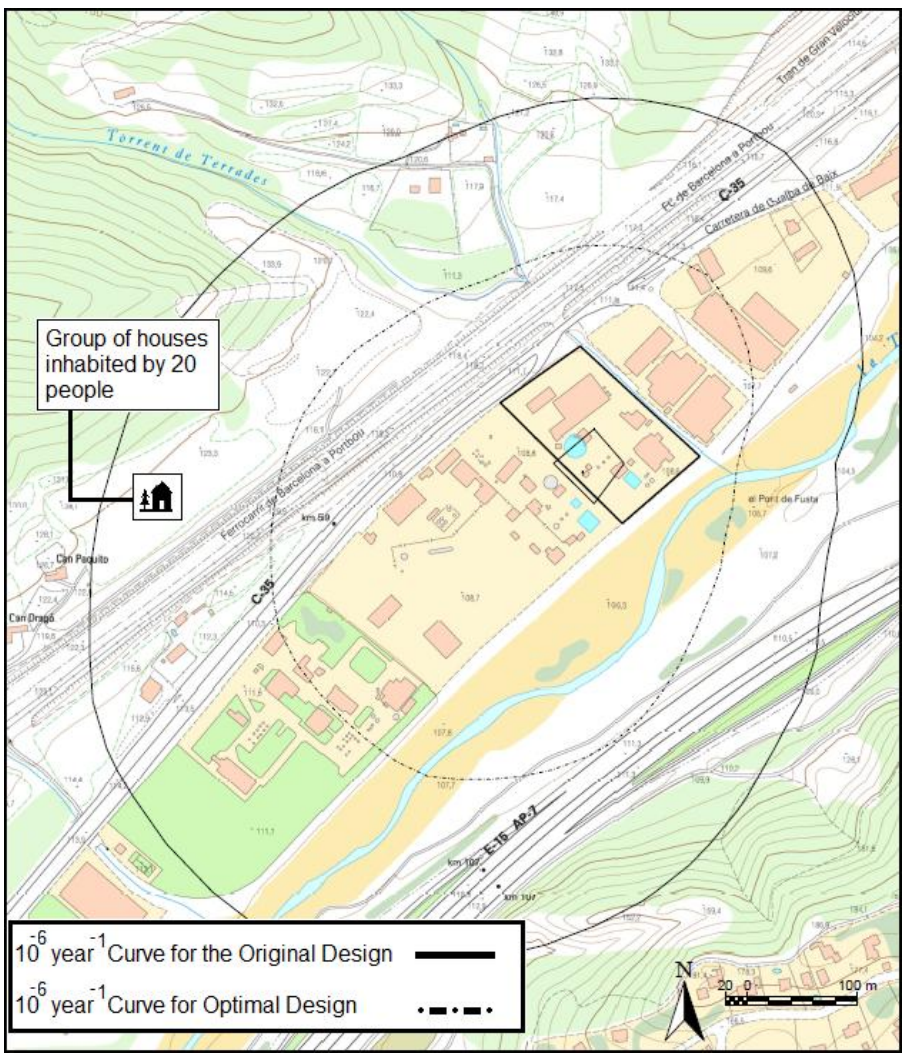


Figure 4.11. Iso-risk curves for chlorine storage case.

4.4. Chapter conclusions

This initial methodology demonstrates that:

- Risk for storage facilities can be quantified by using mathematical programming to explore different possible accidents that can occur in a plant. The probabilities of occurrence of these accidents can be combined with the cost of their consequences to obtain a final risk value that depends on certain aspects of the design.

- The risk function can be used to optimize the design of a facility by studying certain possible accidents that can occur in the type of plant that is being planned.

The methodology can be used as a decision-making tool based on risk analysis that can help improving the design of a storage facility and minimize the associated risk. It also helps understanding the interactions between the frequency, effects and consequences of accidents, the risk of the project and the investment. It is a different approach to the traditional QRA that is designed to offer a more powerful and adaptive decision-making tool.

While traditional quantitative risk analysis is applied on an existing facility or on the late stages of the design of a project, to evaluate the risk it presents to the vulnerable elements that surround it, this new method allows applying aspects of QRA at the initial stages of the project, to help finding an optimum design from a risk point of view, while also taking into account some economic aspects of the project. It is also very adaptive, as it can be applied to different types of installations and using different LUP criteria as restrictions to the optimization.

However, the initial model is limited in the variables it takes into account at the moment of performing the optimization. It does not take the layout of the installation, or

the possibility of domino effect occurrence into account. It is better suited for installations that handle toxic materials than for flammable storage terminals.

The domino effect is a phenomenon of the utmost importance when developing methodologies such as the one presented in this thesis, which can be applied on installations that are highly susceptible to suffering cascading accidents. The domino effect is very difficult to model, and due to the fact that the methodology presented in this chapter represents the initial steps of the larger methodology developed, domino effect was not thoroughly taken into account. Eq. (4.2), which is used to estimate the risk associated to the installation for a specific accident and design, includes the possibility of various tanks suffering occurrences at the same time, although as independent events.

A methodology to model the domino effect and include it into the optimization methodology was developed, and is presented in CHAPTER 5.

NOMENCLATURE

Symbol	Meaning	Units
C_n^{nf}	Combinatory of possible accidents	(-)
C_T	Cost of accident	(€)
C_E	Cost of tank	(€)
f	Frequency of accident	(year^{-1})
n	Number of tanks	(-)
n_f	Number of tanks that suffer accidents at the same time	(-)
n_k	Number of fatalities	(-)
P	Probability of accident occurrence	(-)
r	Risk	(€·year^{-1})
r_i	Individual risk	(deaths·year^{-1})
r_{inv}	Investment risk	(€·year^{-1})

CHAPTER 5. MODELING THE DOMINO EFFECT

The domino effect is defined as a cascade of events in which the consequences of previous accidents are increased both spatially and temporally by following ones, thus leading to a major accident (Devolsalle, 1996). This phenomenon is of the utmost importance at the moment of estimating the risk associated to a specific installation, as it may have a significant effect on the frequencies with which some accidents will occur in the facility.

In this chapter, a methodology for developing accident sequences in storage plants is presented. This method can be used in the estimation of the risk associated to an installation, and is in fact, an instrumental piece of the optimization methodology developed in this thesis. In this model event trees and threshold values for storage tank failures are used to develop accident sequences from generic LOCs for each of the tanks that are part of an installation; the frequency of the accidents in the sequence are obtained by combining the frequency of the initial LOC event with the probability of an accident occurring, and of other tanks being affected by it, and consequently failing and leading to another LOC and further accidents. The methodology has been designed to be easily implemented in a software tool (MATLAB was used for this work), in which the user needs only introduce some data (substance properties, type of tank, distance between equipment) to receive the final frequencies of accident per storage unit.

The domino effect model is instrumental in the design optimization because it allows developing accident sequences which depend on design characteristics of the plant, (layout, capacity of the tanks, number of units or type of tanks used); it also allows knowing the frequencies of each of these possible accidents through the sequence, providing one of the two components of the risk binomial. After the accident sequences and their frequencies are known, the cost of each of the accidents in the sequence has to be estimated in order to evaluate the risk associated to an installation.

Next, a brief review of some historical analysis related to domino effect, as well as a description of some of the models that have been proposed to model this phenomenon in process plants, are presented; after this, the algorithm developed in this thesis to produce accident sequences, is explained. Finally, some case studies are presented, followed by the application of the model to a layout based on the Hertfordshire (Buncefield) oil terminal that suffered a devastating accident in 2005.

5.1. A review of domino effect historical analysis

Historical analysis is the study of accidents that have occurred in systems that share certain characteristics, for example, accidents involving fire, or hazardous events in a specific type of process or unit. This type of study can be very useful at the moment of determining common causes of accident or types of failure through the use of statistical analysis, once a sufficient amount of information has been gathered using a database; however, the most important use of historical analysis is that it can be applied to the calculation of frequencies of initial events and accidents; since it is the only source of experimental data associated to major accidents in process industry, it can be used to validate mathematical models.

A through historical analysis of 225 accidents that have involved domino effect, and that occurred after 1961 was performed by Darbra et al. (2010), analyzing origin, causes, materials involved, effects, consequences and most frequent sequences of accident as the

main factors in the study. The main source of information used was the Major Hazard Incident Data Service (MHIDAS) database (November 2007 version); other sources consulted were the MARS, MAHB, FACTS and ARIA. The accident scenarios considered where processing, loading/unloading, transportation and storage.

The conclusion was that 35% percent of the accidents studied occurred in storage areas, which makes these types of installations the most prone to suffering cascading accidents, followed by process plants with a 28%; the analysis of causes of accidents showed that 30.7% were due to external events, 28.9% to mechanical failure, 20.9% to human factor and 17.8% to impact failure, while the rest were distributed between violent reaction, instrument failure, upset process conditions and services failures. Another important finding was that 89% of the accidents involved flammable materials; LPG was found to be the substance implicated in more events.

The sequences of different domino accidents were analyzed by constructing a relative probability event tree. The most common primary event was found to be fire (probability: 0.524), followed closely by explosion (probability: 0.476). The most frequent sequences of accidents resulted to be explosion-fire (27.6%), fire-explosion (27.5%) and fire-fire (17.8%). The accident with the most disastrous consequences was the event in San Juan Ixhuatepec (Mexico, 1984).

Another important conclusion of the study is the fact that the number of accidents involving domino effect has decreased in the last decades, having reached its maximum during the seventies decade; however, although it has been proved that the number of domino effect accidents is decreasing, the phenomenon is still possible and plants have to be designed taking into account the possibility that it might occur.

A different historical analysis involving domino effect was performed by Gómez-Mares et al. (2008), in which the relation that exists between jet fires and the occurrence of

domino effect was studied. The study was carried out by using different databases like MHIDAS, SRD or MARS. A total of 84 involving a jet fire were identified since 1961, and were included in the study. The analysis of these events allowed the construction of an event tree that was used to determine the most frequent sequences of accidents involving domino effect and jet fires. In 27% of the cases, the sequence was found to be loss of containment to jet fire and later to explosion; 11% were found to be loss of containment to vapor cloud explosion to jet fire. It was determined that when a jet fire occurs it will lead to another accident with severe consequences in approximately 50% of the cases.

5.2. Domino effect models

The modeling of domino effect in process plants is a research theme that has been gaining interest for the last two decades and that has been the subject of various works; investigations on domino effect do not deal only with the modeling of the accident sequences, but also encompass the failure probability of equipment due to the external effects of accidents, like fire, explosions or fragments by use of probit equations or threshold values. It has to be noted that all domino effect models share common aspects, and that the differences normally come in the way in which the accident sequences are developed, or in the models or values that are used to estimate equipment failure.

The first reported tool that could model domino effect was presented in 1997 (Khan and Abassi, 1998) and is called DOMIFFECT; the software tool relies on a model that is capable of estimating: a) the hazards of fire, explosions, toxic releases, or the combination of these phenomena; b) the damage potential of likely accidents; c) the likelihood of a second accident being triggered by the first; d) the scenarios of the second accident, their damage potential, and the probability of other accidents occurring. The work presents models for estimating credible accident sequences that arise from the occurrence of another fire or explosion event, using sophisticated calculation models for the assessment of accident consequences. This work was intended to provide the process industry with a tool that allows predicting if domino effect will occur in an area, and if it does, which are the

most probable sequences, to help in the decision making process of how to prepare for this type of event. This tool is applied to extensive case studies in various works (Khan and Abassi, 2001; Khan and Abassi, 2011), demonstrating the importance of taking domino effect into account in risk calculations associated to a cluster of industries.

Another model dealing with domino effect, this time with the assessment of risk by domino effect in quantitative area risk analysis was presented by Cozzani et al. (2005). This model defines escalation vectors, which are the physical effects responsible for accident propagation (thermal radiation, overpressure wave, etc.), that are generated from the primary scenarios considered in QRA; it uses them to calculate the impact that domino effect could have on individual and societal risk, and to the potential life loss index. This model presents some threshold values for equipment failure due to different effects, but uses probit equations to calculate the probability that an accident escalates. The way in which the frequencies and consequences of domino scenarios are calculated is explained in detail, and various case studies are presented.

A new model for assessing domino effect in process plants has been presented recently by Abdolhamidzadeh et al. (2010), using Monte Carlo Simulation to overcome the limitations of analytical methods at the moment of handling the uncertainty and complexity associated with domino effect phenomena modeling. The model presents an algorithm which relies on ideas similar to those of other domino effect models, but that develops the sequences in a different way, applying a more sophisticated mathematical tool. The proposed model is applied to two case studies, and the impact of the domino effect in risk is established by comparing the individual risk curves with and without taking the phenomenon into account.

Other works are not directly related to domino effect modeling, but deal with the estimation of failure probabilities of equipment due to thermal radiation, overpressure, etc., or with the application of a model to a case study. Some works that deal with the

occurrence of domino effect, or the failure of equipment, due to fire accidents are presented in (Landucci et al., 2009; Zhenyi et al., 2010; Salzano et al., 2003). Other works dealing with domino effect and overpressure are presented by Cozzani and Salzano (2004a, 2004b) or Minnguang and Juncheng (2008); a work dealing with domino effect due to fragments is presented by Xin-Mei and Guo-Hua (2009) while a general approach can be found in the work by Cozzani et al. (2006), in which values are shown for failure of equipment due to different accident effects. The values shown in these works were used to develop an integral part to the methodology presented in this chapter, as is shown in Section 5.3.2.

5.3. Proposed algorithm for developing accident sequences in storage installations

The algorithm (Figure 5.1) that calculates the sequences and final frequencies, the criteria used to develop it and the stages which compose it are explained next.

5.3.1. Input data

The data needed to solve the problem, or that has to be introduced in the program to find the frequencies of accident are:

5.3.1.1. Number of tanks

This variable refers to the quantity of units that exist in the installation, or that are used in its design. For the methodology and program, each tank is assigned a number, which is necessary to generate the domino sequences.

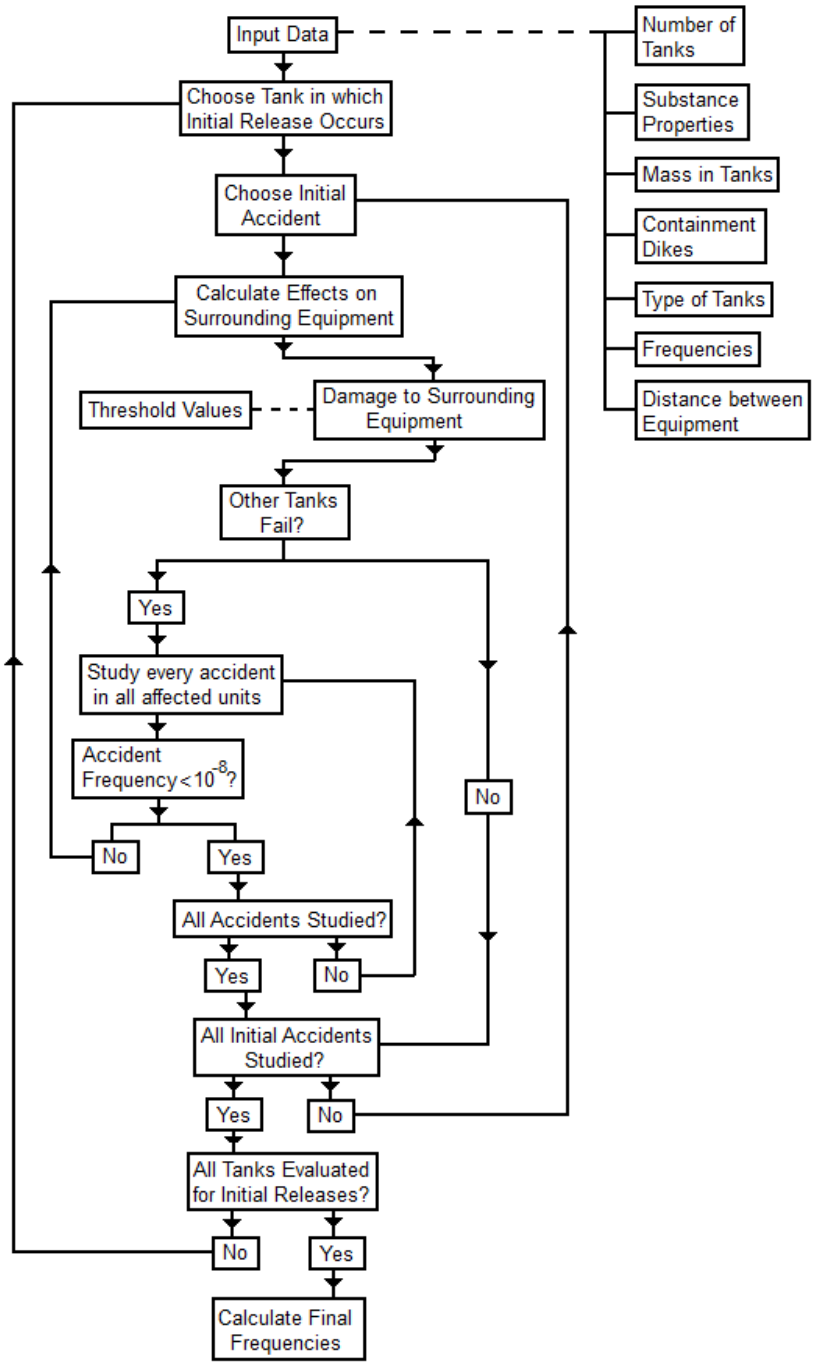


Figure 5.1. Algorithm for development of domino sequences and calculation of final frequencies.

5.3.1.2. Properties of stored substances

To define the possible sequences that can occur in a domino effect event, the different accidents that can occur in each unit, as well as the effects and consequences they may have on the surrounding equipment have to be estimated; to do this, some thermodynamic properties at the storage conditions have to be known, these are: heat of vaporization, density, heat capacity and lower heating value. Other properties, independent of the storage conditions of the substance, are used: boiling temperature, molecular weight and burning velocity.

These properties have to be defined for the substances stored in each tank. For the program developed in MATLAB during this work, they are introduced as a matrix, in which each column represents a property, and each row represents the substance stored in the tank of said number.

5.3.1.3. Mass in each of the tanks

The quantity of mass that is normally stored in each tank. The effects and consequences of an accident are directly proportional to the mass involved in it, which will make this a very important variable in the way in which the domino sequences behave. For the program, these variables are introduced as a vector, in which each position relates to the mass stored in each one of the tanks.

5.3.1.4. Size of containment dikes

Containment dikes are normally used in storage installations to serve as barriers that will enclose the mass of substance in case of a spillage. This type of protection also serves the purpose of saving the surrounding units from being engulfed in flames in case a pool fire occurs in another tank, allowing other safety devices to work and impede the

occurrence of domino effect; it has to be said that sometimes a group of units shares the same containment dike.

A containment dike will define the shape, size and time of the pool fire for the unit it serves, and will significantly affect the sequence of accidents that can be triggered due to this accident. In the program, the size of the dike is introduced as two vectors: one for the width and another for the length. Each position of the vector relates to the tank of that number.

5.3.1.5. Type of each tank

The type of tank refers to some characteristics of the units that can have a significant effect on the risk.

The most important classification is made according to the pressure at which the tank operates; if the tank is pressurized, it is possible that in case of a fire accident, it will be susceptible to suffering a BLEVE incident, something that cannot occur if an atmospheric tank is used. In the program, these two options can be selected for each tank, using a binary variable stored in a vector; as in other cases, each row represents the type of tank for the unit to which that number has been assigned; each position of the vector will be filled with a one or cero, signifying one of them that the tank is pressurized, and the other that its atmospheric.

The tanks can also be classified by their form; in this methodology they are sorted as spheres, vertical and horizontal cylindrical tanks. In the program, the form is inputted similarly to the type of tank by pressure condition, a vector in which each position relates to a tank, and can take three values: one if the tank a sphere, two if it is a vertical cylinder and three if it is a horizontal one.

5.3.1.6. Frequencies of accidents per tanks

This parameter refers to the initial frequencies of an accident occurring in a certain unit; however, before this information can be known, the initial LOCs have to be defined. Those presented in Section 3.1 were used.

Once the LOCs and their frequencies are defined, an event tree detailing the accidents that can occur due to any of them can be developed and used to calculate the probability of occurrence of final accidents in the unit; the probabilities of accident and the initial frequency of the LOC event to which they are related can be combined to calculate the frequency of accident. As has been said, CPR18E (2005) was used in this work as a model to develop event trees and calculate frequencies of accident.

In the program, two matrixes are used to introduce the frequencies of accident. The first one is for the initial accident frequencies for each tank, and is obtained from event trees. The second matrix is for the probabilities of accident in the surrounding units due to external fire resulting from other accident; this is because most tanks have safeguards that can be used to prevent fire triggered accidents, and this has to be taken into account, as it can greatly change the event tree, and thus, the frequencies of final accidents. The rows in both matrixes correspond to each of the tanks in the installation, while the columns will be the frequency of a certain accident, for example an explosion derived from a G.2 scenario or a BLEVE from a G.1 type release.

5.3.1.7. Distances between tanks

The final information that is required to be able to define the accident sequences, and to calculate the final frequencies of accident, is the distance between the tanks that are being evaluated. This information is available from the design of the installation. In the program, the distances are introduced as a matrix, in which the intersections between rows and columns determine the distance between the units.

5.3.2. Development of accident sequences

To develop the domino effect sequence that can occur due to an initial loss of containment in certain equipment, the first necessary step is to determine the accidents and frequencies that can occur because of the release; this step has already been accomplished in advance.

The next step is to calculate the effects that all possible initial accidents in each tank could have on the surrounding units, to know how they are affected and what accidents might happen as a consequence of the initial one. To know how other equipment might be affected, the same LOCs as for the original accident were used, combined with threshold values that allow estimating the level of damaged suffered and the type of release that occurs in the affected units; for example, if a continuous release that leads to an explosion occurs in a tank and the overpressure wave that a second unit receives as a result is higher than a certain threshold value, another release, instantaneous or continuous, depending on the magnitude of the wave will occur on the second tank, which might lead to more accidents occurring. The threshold values used for the model are presented in Table 5.1.

Because of their short duration, flash fires are not considered to have significant effects or consequences on other equipment, even though the radiation they emit might be high (also considered this way by Antonioni et al. (2009)).

Jet fires have been evaluated for domino potential according to their length and the thermal radiation they emit; if a jet fire impinges on a tank, the worst type of domino effect will occur, while if it does not touch the tank, but emits a certain amount of thermal radiation a lesser release will occur in the affected unit or the piping that surrounds it.

Overpressure thresholds have been decided by combining values presented in different literature sources (Antonioni et al., 2009; Khan and Abassi, 2011; Cozzani and Salzano, 2004a).

Table 5.1. Threshold values for damage associated to LOCs.

Accident	Effect	Threshold Values		Consequence
		Pressurized Tanks	Atmospheric Tanks	
BLEVE	**Thermal radiation (kW/m^2)**	≥ 100	≥ 100 (Antonioni et al., 2009)	G.3 type release
		< 100	< 100 (Antonioni et al., 2009)	No consequence
Explosion	**Overpressure wave (kPa)**	≥ 100	≥ 25 (Khan and Abassi, 2001)	G.1 type release
		53 < ΔP < 100 (Cozzani and Salzano, 2004b)	20 < ΔP < 25 (Cozzani and Salzano, 2004b)	G.2 type release
		30 ≤ ΔP < 53 (Cozzani and Salzano, 2004b)	14 ≤ ΔP < 20 (Cozzani and Salzano, 2004b)	G.3 type release
		ΔP < 30 (Antonioni et al., 2009)	ΔP < 14 (Cozzani and Salzano, 2004a)	No consequence
Jet fire	**Jet length (m) Heat Radiation (kW/m^2)**	dj ≥ d (Antonioni et al., 2009)	dj ≥ d (Antonioni et al., 2009)	G.1 type release
		dj < d & I ≥ 40 (Antonioni et al., 2009)	dj < d & I ≥ 10 (Antonioni et al., 2009)	G.3 type release
		dj < d & I < 40 (Antonioni et al., 2009)	dj < d & I < 10 (Antonioni et al., 2009)	No consequence
Flash fire	-	-	-	No consequence
Pool fire	**Thermal radiation (kW/m^2) Pool duration (min)**	dp ≥ d (Antonioni et al., 2009)	dp ≥ d (Antonioni et al., 2009)	G.1 type release
		60 ≤ I & tp ≥ 10 & dj < d (Landucci et al., 2009)	15 ≤ I & tp ≥ 10 & dj < d (Landucci et al., 2009)	G.2 type release
		I ≥ 8 & dj < d	I ≥ 8 & dj < d	G.3 type release
		I < 8 & dj < d	I < 8 & dj < d	No consequence

dj = jet length; dp = pool diameter; d = distance between tanks; tj = duration of jet fire; tp = duration of pool fire

Finding threshold values for failure due to the radiation emitted by a pool fire can be difficult; for this work, the only way in which a G.1 type release may occur due to a pool fire, is if the fire engulfs the affected unit, while it will suffer a G.2 LOC event if exposed to a certain radiation intensity during a certain amount of time (Cozzani and Salzano, 2004b); therefore, if tanks are in separate containment dikes, it will be almost impossible for a G.1 type release to occur in any of them due to an adjacent pool fire (tilting of the flame by wind effect is not considered). The value for the G.3 type release is the radiation

intensity at which domino effect may start occurring as specified in the Spanish legislation. It has to be said that different type of equipment might fail at different values, that threshold criteria can vary significantly according to different sources, and that this table presents only some guide values used in this work, but that can be changed when applying the methodology.

An example to illustrate the use of the shown threshold values is: if a pool fire occurs from a G.1 type release in a tank, and a surrounding pressurized unit receives the equivalent thermal dose to 60 kW/m^2 during 10 minutes, a G.2 release will occur; this might result in another one of the final events related to a G.2 type event in a pressurized unit, unleashing new accidents that can affect other equipment.

The domino sequences in this model are arranged as event trees in which the probabilities of accidents are dragged through every level, so that the next one will have a lower probability as more levels are generated; for example, if a G.3 release occurs in a tank, resulting from a G.1 release in another, the event tree of the G.3 scenario will incorporate the probabilities of the initial one, and the frequency of the first release.

When an accident down the domino sequence occurs with a probability lower than $1x10^{-8}$ it is no longer taken into account as a possible initiator of other accidents; in this way, the sequence may stop, even though not all units may have been affected. The sequences will be generated for each initial type of release, in each one of the units that are part of the study.

5.3.3. Calculation of final frequencies

Once all the domino sequences and the frequencies in each level for every unit and LOC have been defined, the frequencies for each accident according to the unit in which it occurs will be summed; for example, every time a flash fire occurs in a certain tank due to a specific release, the frequency associated to it will be registered, and at the end, summed

to obtain the final value associated to a flash fire in said tank. These are the final frequencies that will be introduced in the risk analysis software to obtain the iso-risk curves that take into account the possibility of domino effect.

5.4. Case studies

Three cases studies are presented, the first dealing with propylene and ethylene storage in two units; the second with a facility in which different types of oil derivatives are stored in six atmospheric tanks; the last deals with the oil storage terminal involved in the Buncefield fire (2005). Domino effect sequences for the cases are developed using the proposed method and the final frequencies are entered into RISKCURVES 7.6 to generate the iso-risk curves associated with the facilities. The curves are compared with those derived from traditional analysis. Hence, the potential impact of the domino effect on the curves and the risk associated with the plants can be determined.

The two first cases are treated in a different way than the third one; this is because they are not based in real accidents, although the layouts presented in them are real. As it deals with a real situation, the Buncefield case study has been approached from a different point of view, and therefore, different conclusions are obtained from it.

5.4.1. Propylene and ethylene storage plant

A facility in which ethylene and propylene are stored is evaluated. A total of 2.42×10^6 kg of propylene are stored in a refrigerated sphere of 5,450 m^3 and 4.71×10^6 kg of ethylene are stored in a vertical tank with a capacity of 9,775 m^3 at cryogenic and atmospheric conditions. Case conditions, the frequencies of initial LOCs, accident probabilities and the layout of the installation are presented in Table 5.2, Table 5.3 and Figure 5.2 respectively.

Table 5.2. Case study conditions.

Tank parameters		
	Tank1	**Tank 2**
Substance	Propylene	Ethylene
Type of tank	Pressurized/sphere	Atmospheric/vertical
Volume (m3)	5,450	9,775
Mass (kg)	2,424,700	4,718,500
Containment size (m)	38 x 38	58 x 65
Pressure (bar)	9.5	0.1
Temperature	271	170
Atmospheric conditions		
Temperature (K)	283.15	
Wind velocity (m/s)	4.5	

Table 5.3. Frequencies of accidents due to initial LOCs.

LOCs	**Frequency (y^{-1})**		**Accident**	**Probability of occurrence**	
	Tank 1	**Tank 2**		**Tank 1**	**Tank 2**
G.1	$5x10^{-7}$	$5x10^{-6}$	BLEVE	$2.45x10^{-2}$	0
			Explosion	$1.62x10^{-2}$	$1.2x10^{-2}$
			Flash fire	$4.05x10^{-2}$	$0.3x10^{-1}$
			Pool fire	0	$7.0x10^{-1}$
G.2	$5x10^{-7}$	$5x10^{-6}$	Explosion	$1.2x10^{-2}$	$1.2x10^{-2}$
			Flash fire	$0.3x10^{-1}$	$0.3x10^{-1}$
			Pool fire	$7.0x10^{-1}$	$7.0x10^{-1}$
G.3	$1x10^{-5}$	$1x10^{-4}$	Flash fire	$0.8x10^{-1}$	$0.8x10^{-1}$
			Pool fire	$2.0x10^{-1}$	$2.0x10^{-1}$

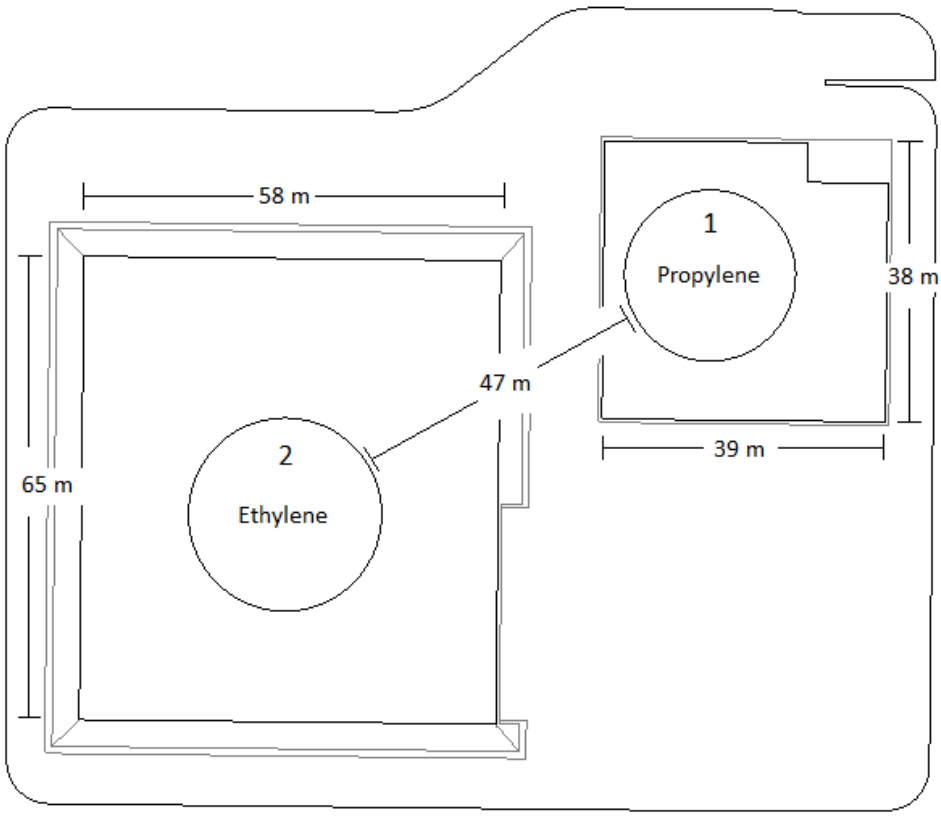


Figure 5.2.Layout of the installation.

The facility is equipped with a fire protection system (FPS) with a probability of failure on demand (PFD) of 5%. All the accidents triggered by a previous fire event have a 95% lower probability of occurrence. If a fire accident occurs in Tank 2, the FPS system in Tank 1 will start operating, and the probability of the domino effect occurring will decrease. Accident probabilities will be multiplied by 0.05 in cases preceded by an external fire. A reduction in the probabilities due to the FPS is not taken into account in initial accidents, as it will stop fires from developing, but not from starting. The FPS is only considered in initial accidents for events that can occur after the immediate ignition of contents spilled after a release, such as a BLEVE in Tank 1. For this case, domino

sequences are developed with and without the FPS, to compare the effect it has on the risk associated with the facility.

Domino sequences obtained using the model for the case of G.1 events in Tanks 1 and 2, with active FPS, are presented in Figure 5.3. When an instantaneous release occurs in Tank 1, a BLEVE, an explosion or a flash fire might occur. If a BLEVE happens, Tank 2 will suffer damage to its piping or structure that will lead to a release through a 10 mm hole (the fragment projection is not evaluated), which subsequently can develop into a pool or flash fire. If an explosion occurs after the G.1 release in Tank 1, Tank 2 will be severely damaged. This will lead to a G.1 release, which can then develop into another explosion, flash fire or pool fire. The sequences involved in the instantaneous release of the contents of Tank 2 can be described in a similar way.

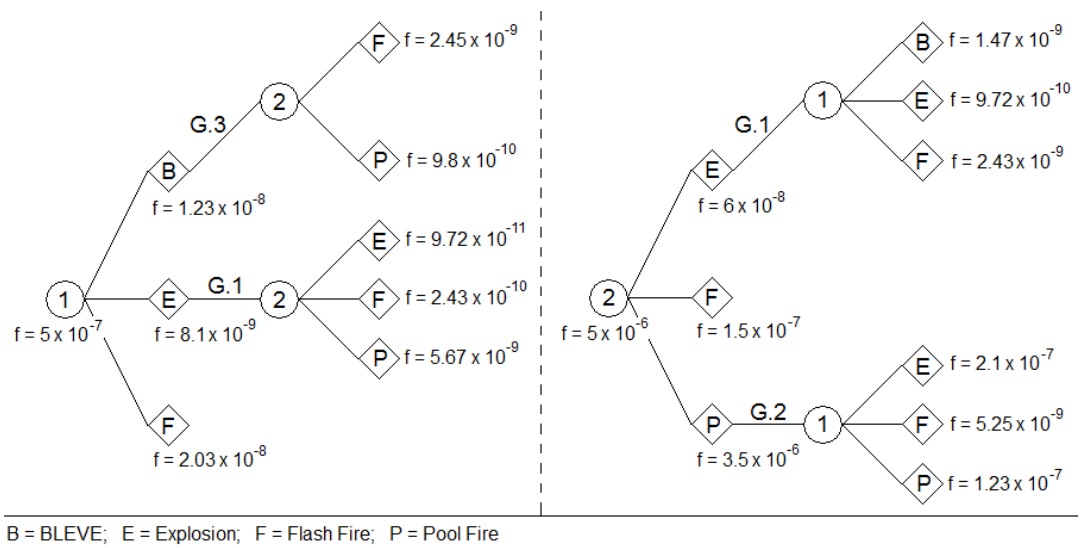


Figure 5.3.Domino sequences for the G.1 type release.

The final frequencies are shown in Table 5.4 Some accident frequencies increase significantly when the domino effect is taken into account and rise further when the FPS is not considered. The accident frequencies that are most affected by considering the domino effect are those associated with G.1 and G.2 releases in Tank 1. Explosions are the

accident that is most affected by both LOCs. This could be due to various factors. First, the proximity of the tanks means that if an accident occurs in one of them, the other will probably be majorly affected. This explains why the frequencies of G.3 derived accidents do not increase for Tank 1. The second factor is that Tank 2 is cryogenic, and therefore has initial accident frequencies that are one order of magnitude higher than those of Tank 1. Frequencies resulting from accidents caused by the domino effect in this unit are insignificant compared to those of the initial accidents. Nevertheless, there is an increase in accident frequencies, which is not appreciable because of the difference in initial accident frequencies between pressurized and cryogenic storage. This also works in the opposite direction, resulting in a very significant increase in the frequencies for Tank 1 because the rate of accident frequency in Tank 2 is higher, and now influences and causes accidents in the other unit.

Table 5.4. Final frequencies for case study 1.

LOCs	Accident	Frequency (y^{-1}) No domino effect		Frequency (y^{-1}) Domino effect and FPS		Frequency (y^{-1}) Domino effect and no FPS	
		Tank 1	Tank 2	Tank 1	Tank 2	Tank 1	Tank 2
G.1	BLEVE	$1.23x10^{-8}$	0	$1.52x10^{-8}$	0	$3.03x10^{-7}$	0
	Explosion	$8.10x10^{-9}$	$6.00x10^{-8}$	$1.00x10^{-8}$	$6.02x10^{-8}$	$5.90x10^{-8}$	$6.06x10^{-8}$
	Flash fire	$2.03x10^{-8}$	$1.50x10^{-7}$	$2.51x10^{-8}$	$1.50x10^{-7}$	$1.48x10^{-7}$	$1.52x10^{-7}$
	Pool fire	0	$3.50x10^{-6}$	0	$3.51x10^{-6}$	0	$3.54x10^{-6}$
G.2	Explosion	$6.00x10^{-9}$	$6.00x10^{-8}$	$1.02x10^{-8}$	$6.02x10^{-8}$	$9.00x10^{-8}$	$6.42x10^{-8}$
	Flash fire	$1.50x10^{-8}$	$1.50x10^{-7}$	$2.55x10^{-8}$	$1.51x10^{-7}$	$2.25x10^{-7}$	$1.61x10^{-7}$
	Pool fire	$3.50x10^{-7}$	$3.50x10^{-6}$	$5.95x10^{-7}$	$3.51x10^{-6}$	$5.25x10^{-6}$	$3.74x10^{-6}$
G.3	Flash fire	$8.00x10^{-7}$	$8.00x10^{-6}$	$8.00x10^{-7}$	$8.00x10^{-6}$	$8.00x10^{-7}$	$8.04x10^{-6}$
	Pool fire	$2.00x10^{-6}$	$2.00x10^{-5}$	$2.00x10^{-6}$	$2.00x10^{-5}$	$2.00x10^{-6}$	$2.01x10^{-5}$

The effect of the FPS is more significant in Tank 1 and reduces the frequency of accidents by almost one order of magnitude for every G.1 and G.2 accident, except the explosions. However, the FPS does not have a significant effect on the frequencies for Tank 2. This is an interesting result, as it reflects the design intention of the FPS for the propylene sphere, which is to cool it in the case of external fire, preventing the occurrence

of a BLEVE or another kind of explosion. The FPS does not seem to be very important for the ethylene tank because it is not taken into account in calculations of the frequencies of initial events, which are the most important for the final frequency calculation. Therefore, removing the FPS has no real impact on the case study results for this tank, although it would have an effect on the real facility.

The way in which frequency increases from the initial scenario, in which no domino effect is considered, to the others (in which the domino effect is taken into account with and without the FPS) has been calculated for each accident in each tank. Final frequencies are divided by those of the initial scenario for each tank and accident. The results are presented in Figure 5.4 as a bar chart, so that the increments can be observed clearly; it shows that for Tank 1, the increment in frequencies between Scenarios 1 and 2 ranges from a 20% increase for G.1 accidents to almost a 50% rise for G.2 events, with no variation in G.3 release. There are significant differences between the third scenario and the other two for the G.1 and G.2 releases.

The BLEVE frequency increases by a factor of approximately 25, the G.2 accidents by a factor of 15, and the G.1 explosion and flash fire by a factor of 7.

An interesting result that cannot be determined easily by analyzing Table 5.4 is that apart from the BLEVE in Scenario 3, all the accident frequencies are increased by very similar factors depending on the type of initial release. This can be better explained in the second case study, though it could be said that the frequency of BLEVE in Scenario 3 behaves in a different manner because the branches of the event trees associated with it vary in a special way that is different to that of other accidents. The frequencies do not vary significantly for Tank 2, due to the factors explained before.

The iso-risk curves for the case study can be produced by entering the new frequencies obtained by the method into RISKCURVES 7.6 for the same accidents that

were studied in the original QRA. The curves for the scenarios are presented in Figure 5.5, Figure 5.6 and Figure 5.7.

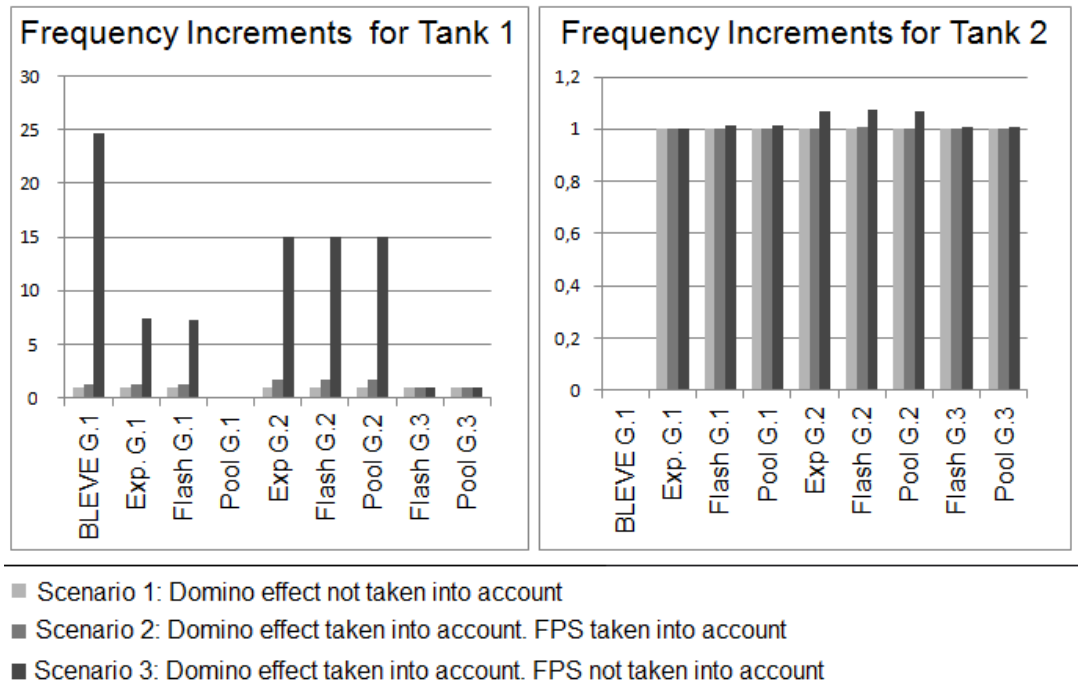


Figure 5.4.Frequency increments.

Figure 5.5 shows a difference between the risks that each scenario represents. However, the difference is not significant for this level of risk, as the increment in the distance between the curves is some 30 m at most.

Figure 5.6 presents a very different outcome, in which the variation between the results of the common QRA procedure and those obtained using the domino effect model is minimal, unless comparisons are made with the curve obtained for the domino effect without the FPS. In this case, the variance between the results is dramatic. This is crucial when we consider that the probability of safety measures such as an FPS failing may increase due to the chain of accidents in a domino effect, leading to a dangerous situation for which there is no protection. Consequently, safety measures in process plants should be

designed to withstand major accidents, so that they are also effective in the event of a domino effect.

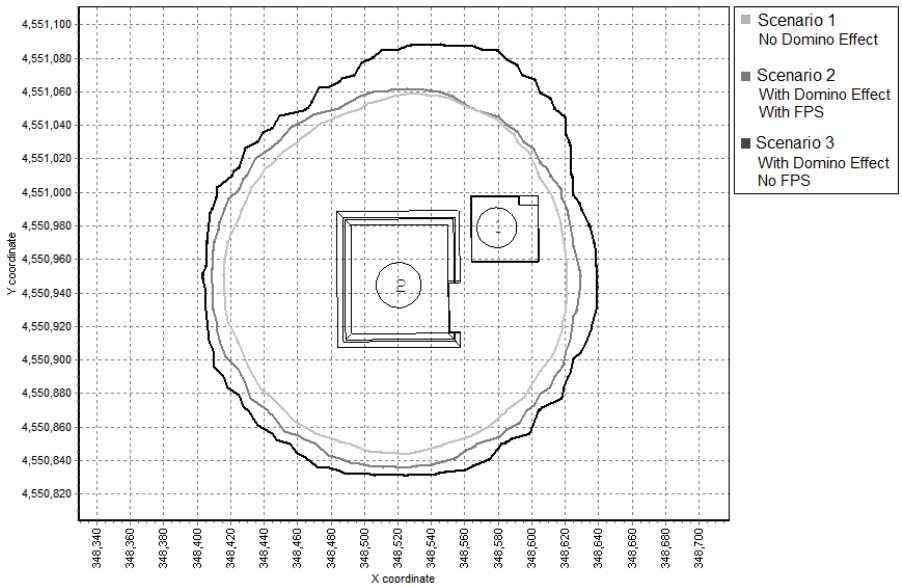


Figure 5.5. 1x10^{-6} iso-risk curves for case study 1.

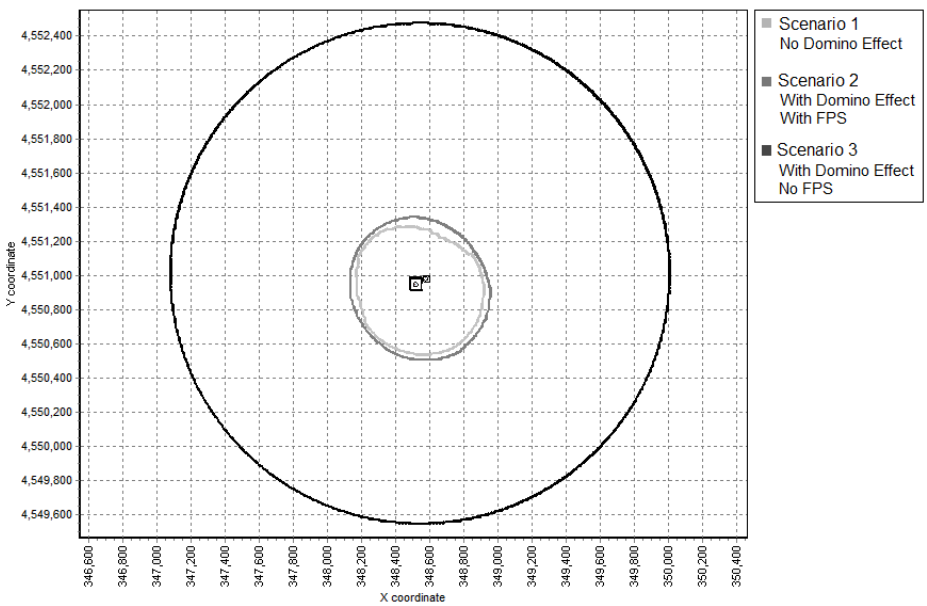


Figure 5.6. 1x10^{-7} iso-risk curves for case study 1.

A comparison of the three scenarios reveals considerable differences in the $1x10^{-8}$ curve. The difference between the first two is 100 m, while the curve for the third scenario is at a distance of approximately 600 m from the second one. Once again, the major difference appears when the domino effect is taken into account without the protection of the FPS.

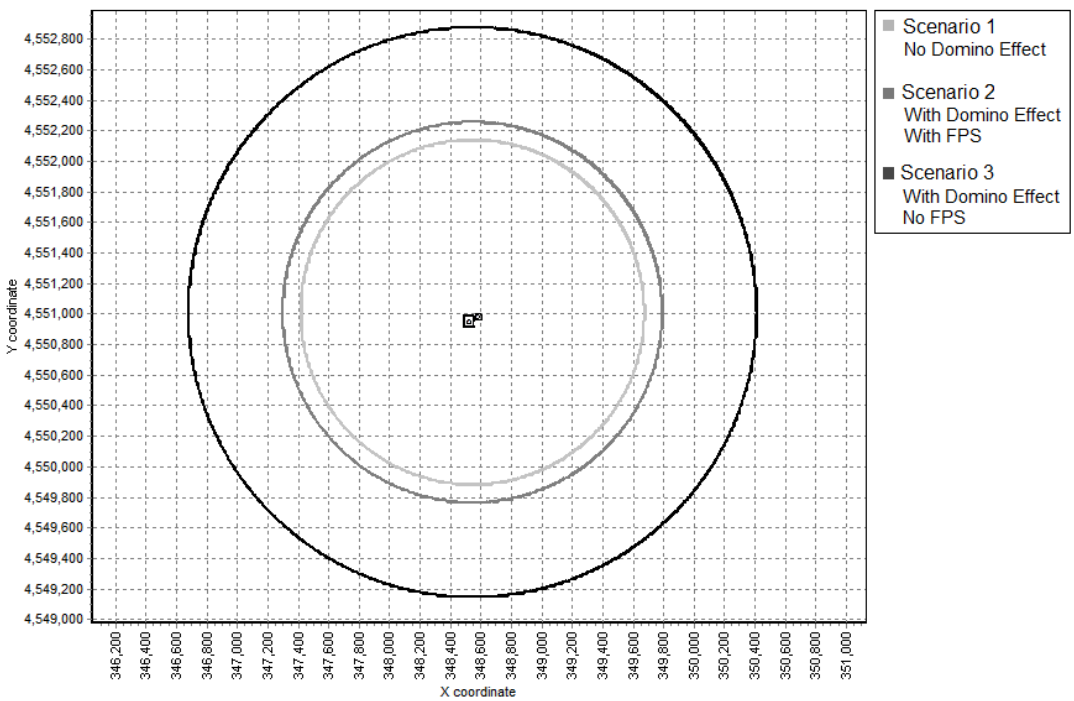


Figure 5.7. $1x10^{-8}$ iso-risk curves for case study 1.

Figure 5.8 shows the comparison of f-N societal risk curves for each of the scenarios. It can be seen that only the frequency factor of the curves is altered. This point is further discussed in Section 5.4.3

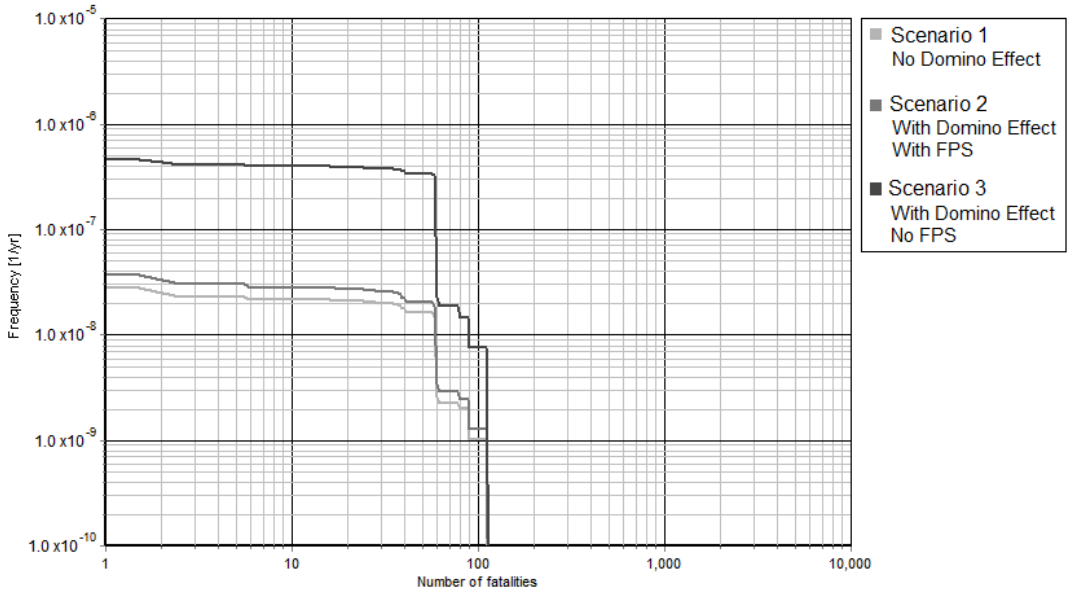


Figure 5.8. f-N curves for case study 1.

5.4.2. Gasoline and naphtha storage plant

Oil-derived products are stored in six floating roof tanks. Tanks 1 and 2 are used for naphtha, while 3–6 store gasoline. The layout of the plant is shown in Figure 5.9.

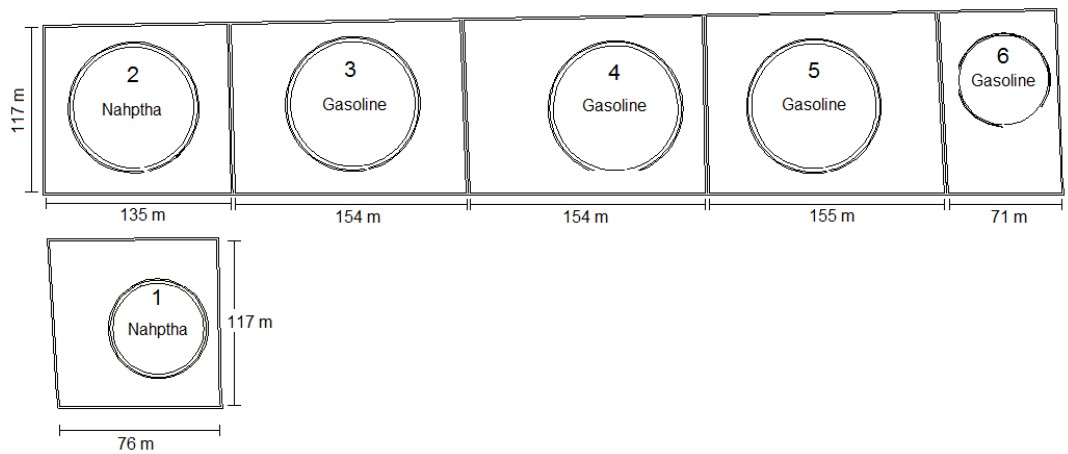


Figure 5.9. Layout of oil storage installation.

All containment dikes can hold the total amount of mass stored in each tank. The facility is equipped with an FPS similar to that in the facility presented in Case 1, with a PFD of 5%.

Naphtha and gasoline will be modeled as n-pentane in this case. The storage and atmospheric conditions are shown in Table 5.5, the distances between tanks in Table 5.6, and the frequencies of LOCs and probabilities of accidents due to initial LOCs or after a fire accident in Table 5.7.

Table 5.5. Case study conditions.

Parameter	Tank					
	1	2	3	4	5	6
Type of tank	Floating roof					
Mass (kg)	$3.17x10^7$	$7.25x10^7$	$8.77x10^7$	$8.75x10^7$	$8.31x10^7$	$3.72x10^7$
Containment size (m)	117 x 76	117 x 135	117x154	117x154	117x155	117x71
Pressure (bar)	1.01					
Temperature (K)	288.15					
Wind velocity (m/s)	4.5					

Table 5.6. Distances between tank shells (m).

Tank	6	5	4	3	2
1	539	395	300	138	78
2	519	367	239	59	
3	368	217	90		
4	190	38			
5	63				

Table 5.7. Frequencies of accidents due to initial LOCs.

LOCs	Frequency of LOC ($year^{-1}$)	Accident	Probability of occurrence	
			With FPS	Without FPS
G.1	$5x10^{-6}$	Explosion	$1.87x10^{-3}$	$3.74x10^{-2}$
		Flash fire	$4.68x10^{-3}$	$9.35x10^{-2}$
		Pool fire	$3.25x10^{-3}$	$6.50x10^{-2}$
G.2	$5x10^{-6}$	Explosion	$1.87x10^{-3}$	$3.74x10^{-2}$
		Flash fire	$4.68x10^{-3}$	$9.35x10^{-2}$
		Pool fire	$3.25x10^{-3}$	$6.50x10^{-2}$
G.3	$1x10^{-4}$	Flash fire	$4.68x10^{-3}$	$9.35x10^{-2}$
		Pool fire	$3.25x10^{-3}$	$6.50x10^{-2}$

Since the substances have similar properties and the tanks are similar and protected equally, the frequencies and probabilities will be identical for every tank.

The method was applied to the case and the domino sequences were developed. The final frequencies found are shown in Table 5.8. The case was solved with and without taking into account the FPS, to study the effect that its presence can have on accident frequencies. The domino sequence tree for the case of a G.1 LOC event in Tank 2 is shown in Figure 5.10, as a representative tree for this case.

Table 5.8. Final frequencies for the second case study.

Domino effect	Tank	G.1			G.2			G.3	
		Exp.	Flash	Pool	Exp.	Flash	Pool	Flash	Pool
fx10^7 (y^{-1}) No domino	**All**	1.87	4.68	3.25	1.87	4.68	3.25	93.5	65
fx10^7 (y^{-1}) with domino effect and FPS	**1**	2.28	5.72	3.97	1.96	4.91	3.41	93.6	65.2
	2	2.35	5.89	4.10	2.03	5.08	3.53	93.5	65.0
	3	2.42	6.07	4.22	1.91	4.79	3.33	93.6	65.1
	4	2.14	5.37	3.73	2.17	5.43	3.78	94.2	65.5
	5	2.28	5.72	3.97	1.90	4.77	3.31	93.5	65.0
	6	2.21	5.54	3.85	2.03	5.08	3.53	93.5	65.0
fx10^7 (y^{-1}) with domino effect and no FPS	**1**	2.29	5.74	3.99	2.49	6.23	4.33	93.6	65.1
	2	2.38	5.96	4.14	2.53	6.33	4.40	94.7	65.8
	3	2.43	6.09	4.23	2.87	7.17	4.99	93.5	65.0
	4	2.17	5.44	3.78	2.71	6.79	4.72	96.0	66.7
	5	2.30	5.76	4.01	2.66	6.65	4.62	93.5	65.0
	6	2.24	5.61	3.90	2.53	6.32	4.39	93.5	65.0

All evaluated units are alike and contain similar substances, so there are no issues related to differences in initial release frequency, as in the first case. Accident frequencies increase when the domino effect is taken into account, though not dramatically. As in Case 1, the increase in frequencies is equal for all accidents caused by a common release type, so instead of stating that the frequency of the G.1 explosion in a unit increases by a certain factor, it could be said that the frequencies of G.1 derived accidents increase by a factor; this increase is the value obtained by dividing the new frequency by that in which no domino effect is considered.

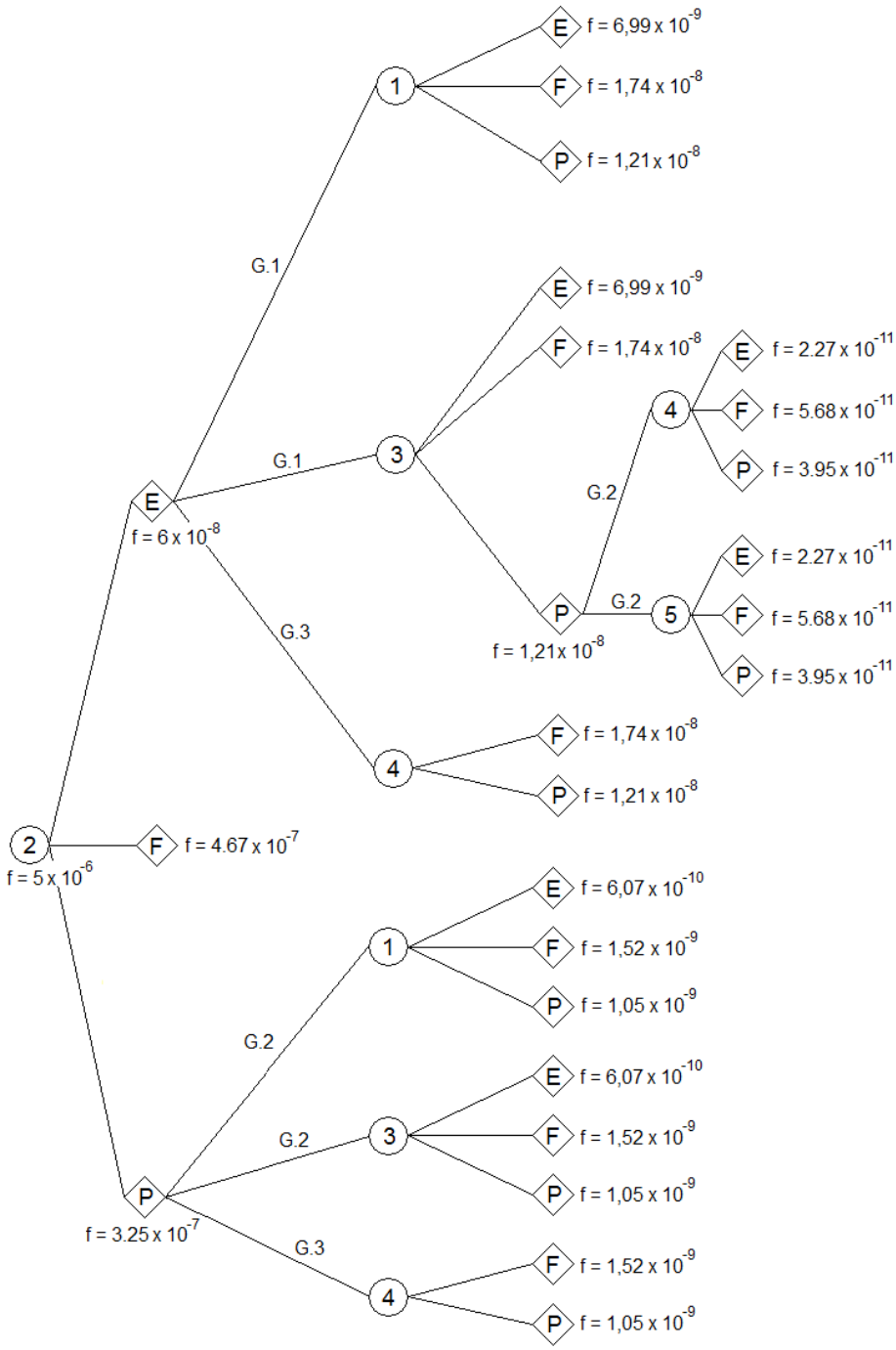


Figure 5.10. Domino effect sequences for G.1 release in Tank 2.

Figure 5.11 shows frequency increments for all tanks and types of releases for the scenarios considered in this case, compared with the original values in which no domino effect is considered. Frequency increments are equal for different accidents derived from the same LOC event because the domino effect in this model generates other releases in other units, which can then develop into accidents with a defined probability from the same point of origin. Therefore, increases in frequencies are really associated with different types of releases, and not with the accidents that can occur subsequently.

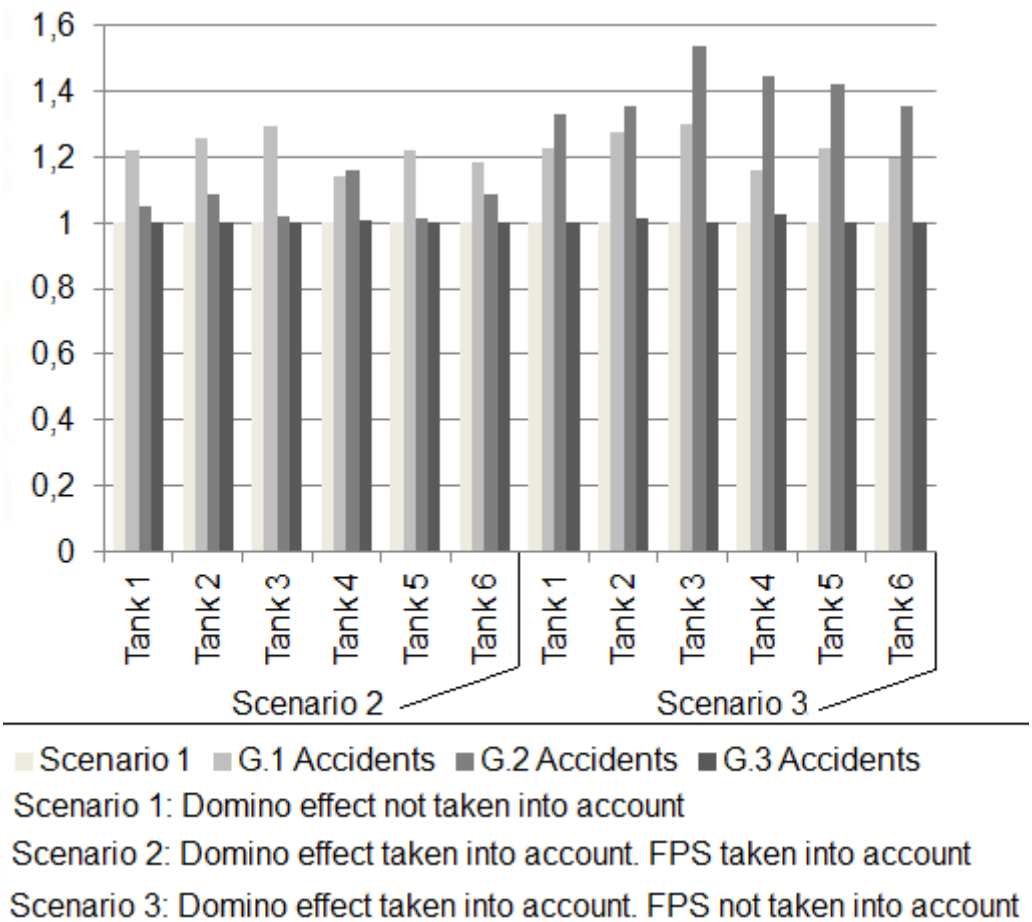


Figure 5.11. Frequency increments for case 2.

For the scenario in which the FPS is considered, the frequencies of G.1 accidents increase by a range of 18% to 30%, the frequencies of G.2 by a range of 5% to 16% and the increase in G.3 accident frequencies is almost negligible. In this facility, few G.3 accidents occur due to the domino effect. When the FPS is not considered, G.1 accident frequencies do not increase significantly, as the layout, model and the selected threshold values only allow for this type of release to be caused by explosions, which cannot initially be remediated through the use of a FPS. Subsequent explosions will be less likely if the FPS is active, but only those generated by fire accidents in other units. In total, these do not have as great an impact on the overall frequency increment as accidents preceded by other explosions. In contrast, the frequencies of G.2 accidents do increase considerably (from 30% to 50%) when the FPS is not considered, as G.1 and G.2 derived pool fires in this facility will normally lead to G.2 type releases in surrounding units. The frequencies of G.3 accidents are not affected, as they do not increase when the domino effect is accounted for.

Frequencies in Scenario 2 increase from Tanks 1 to 3, decrease for 4, climb again for 5 and drop for 6. For Scenario 3, the frequencies increase from Tanks 1 to 3 and then decrease from 4 to 6. These values are influenced by the tank positions, the amount of product stored, the sizes of containment dikes and other variables inherent to the design. If the facility had a different design, for example with tanks sharing containment dikes, the results would vary greatly.

The same process as in Case 1 is followed to obtain iso-risk curves. There are no significant differences between the curves obtained for this case, as the frequencies do not increase by at least an order of magnitude for any of the accidents, which makes it difficult to appreciate discrepancies in the curves. These are shown in Figure 5.12. For this case study, there was no population in the vicinity of the facility, so the f–N curves do not show any information.

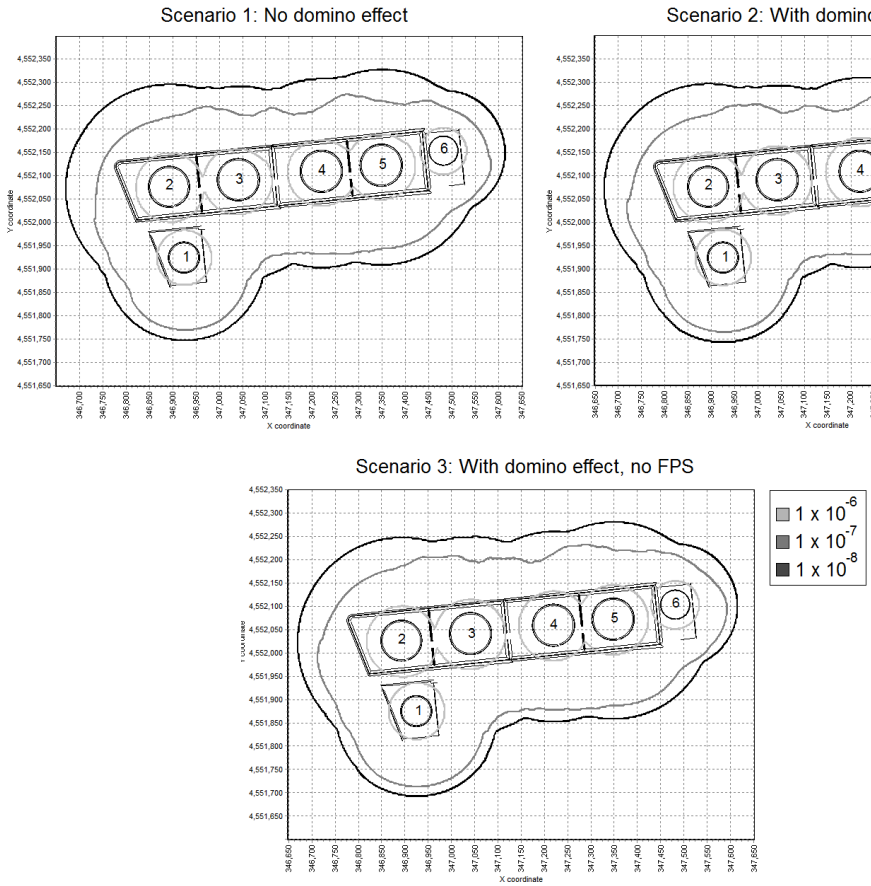


Figure 5.12. Iso-risk curves for case study 2.

5.4.3. Discussion of the two first case studies

For the cases studied the frequencies of G.1 accidents, when the facilities have the appropriate safety systems, increase by a maximum of 30% if the domino effect is taken into account depending on the type of units. The frequencies of accidents derived from G.2 releases can increase by up to 70% for the pressurized sphere in Case 1, but by an average of 14% when both cases are taken into account. The frequencies of G.3 related accidents show no change for the cases studied. These frequency increments are significant, but are well within the parameter used to include the domino effect in QRA in Spain, which is to multiply the frequencies of accidents by a factor of 2 (an increment of 100%).

The method suggests that a well-designed FPS, with a low PFD, can significantly decrease the probability of domino effect occurrence, especially for BLEVE scenarios in pressurized tanks and for accidents caused by pool fires. This has been proven in real facilities many times; however, it is clear that safety measures must be designed to withstand major accidents, so that they can prevent the escalation of the domino effect. If a facility's safety measures do not operate when necessary, the probability of more accidents occurring increases dramatically, as does the risk associated with the facility.

Pressurized containers should not be placed in the same area as atmospheric or cryogenic ones, as they have different failure rates. Accidents occur more frequently in atmospheric tanks than in pressurized ones, therefore, it is a hazard for pressurized units to be placed near atmospheric tanks. As with the FPS, this is a known fact, and pressurized tanks are normally placed apart from other types of containers, as much to protect pressurized containers from the others, as to protect others from the fragments that might be projected if an explosion occurs in the pressurized unit.

An important issue is the impact of the methodology on individual and societal risk. Individual risk increases when the method is applied, as can be seen in the iso-risk curves. This is due to the fact that the probability of a person in the vicinity of the facility dying as a consequence of a possible accident will rise as the frequencies of the different accidents increase. Societal risk will be affected in a different way; the application of the method does not take into account the fact that the occurrence of the domino effect may trigger accidents that could have more serious consequences than those that are part of the traditional QRA; therefore, the maximum number of deaths obtained in the original QRA will be maintained when the methodology is applied, even though the frequencies of the accidents may increase. Only the frequency factor of societal risk will change, which will mean that the ratio between frequencies and numbers of death will also be altered, as shown in Figure 5.8.

For the overall number of fatal victims to vary, new scenarios with more severe accidents than those originally presented would have to be defined. This implies a fundamental change in the method's approach, as it is designed to use the same scenarios as those defined during the QRA to introduce the domino effect without incurring the greater time and resource costs that the creation of new scenarios would imply. Another problem would be the uncertainty in these calculations. For example, it would be difficult to predict how two or more different releases would behave in the event of one of them igniting or if the overlapping of two simultaneous accidents would result in more serious consequences. These are the reasons why the methodology is performed with the accidents that would appear in a regular QRA.

The main advantage of the model is that it can include, or account for, the possibility of a domino effect in the calculations performed during the QRA of storage facilities. The model is easy to use and little time is needed to correct the accident frequencies and reevaluate the risk. This is because it has been devised to work in the same systematic order as a QRA. It can be applied to a facility by performing a new QRA or by using the information produced by previous assessments. Another advantage is that it is a very adaptable tool, which could be modified in different ways depending on the type of equipment, the threshold values for equipment failure, the way of developing the event trees or the accident frequencies. Thus, it can be adapted to diverse perspectives and requirements.

On the downside, the method is constrained by the inherent complexity of the domino effect phenomenon and QRA. It has been developed on the basis of some simplifications (those used in the thesis), for example, explosions or flashes are modeled as generated in the tank that suffers the release (possible ignition points are not taken into account). If an accident is caused by an adjacent fire, the probability of immediate ignition will generally be higher than that used in the model. However, this could be addressed

easily if data were available, by developing event trees with new probabilities and changing the frequencies of accidents caused by fire.

Finally, a comparison can be made between the results presented in these cases and those obtained by other authors, such as Cozzani and Abassi. However, this comparison is only superficial, as the methodologies vary in their treatment of sequences and accidents, and the case studies can be very different in scope. Nevertheless, the results from all the methods clearly show that the domino effect has a significant impact on the risk associated with a facility and should be considered when risk analysis studies are carried out.

5.4.4. The domino effect model applied to the Buncefield oil storage terminal

On December 11, 2005, a series of explosions occurred at the Buncefield Oil Storage Terminal, located in Hemel Hempstead, Hertfordshire, England. The explosions resulted in large fires which spread throughout the installation, causing more than 40 injuries, the destruction of most of the installation and the emission of large clouds of black smoke to the atmosphere; the accident also caused significant damage to residential and commercial properties in the vicinity of the terminal, the evacuation of population centers near the terminal, and an overall economic loss estimated at close to £ 1 billion (The Final Report of the Major Investigation Board, 2008).

The Buncefield disaster is a perfect example of domino effect in the oil industry; the initial explosion, which was caused due to the overflow of one of the tanks in the installation and the subsequent formation and ignition of a flammable cloud, caused fires that engulfed more than 20 storage tanks in the terminal, and resulted in the destruction of a significant part of the facility.

One of the characteristics that made this accident the object of many researches, was that the overpressure wave ensuing from the first explosion was much higher than would be expected from a VCE; however, the aim of this case is not to model the exact explosion

that occurred or to determine the reasons that caused the overpressure resulting of the initial explosion to be higher than expected, as much works have been dedicated to this endeavor, producing satisfactory conclusions to the phenomenon. The objective of this case study is rather to use the Buncefield Terminal layout to test the domino effect model, simulating possible accident sequences after an explosion to ascertain if they are similar to the chain of accidents that took place during the real event; also, QRAs will be performed using the layout, one in a traditional fashion (CPR18E, 2005) and without taking domino effect into account, and another taking domino effect into account through the application of the proposed model, to analyze the change in the iso-risk curves obtained for both QRAs.

5.4.4.1. Description of the accident

A brief abstract of the incident as described in Volume 1 of The Final Report of the Major Incident Investigation Board (2008) is presented next. Figure 5.13 and Figure 5.14 show the facility before and after the accident, respectively.

Figure 5.13. State of the terminal before the accident (The final report of the Major Incident Investigation Board, Volume 1).

On Saturday 10, December 2005, a delivery of unleaded petrol started to arrive at Tank 912 in bund A. At about 05:30 on 11 December, the safety systems that prevented the overfilling of the tank failed to operate. Petrol cascaded down the side of the tank and was collected in Bund A. As the released continued, a vapor cloud mixture of fuel and vapor was formed and started dispersing westwards. Up to 300 tons of petrol were released, and about 10% turned to vapor and mixed with air, eventually reaching dangerous concentrations. At 6:01 on Sunday 11, December 2005, the first, in a chain of explosions, occurred. The explosions caused a huge fire which engulfed more than 20 tanks and burned for 5 days, destroying great part of the terminal.

Figure 5.14. State of the terminal after the accident (The final report of the Major Incident Investigation Board, Volume 1).

5.4.4.2. Modeling the installation

To model the installation, the "Google Maps" tool was used to view the current state of the terminal and obtain measures similar to those of the tanks that were destroyed and of those that are still standing; the distances between the tanks and the dimensions of the containment bunds were also estimated. Figure 5.15 shows, on top, the latest image found of the state of the installation and on the bottom, the distances and dimensions used to model the installation. After estimating the dimensions of the installation, the tanks and bunds were renumbered for the application of the model; for example, Tank 912 becomes Tank 3, and Bund A is called C2.

5.4.4.3. Approaches to accident modeling

The vapor cloud that resulted in the explosion in the Buncefield Terminal is thought to have ignited at the emergency pump house located close to the containment bund in which Tank 912 was located, as shown in Figure 5.15. Since the domino effect model works by going through a fixed set of possible accidents in each of the tanks, the approach followed to produce the accident sequences was to define a fictional "Number 30" tank in the area in which the ignition of the flammable cloud is thought to have occurred, containing a mass close to 150,000 kg of pentane.

This approach was followed to produce the accident sequence, but not to develop the QRAs, which will be completed using the layout proposed in Figure 5.15, with all the tanks filled at full capacity.

5.4.4.4. Accident sequence

Figure 5.16 shows the most probable incidents in the sequence produced when the domino effect method is applied to the case of an explosion derived from a G.2 type release in Tank 30, which is the fictional tank created to model the initial explosion.

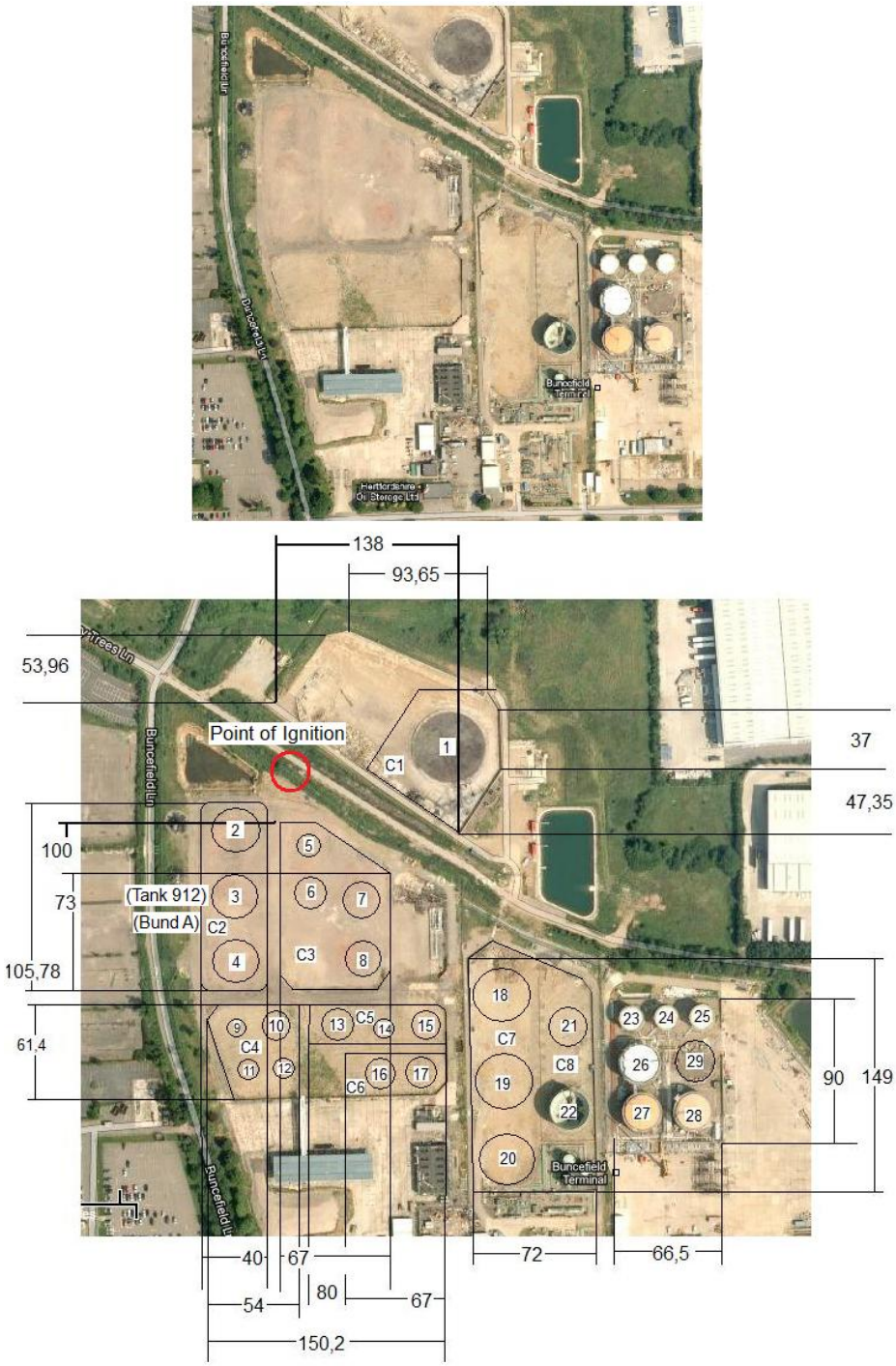


Figure 5.15. Current state of the terminal and layout used.

The tanks are represented inside circles, while the possible accidents are shown inside diamonds (E stands for explosion, P for pool fire). The lines generated in the accident diamonds represent the level of damage caused by an event; these lines later divide, reaching different tanks, which means that the tank suffers the associated type of release after the previous incident. All the lines shown in the figure represent possible accidents identified by the methodology. The continuous lines represent the most probable accidents, which derive in the destruction or heavy damage of the affected unit. The dotted lines represent accidents that do not cause catastrophic damages, or that are less probable; however, they are presented to show other possible scenarios produced when applying the algorithm. Once a tank is reached by a continuous line, it means that it has suffered a level of damage which will result in its destruction.

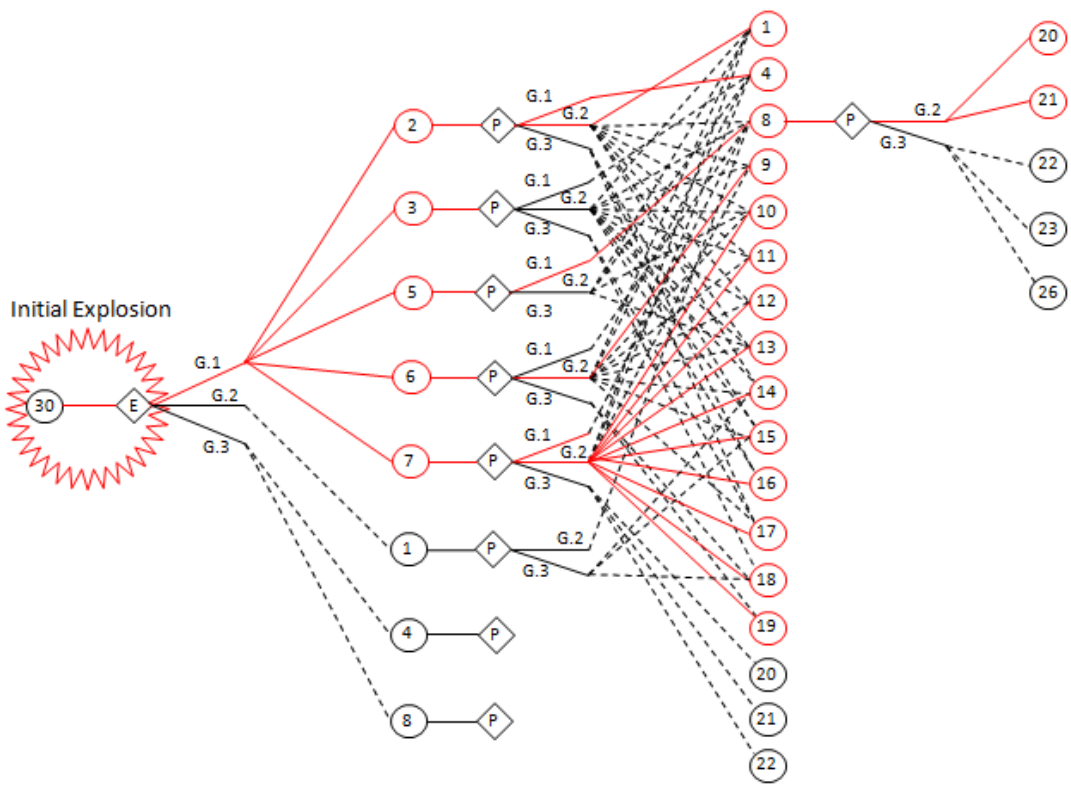


Figure 5.16. Accident sequence developed using the domino effect model.

When the explosion after the continuous release of the complete contents of tank 30 occurs, the overpressure wave affects tanks 2, 3, 5, 6 and 7 in a catastrophic way, tank 1 suffers damages that lead to a G.2 release and tanks 4 and 8 are affected in a minor way. This is the first sequence of accidents, and it is understood that the failures and later releases occur almost simultaneously. After the mentioned tanks fail due to the explosion, other accidents will generate in each of them, specifically, explosions, flash fires or pool fires; since these last type of accident will be the most probable one (according to the event trees used to produce the sequences), it will be shown for each of the affected tanks.

In the case that a pool fire occurs in Tank 2, Tank 4 will fail catastrophically due to the thermal radiation load it receives, while Tank 1 will also be affected in a major way, and also fail. There are other affected tanks, but these possible paths are not explored in detail here. It has to be noted that by the time Tank 2 fails, Tank 3 is also failing. A catastrophic failure in Tank 3 would also result in a pool fire that would further the chain of accidents, but none of these occurrences is explored. Pool fires in tanks 5, 6 and 7 would, according to some paths of the sequence obtained, result in the failure, and grievous damage of tanks 8 through 19. If the sequence is furthered following a pool fire in Tank 8, tanks 20 and 21 would be damaged beyond repair, while tanks 22, 23 and 26 would suffer minor damages. It has to be noted that in the sequence explored, tanks 24, 25, 27, 28 and 29 do not suffer damages.

The sequence of accidents explored, which is the one that presented higher frequencies in each of its events, results in the destruction of 21 out of the 29 tanks that are part of the installation, which is in accordance to the level of damage in the real Buncefield terminal after the situations resulting from the explosion were controlled. It has to be said that this is one of many possible sequences produced by the algorithm, several of which are different from the real occurrence; however, branches of the possible sequences could be trimmed, in order to choose occurrences that are deemed to be possible.

5.4.4.5. Application to QRA

Two QRAs were performed using the layout presented in Figure 5.15, the first using the normal procedure, and the regular frequencies obtained from the original LOCs and the event trees; the second, using the frequencies of accident obtained from applying the domino effect model. The iso-risk curves obtained for the studies are presented in Figure 5.17 and Figure 5.18.

Figure 5.17. Regular iso-risk curves.

It is clear when observing the figures presented above, that the individual risk associated to the installation increases when the domino effect methodology is applied. When regular frequencies are used, only 10^{-5} and 10^{-6} curves appear, while a 10^{-4} curve appears when using the modified frequencies, encompassing the complete layout of the installation, and in some points, extending some 80 m from the limits of the terminal. The

10^{-4} increases it size so much because many lesser accidents with low frequencies appear in the accident sequences generated by the algorithm. The 10^{-5} curve also increases its area significantly, growing to the point of covering the complete evaluated installation, and reaching close to a 100 m from the limit of the terminal on its furthest point. The 10^{-6} curve is the one that presents a less appreciable change; to the north of the installation the curve suffers almost no alteration, to the south, it increases its length some 30 m and to the east and west, it increases some 20 m in each direction.

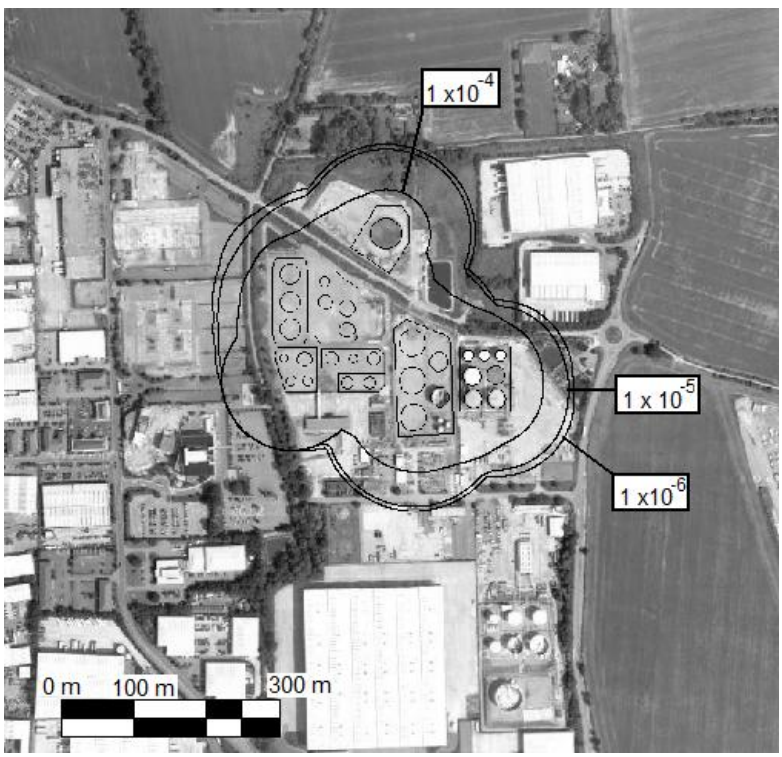


Figure 5.18. Iso-risk curves accounting for domino effect.

It is interesting to note that when performing a QRA of a storage installation composed of atmospheric tanks, the accidents with highest frequencies of occurrence are the pool fires, followed by flash fires and at the last, by explosions. This means that the iso-risk curves related to the type of installation studied will not extend over great distances, as occurs when evaluating installations that store pressurized flammable liquids

or toxic gases. Therefore, although the increase in the 10^{-6} curve, which, in many European countries is the most representative at the moment of evaluating external affectation, seems marginal, it is important, due to the type of installation that has been evaluated.

5.4.4.6. Conclusions of the Buncefied case study

The domino effect model applied to a layout similar to that of the old Buncefield terminal produced many accident sequences, one of which is thought to be similar to the real accident that occurred in the facility in 2005. This means that the model is indeed suitable to be applied on real layouts, and that it can be used to help assess the risk related to a projected or existing installation, taking into account the possibility of domino effect occurrence.

An increase in the risk associated to the installation was observed when the domino effect frequencies were used, in contrast to the results obtained when the regular QRA methodology was applied. The10^{-6} curve does not suffer a significant increase in size due to the nature of the installation and its equipment.

5.5. Chapter conclusions

Domino effect has occurred in some of the worst accidents in the history of the process industry. This effect has a significant impact on the risk associated with storage facilities; however, it can be avoided or mitigated up to a point by applying correct design criteria and implementing safety measures such as fire protection systems that are reliable and can cope with the worst-case accident scenarios.

The method developed during this thesis can be applied rapidly to different types of storage facilities. Less time is required than that needed to perform the complete QRA. As in real life, the results obtained with the method vary considerably depending on the type and design of the facility.

According to the method described in this paper, accident frequencies can vary considerably if the domino effect is taken into account during a QRA. However, this effect can be mitigated by an appropriate facility design and reliable safety measures on site.

The method allows variations in accident frequencies to be introduced easily into QRA calculations, without increasing the time needed to perform the study.

CHAPTER 6. INCLUDING ISD AND DOMINO EFFECT. THE FINAL OPTIMIZATION METHODOLOGY

Once a method to model the domino effect in storage terminals has been developed, it can be combined with the algorithm (Figure 4.1) of the initial optimization methodology proposed in CHAPTER 4. In this way, the optimization will be able to use more decision variables, becoming a more powerful tool; among these new variables are the layout of the installation and the technology used. In order to produce better designs and make the optimization more effective, the strategies of ISD can be applied, so that safer technologies and layouts are chosen from the beginning of the design process.

Next, a proposal for the application of ISD strategies to storage terminals is explained, followed by the presentation of the final algorithms for the design optimization of storage facilities. Finally, the methodology is applied to different types of installations in some case studies. One of these examples is based on the LPG storage terminal in which the San Juanico tragedy (Mexico, 1984) occurred; this particular case will be crucial at the moment of demonstrating that the methodology developed can be used to optimize the design of a storage facility, while minimizing the risk associated to it.

6.1. Application of ISD strategies to storage installations

The four current ISD strategies (substitution, minimization, moderation and simplification) have been observed from the unique perspective of storage installations and of the proposed optimization, in order to make it possible to integrate them into the methodology.

6.1.1. Substitute

The proposed method is supposed to be used in storage installations, in which it is absolutely necessary to keep a specific substance, making it impossible to use the substitution approach in regards to the chemicals used in the process. Yet, the method does have a way in which this strategy might be used, and that is technology substitution, changing the way in which the substance is stored; for example, when storing Liquefied Petroleum Gas (LPG) it may be decided, depending on the quantity, to store it in a pressurized above ground sphere or in an mounded bullet, which would reduce the risk of BLEVE, making this design inherently safer from this point of view.

6.1.2. Minimize

Once again, minimization of the quantity of substance is not possible, as the method is applied on storage installations that are required to have a fixed maximum capacity. One of the variables of the function used to minimize risk is the number of tanks present in the plant; when the mass stored is fixed, increasing the number of tanks means that each one of them will be smaller, so that if an accident occurs in any of them, and there is no domino effect, the consequences of the accident will be less severe; thus, by minimizing the size of equipment, hazards may be diminished.

6.1.3. Moderate

Some hazardous conditions may be reduced during storage by changing the process conditions. For example, liquefied propane or ammonia can be stored as refrigerated liquids at atmospheric pressure instead of as pressurized liquids at ambient temperature.

6.1.4. Simplify

Storage plants in which a wide variety of substances are stored, or in which many operations that require moving product between tanks, or loading and unloading from different tanks are performed, may be more prone to suffer overfilling or other less serious accidents than other more simpler facilities. However, these hazards may be intrinsic to the facility and vital to its profitable operation, and the way to reduce them would be through the implementation of an automated management system, the minimization of manual operations or the preparation and implementation of correct operating procedures. The method proposed does not incur in the analysis of loading or unloading operations or other conditions that could be simplified in a storage installation. However, the layouts proposed during the optimization will be intended to be as simple as possible.

6.2. The final optimization methodology

As has been explained previously, the final optimization method is a combination of the initial proposal (Figure 4.1) and the domino effect model presented in the previous chapter. A diagram of the final optimization algorithm is presented in Figure 6.1.

As in a QRA, the initial stage of the method is to introduce some information that is necessary to solve the design problem. Of course, it is essential to know the substance(s), or at least, the type of materials that will be stored in the installation. The space available will also be required, as it will be an important factor at the moment of designing the layout of the terminal and selecting the number of tanks. Another piece of information that

is crucial for the resolution of the problem is the description of the vulnerable elements surrounding the installation; it is absolutely necessary to know the number of people residing near the terminal, as well as the number of houses they inhabit (environmental vectors are not considered, as explained in CHAPTER 3).

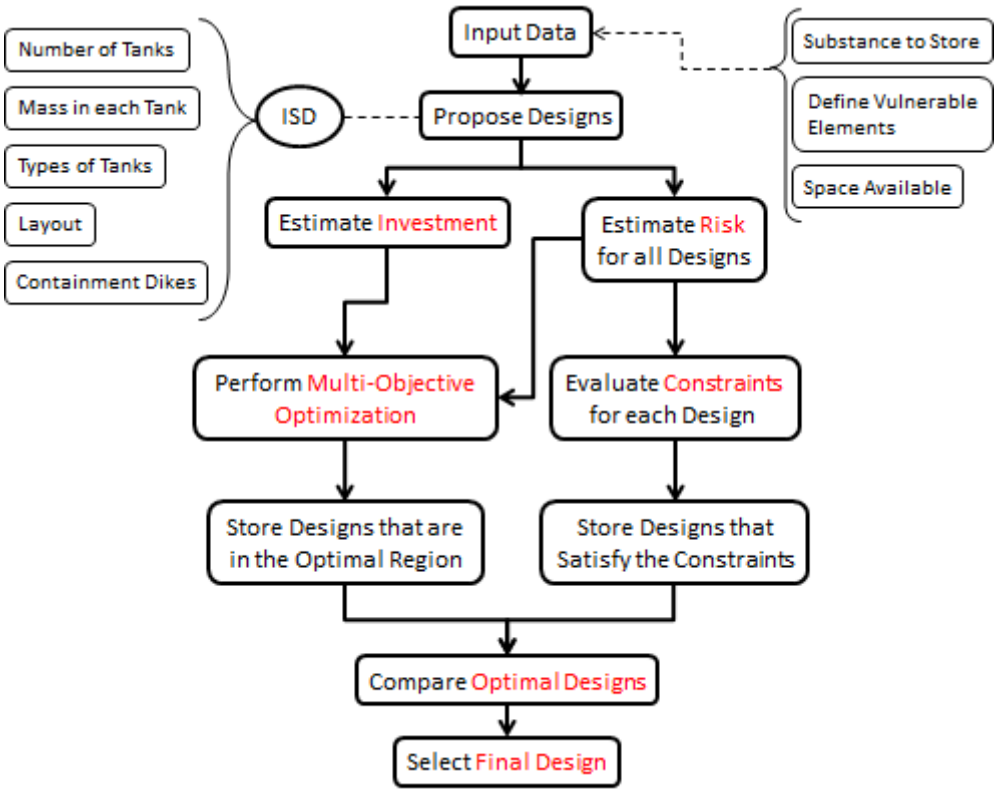


Figure 6.1.Final optimization methodology.

The following step is to propose a battery of designs for the terminal by applying the principles of ISD. Some of the decisions that will have to be made during this stage are the number of tanks to use, their size (mass in each of them), the types of tanks to use and the layout of the installation (on important factor is the number and characteristics of containment dikes). By applying ISD in this stage, the optimization can become mucho more effective, as fewer designs will have to be evaluated in order to obtain one which minimizes risk.

After a new design has been proposed, the investment required for it has to be estimated, for example, as shown in Section 3.7. At this moment, it is also necessary to estimate the risk associated to the design; since much of the complication of the methodology resides in this point, it will be explained in Section 6.2.1 for terminals in which there is possibility for domino effect (for example, those in which flammable or pressurized substances are stored) and in Section 6.2.2 for installations in which a domino effect scenario is not credible (for example, installations storing non-pressurized toxics or non-flammable materials).

Once the risk for the design has been estimated, it has to be confirmed that it complies with the constraints; in this work, the individual risk; the designs that satisfy the constraint are stored along with their associated risks. At this point the multi-objective optimization can be performed using the risks and costs of investment of the different evaluated designs; those designs that falls into the optimal region will be considered for the final decision.

The final stage is to select one of the designs that are in the optimal region and satisfy the constraint; this decision will have to be made by the team of people involved in the design of the storage terminal; however, the algorithm does select the design that is closer to the utopia point in the multi-objective optimization as the first choice.

As can be seen in Figure 6.1, the optimization is not an automatic procedure in which the characteristics of the problem are introduced and a final solution obtained. The user has to propose several designs and will obtain the one that has the best risk-investment relation while complying with the individual risk restriction. In this way, the user can evaluate as many designs as desired until the safety requirements are satisfied.

6.2.1. Estimation of risk with domino effect

The procedure through which risk is estimated for a specific design is completely based on the domino effect algorithm presented in Figure 5.1. It follows the procedure of accident sequence development, calculating at the same time the frequencies, cost and risk associated to each of the accidents in each of the steps of the sequence; Finally, all the risk are added in order to obtain the final risk associated to the installation (Figure 6.2).

Initially, the LOCs associated to each tank, along with their frequencies, must be defined. After this, one of the tanks must be selected to initiate the accident sequence; the first release is modeled and at this moment, the cost associated to this release is estimated and its risk calculated; this value is stored for later use.

After the initial release, the first accident must be modeled, and the costs associated to it, as well as its frequency must be estimated; the risk for the initial accident is calculated and stored. The effects of the initial accident on surrounding equipment must be estimated, in order to decide the level of damage suffered by the other tanks due to the event. If no surrounding tanks fail, the algorithm jumps forward to the point of asking if all the initial accidents in the tank have been studied. If other tanks do fail due to the initial accident, the algorithm enters a loop in which most of the accident sequence is developed.

In this cycle, the algorithm must study the accidents caused in surrounding equipment due to the initial event one by one, always estimating frequency and consequences in order to obtain risk. If the frequency of the studied accident is lower than 10^{-8}, or all the tanks are affected, the cycle breaks. If not, the algorithm must once again estimate the effects of the current accident on the surrounding equipment and continue furthering the sequence; this must be done until the frequency of the accident is low enough or all tanks have been affected in a major way.

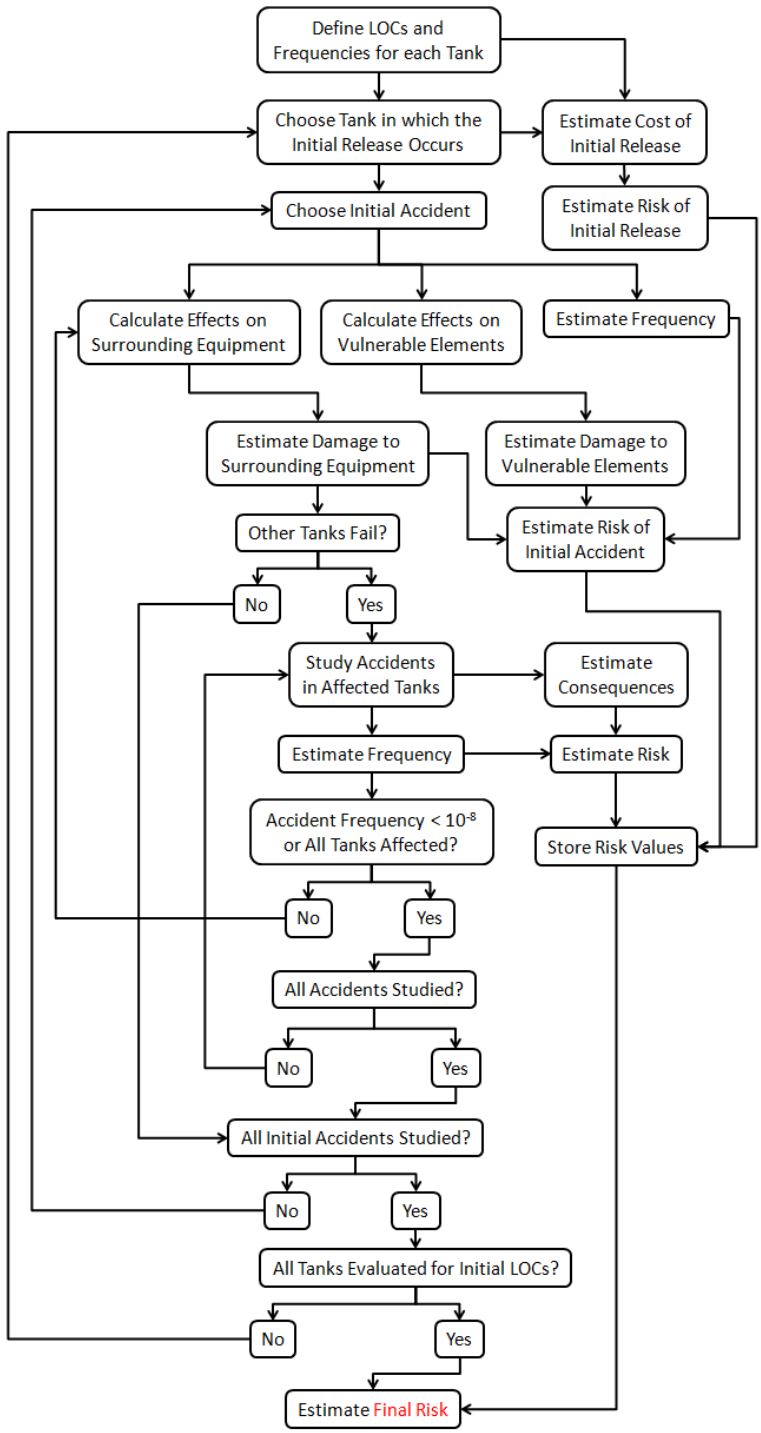


Figure 6.2.Risk estimation for installations with possible domino effect

Once the frequency is low enough or all the tanks have been affected, the algorithm goes to ask if all possible accidents in the previous stage of the sequence have been studied. If they have not been considered, the algorithm will once again enter the previous cycle, generating more accident sequences until the conditions have been satisfied.

If all accidents in the previous stage have been studied, the algorithm goes to ask if all the possible accidents for the initial tank have been considered as initiators. If not, the algorithm goes to the stage of choosing an initial accident. If so, the algorithm continues to ask if all tanks have been evaluated for initial release. In the case that they have, it can proceed to calculate the risk associated to the installation by adding the risks that have been stored during the procedure. In the negative case, the algorithm goes to the initial stage and chooses the next tank to continue the procedure.

6.2.2. Estimation of risk without domino effect

Estimating the risk associated to an installation in which domino effect is not expected is a much less complicated procedure than the one explained previously. The methodology is basically the same, but many cyclic operations are eliminated (Figure 6.3).

The initial step is to define the LOCs and their frequencies for each tank in the installation, to later decide the tank in which the initial release occurs. At this moment, the costs of the initial release are calculated and the risk of this occurrence estimated.

Afterwards, an accident in the first tank is selected and its consequences on the vulnerable elements, as well as its frequency estimated; these values can be used to estimate the risk associated to the accident. If all accidents in the tank have been studied the algorithm moves on to ask if all the tanks have been evaluated for initial LOCs. If not, the algorithm goes to study a different accident in the initial tank.

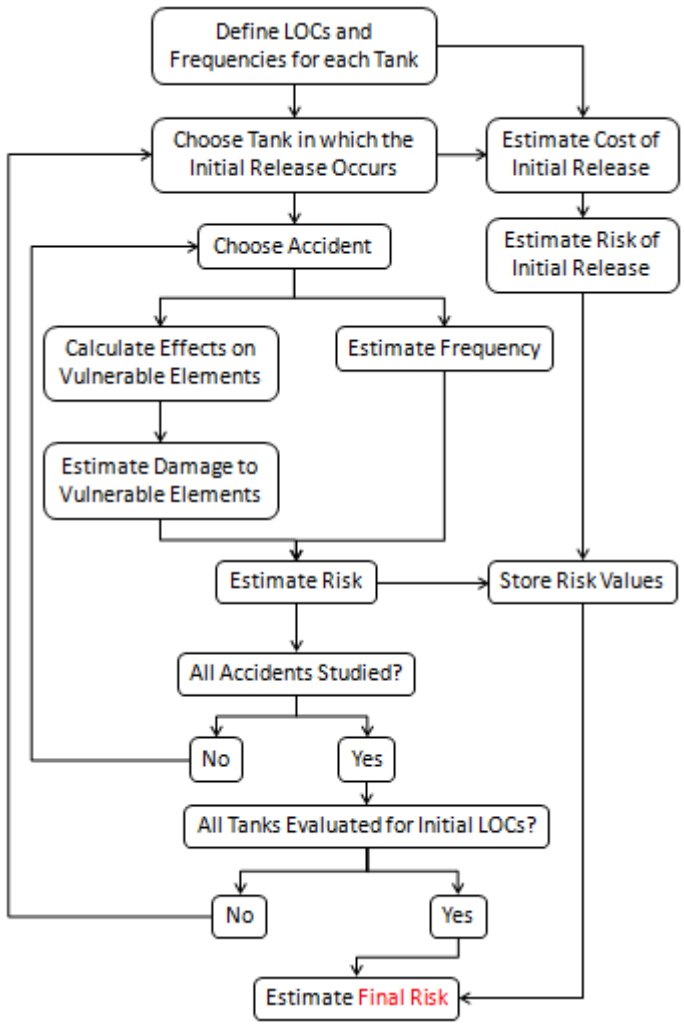


Figure 6.3.Risk estimation for installations without possible domino effect.

When all tanks have been evaluated for initial LOCs, all the risks that have been stored for the different accidents in the different tanks can be summed to obtain the risk associated to the storage terminal.

6.3. Case studies

6.3.1. Chlorine storage plant

In this case study a chlorine storage installation with a capacity of 120,000 kg is studied. The objective of this case is to find an inherent safer design for the installation, knowing that there is a group of houses in which 20 people live 800 meters to the west of the installation, while maintaining the total volume of the substance (understanding that it cannot be minimized), but varying the number of tanks and the storage conditions between pressurized and cryogenic. The storage conditions for both evaluated possibilities and the atmospheric data for the study are presented in Table 6.1 and Table 6.2.

Table 6.1. Storage conditions for chlorine case study.

Property	Pressurized Storage	Refrigerated Storage
Pressure (bar)	5.9	1.01
Temperature (K)	283.15	239.1

Table 6.2. Atmospheric conditions for chlorine case study.

Temperature (K)	283.15
Relative humidity (%)	70
Atmospheric stability class	D
Wind velocity (m/s)	4.5
Ground roughness coefficient	10

The ISD techniques applied in this case study are minimization and moderation; minimization as the number of tanks will be increased in order to decrease the mass stored in each unit, and moderation, when changing the type of storage from pressurized to cryogenic. However, the layout of the plant will become more complicated as more tanks are used, meaning that more instrumentation, maintenance and probably loading/unloading operations will be necessary during the life cycle of the installation, which goes against the simplification principle. It has to be understood that, for the proposed method, risk in this type of installation is derived from the dispersion of the toxic substance and its affectation on the surrounding vulnerable elements, and on the loss of product and the damage to the tanks when the LOCs occur.

The toxic chlorine dispersions are calculated using Aloha v.5.4.3, with the atmospheric conditions shown in Table 6.2 and wind coming from the east. As stated by Marshall et al. (1995) a chlorine release from a pressurized container through a hole will result in a two-phase jet, while for a cryogenic tank, loss of containment will result in the chlorine being released as a liquid and forming a pool, which will later evaporate; these two phenomena will result in a very different type of dispersion, with different affectations to the population surrounding the installation. The lethality consequences on humans were estimated using the probit equation Eq. (3.33), with the values shown in Table 3.5 for chlorine.

For this case, the LOCs applied for the pressurized storage are those defined in Table 3.1; for the cryogenic storage it was decided to use tanks with protective outer shells, as defined in Section 3.2.2 of the Purple Book (2005); the LOCs and frequencies associated to this type of storage are presented in Table 3.2. There is no possibility of domino effect occurrence from the LOCs defined for the case.

To apply the methodology the value of human life was set as shown in section 3.6.1, the costs for pressurized tanks were obtained from http://www.matche.com/EquipCost/Vessel.htm using stainless steel as construction material and for the cryogenic storage the costs are those found in http://www.matche.com/EquipCost/Tank.htm for atmospheric stainless steel tanks. The cost of chlorine (to estimate cost of product loss) was set at 0.15$ for 100 g. When the methodology is applied the results presented in Table 6.3 and Figure 6.4 are obtained; G.1b, G.2b and G.3a releases for cryogenic storage are not presented in the figure, as they do not contribute to risk in a significant way.

Table 6.3. Risk results for pressurized and cryogenic chlorine storage.

n	Risk (€/y)									
	Pressurized				Cryogenic					
	G.1	G.2	G.3	Total	G.1a	G.1b	G.2a	G.2b	G.3b	Total
1	7.19	7.21	0.64	15.04	4.80	0.081	5.72	0.045	2.78	13.43
2	3.07	4.93	0.99	8.99	1.26	0.128	3.13	0.070	4.61	9.20
3	1.39	2.78	1.32	5.48	0.81	0.187	1.80	0.103	6.66	9.55
4	0.87	1.87	1.63	4.36	0.68	0.240	1.20	0.132	8.43	10.68
5	0.71	1.34	1.95	4.01	0.59	0.220	0.89	0.121	8.75	10.57
6	0.64	1.07	2.26	3.96	0.60	0.263	0.76	0.145	10.32	12.09
7	0.61	0.88	2.56	4.05	0.61	0.281	0.68	0.155	11.34	13.07
8	0.60	0.76	2.86	4.22	0.62	0.298	0.62	0.164	12.33	14.03
9	0.60	0.68	3.16	4.44	0.63	0.314	0.58	0.172	13.28	14.98
10	0.60	0.64	3.46	4.70	0.65	0.328	0.55	0.180	14.20	15.91

The most prominent result is that for both types of storage, risk reaches a minimum as more tanks are used to store the same volume of product, and afterwards increases; this is because for a low number of tanks, the consequences on people will be more serious as G.1 or G.2 types of events take place, but as more tanks are used, the consequences on human life will be less serious as the mass of the releases becomes smaller (the effects eventually becoming negligible) and the economic consequences (equipment damage and loss of product) related to smaller but more frequent releases will increase. There is evidence of this tendency in Figure 6.4, in which it can be observed that for both storage options the risk associated to G.3 releases increases with the number of tanks, as opposed to the G.1 and G.2 types.

Initially, risk is higher for the pressurized storage option, but as more units are built, the cryogenic storage seems to become more hazardous; this result is completely derived from the frequencies of the LOCs for each type of storage. As can be seen in Table 6.3, risk related to G.1 and G.2 types of releases is higher for pressurized storage up to 8 tanks, due to the different chlorine concentrations and affectation of population that will result from the pressurized or cryogenic storage; afterwards, both types of storage have very similar values (differences coming from the diverse equipment costs). However, the risks related to G.3 releases are always much higher for the cryogenic storage, as is the rate at

which they augment as more tanks are used. For this case study, G.3 releases pose no threat to the evaluated population (even when using 1 tank), however, as more tanks are used, the cost associated to the loss of product and the damage to the equipment increases, and as the frequency of G.3b releases for atmospheric tanks with protective outer shells is one order of magnitude above the G.3 releases for pressurized vessels, risk for the cryogenic storage for this type of releases will always be higher than for the pressurized option.

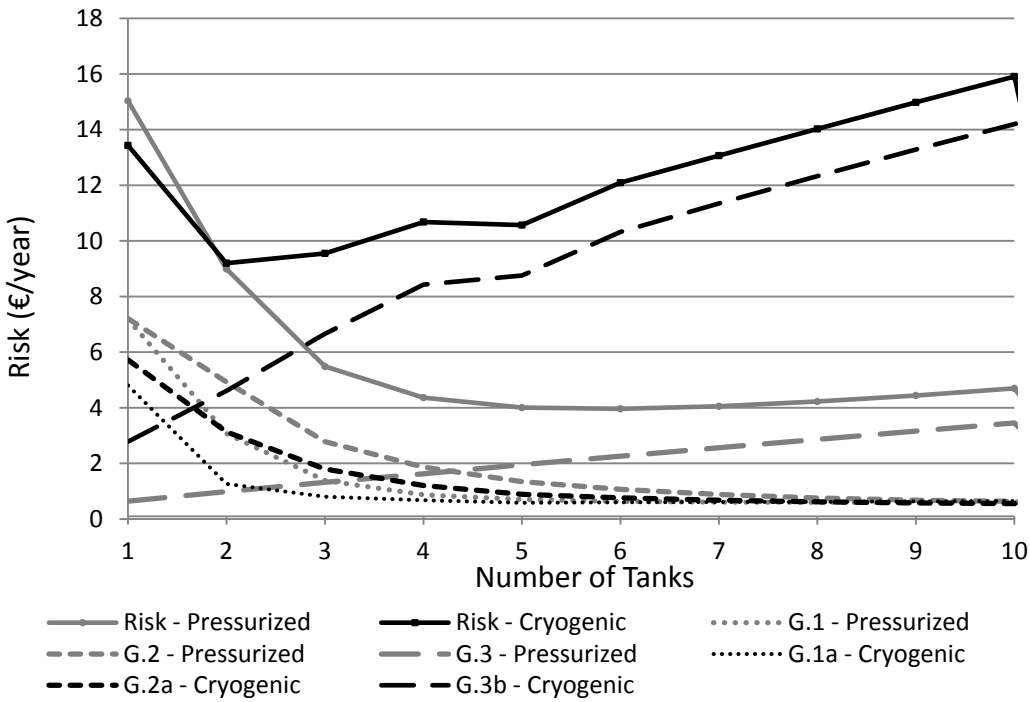


Figure 6.4.Risk vs. number of tanks for pressurized and cryogenic storage of chlorine.

The minimum risk for pressurized storage is achieved when using 6 tanks (containing 20,000 kg each), while for cryogenic, the minimum objective is obtained for 2 tanks (60,000 kg each); the decision that minimizes risk for the installation is to use 6 pressurized tanks. Though this decision minimizes risk, it may not be the best one at the moment of performing an investment; it is possible that other options involving

pressurized or cryogenic equipment present a better risk-investment ratio while maintaining risk at tolerable levels. It is also possible that some designs do not comply with the proposed constraint. In order to make the final decision a multi-objective optimization will be performed and iso-risk curves will be obtained for the case.

6.3.1.1. Multi-objective optimization. Investment vs. Risk

To perform the risk-investment optimization, a similar procedure to the one used in the San Juanico case study was followed, varying the percentages used for calculation of installation cost. As more associated equipment, services and instrumentation are required for an installation using cryogenic tanks, the highest possible values were assigned to this type of installation, and the values used for above ground pressurized storage in the previous case study were maintained. The percentages used are presented in Table 6.4.

Table 6.4. Percentages of costs for different types of storage in the chlorine case study.

Operation	% of equipment cost	Type of Tank	
		Pressurized	Cryogenic
Equipment Installation	30-60%	30%	60%
Insulation Costs	8-9%	8%	9%
Instrumentation and Control	6-30%	25%	30%
Piping	60%	60%	60%
Electrical Installation	10-15%	15%	15%
Service Facilities	8-20%	20%	20%
Land	4-8%	8%	8%
Engineering and Supervision	30%	20%	30%
Construction Expense	4-21%	15%	21%
Contractor Fees	1.5-6%	6%	6%
Contingencies	6%	6%	6%
Startup Expense	6%	6%	6%

As can be seen in Table 6.5, the costs of the installations become higher as more tanks are used; for less than 4 tanks it is less expensive to use cryogenic equipment, and after this, it is cheaper to go with the pressurized options. Having the risks and costs associated to the different decisions of type of storage and number of tanks, the multi-objective plot can be made; it is presented in Figure 6.5, in which the different options are

represented by the number of tanks used and the letter P for pressurized and C for cryogenic storage.

Table 6.5. Cost of the installations for the possible designs.

N	Pressurized	Cryogenic
1	2.68×10^5	1.51×10^5
2	3.15×10^5	2.37×10^5
3	3.48×10^5	3.46×10^5
4	3.65×10^5	4.45×10^5
5	4.01×10^5	4.07×10^5
6	4.20×10^5	4.89×10^5
7	4.40×10^5	5.21×10^5
8	4.59×10^5	5.52×10^5
9	4.78×10^5	5.82×10^5
10	4.93×10^5	6.09×10^5

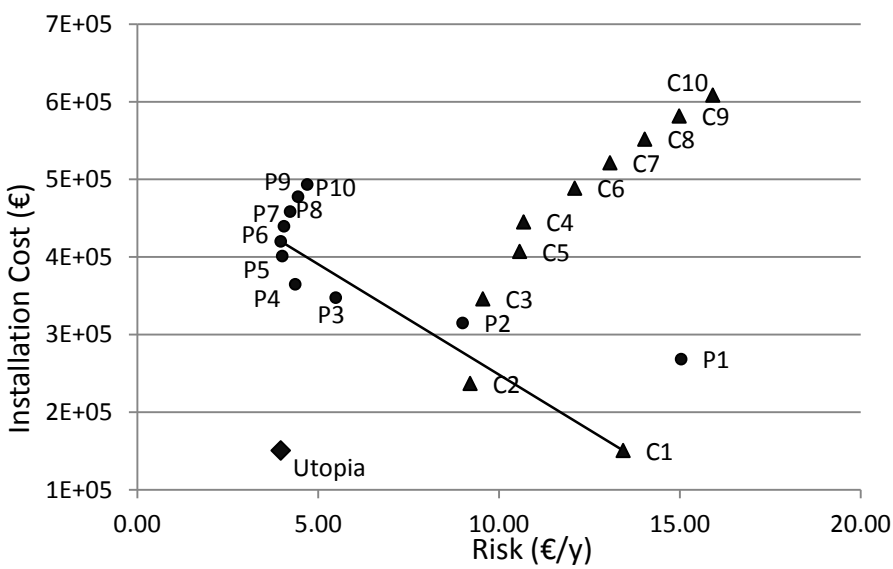


Figure 6.5. Investment cost vs. risk for the different chlorine storage designs.

From Figure 6.5 it can be gathered that using up to 2 cryogenic tanks and from 3 to 6 pressurized tanks are the options that can be said to be optimal from the risk-investment point of view. Of these decisions, the closest to the utopia point is using 2 cryogenic tanks with a capacity of 60,000 kg each to store the complete chlorine volume; however, as has

been said previously, the final decision will depend on the constraint (iso-risk curves) and on the weight that is given to each objective.

6.3.1.2. Iso-risk curves for the chlorine storage case study

To produce the curves, the dispersions were once again modeled using ALOHA 5.4.3, and the curves were plotted using Riskcurves 7.6, applying the same conditions and scenarios that were used for the proposed method. The results are presented in Figure 6.6. In this figure only four curves appear, although six designs were proposed; this is because the cryogenic storage options did not produce 10^{-6} curves, which automatically means that any of the two possible cryogenic designs could be used.

The curves for the pressurized storage designs seem to increase in size as more tanks are used. This results of the fact that as more tanks are built, since the mass is divided in equal parts, the difference in the effects between one decision and the next will become almost asymptotic, as opposed to the frequency of accidents, which increases in a proportionally direct way against the number of tanks. In this way the fact that the curves for 3 and 4 tanks are almost the same size, but that for 5 and 6 tanks they increase is explained. However, none of the curves are close to affecting the vulnerable elements, which means that any of the designs in the optimal region in Figure 6.5 can be used.

For this case, the iso-risk curves for pressurized designs from 3 to 6 tanks do not share the tendency with the risk values obtained using the proposed method, in which the minimum risk is obtained for 6 tanks. This is because the method takes into account the consequences of the possible accidents on material property like equipment (which for this case represent higher costs, as people are not affected in a significant way), and the iso-risk curves are produced taking into account only the affectation to people.

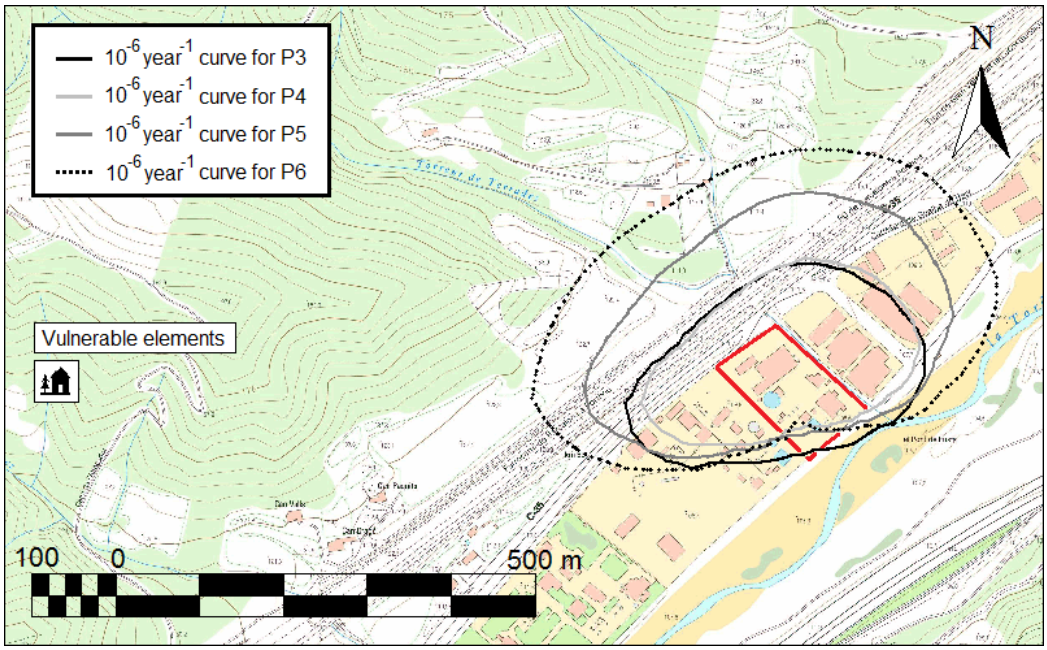


Figure 6.6.10^{-6} Iso-risk curves for the chlorine storage case study.

6.3.1.3. Selection of the optimal design

Once the risk in €/year has been calculated for all possibilities, the multi-objective optimization has been performed, and the constraint for the problem has been checked, the final decision of which design represents the best option can be made. In this case it is clear that since all optimal designs comply with the individual risk constraint, the best decision would be to use the one that represents the lower investment, which would be the installation of two cryogenic tanks. However, this option may have other associated risks that should also be studied, which could lead to another decision being made; as stated before, the most important thing at the moment of designing the installation and making the final decision is that an ISD approach is taken during all the stages of the process, and that hazards are properly identified, evaluated and managed, taking special care with population and environmental affectation.

6.3.2. Application to the San Juanico disaster (Mexico, 1984)

6.3.2.1. Original installation and accident description

The PEMEX (Mexican Petroleum) plant installed in the San Juan de Ixhuatepec (San Juanico) locality in Mexico City was a LPG storage terminal. It was used to store mainly propane and butane mixtures and to distribute the LPG, which was received through gas ducts from different refineries. The capacity of the installation was of approximately 16,000 m^3, distributed between 6 spheres (four with a volume of 1,600 m^3 and two with a volume of 2,400 m^3) and 48 cylinders of different capacities.

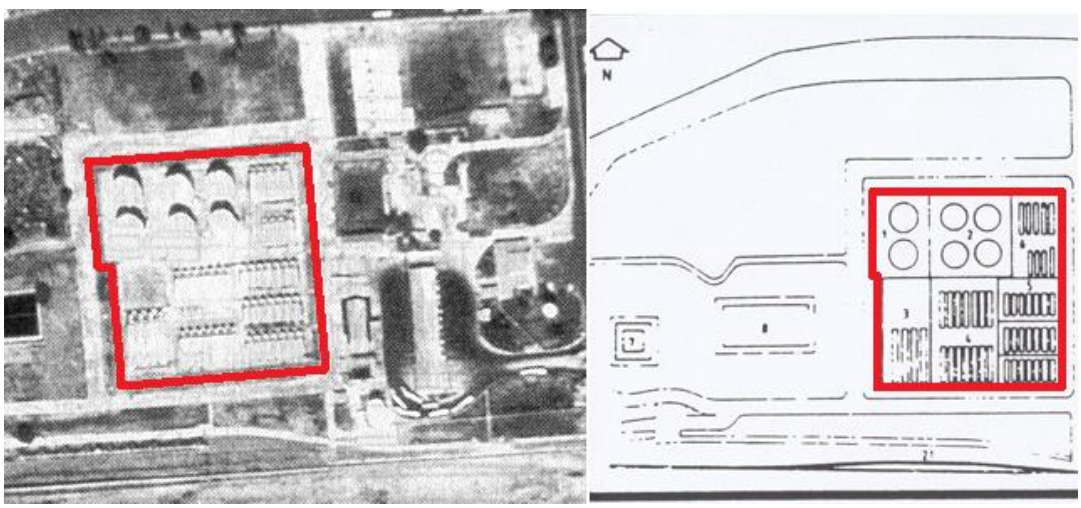


Figure 6.7.Original layout of the LPG storage facility.

The plant had been built according to API (American Petroleum Institute) codes and its surface was of approximately[2] 13,000 m^2. A picture of the installation is shown in Figure 6.7. The town of San Juan Ixhuatepec surrounded the installation and consisted of approximately 40,000 residents, mostly living in one-story houses with brick walls and roofs of iron sheets; some of the houses were located at a distance between 130 and 300 meters close to the plant.

[2] http://www.unizar.es/guiar/1/Accident/San_Juan.htm

At some moment of November 19, 1984, a LPG leak occurred in the plant and a vapor cloud formed and started drifting towards the ground-placed flare pit in the western part of the installation. The cloud ignited around 5:40 a.m. and was followed by an extensive fire. The first explosion was registered at 5:44 a.m.; a dozen more were reported during the next hour, some of them BLEVEs due to the catastrophic rupture of some of the tanks, pieces of which were propelled to a distance of 1,200 m. The blast waves from the explosions destroyed a number of houses on the town, and shifted many cylinders from their supports, adding more flammable material to the already burning atmosphere. Several people died due to exposure to the thermal radiation of the fires caused by the different explosions; burning gases reached the town, escalating the consequences of the initial event. The overall accident resulted in approximately 650 deaths and more than 6,000 injuries, as well as the evacuation of the complete population and the destruction of the majority of the town. Damage to the plant was estimated in $ 31.3 million (AcuSafe, 2012).

6.3.2.2. Modeling the installation

To reproduce the PEMEX installation, a research of the event and layout of the original installation was performed, obtaining approximate sizes and capacities of the different tanks and containment dikes, as well as the distances between the units. In order to simplify the problem, the stored substance is changed from a propane/butane mixture to propane. Figure 6.8 shows the layout used, with some of the distances and dimensions for the different tanks.

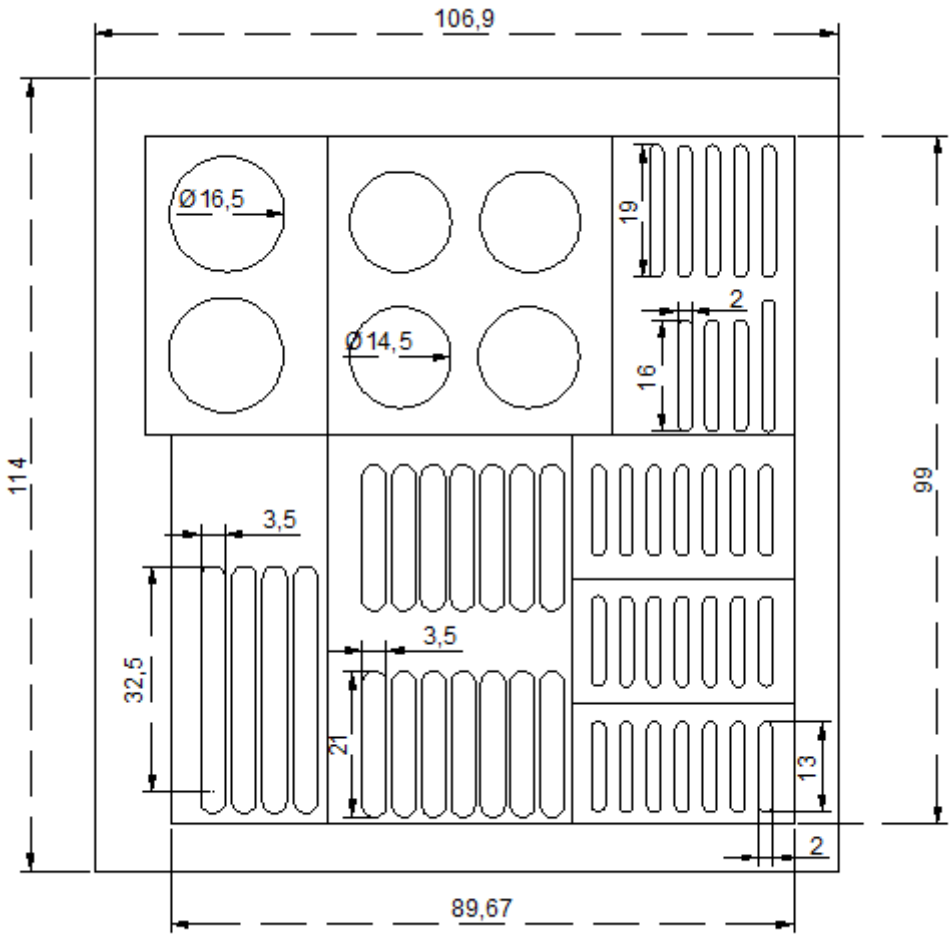


Figure 6.8.Layout used to model the installation.

One of the most important aspects of this accident was its effect on the nearby community; to account for this parameter, a simplistic approach was followed: to place the vulnerable elements (people and houses) north of the installation, and that the population would consist of 40,100 people; the number of houses was calculated by dividing the number of people by 4 (4 persons per house), resulting in 10,025 houses. Of the people, 20% are said to be outdoors and the rest indoors; only the people outdoors will be taken into account at the moment of calculating fatalities. The distribution and the distances at which the people and houses are located were chosen using a BLEVE accident involving

1,500 m^3 of propane to calculate the number of deaths that would result from the thermal radiation emitted by a fireball, in order to obtain results similar to the consequences of the real disaster. Figure 6.9 shows how, for the proposed accident, the percentage of fatalities decreases as the distance from the fireball increases.

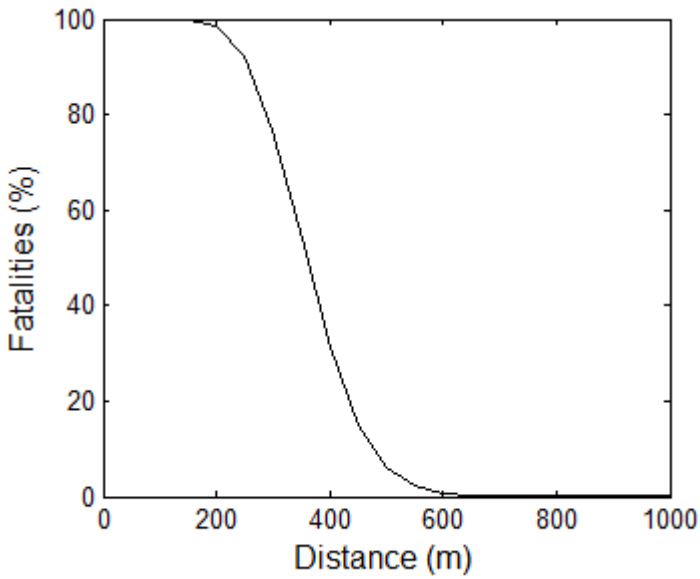


Figure 6.9.Distance vs. percentage of fatalities for the studied fireball.

Based on Figure 6.9, the population/distance relation presented in Table 6.6 was used to obtain figures similar to the ones reported in the San Juanico disaster, starting at the closest reported distance to the installation (130 m) to a kilometer far. Table 6.7 shows the storage and environmental conditions used in the case study.

Table 6.6. Population distribution vs. distance for the case study.

Distance (m)	130	200	300	400	500	600	700	800	900	1000
Number of people	70	170	280	380	520	710	940	1250	1700	2000
Number of houses	87	213	350	475	650	888	1175	1563	2125	2500

Table 6.7. Storage and atmospheric conditions for the San Juanico case study.

Storage conditions	
Pressure (bar)	9.53
Temperature (K)	298.15
Atmospheric conditions	
Temperature (K)	298.15
Relative humidity (%)	70
Atmospheric stability class	D
Wind velocity (m/s)	4.5
Ground roughness coefficient	10

6.3.2.3. Formulation

The purpose of this case study is to obtain a design, which minimizes risk, managing to store the same amount of product in the same space as the original PEMEX plant. To achieve this, different designs were proposed, all of which have been made taking into account the NFPA 58 standard (NFPA, 2011). Later, risk was estimated for each of them (including the original) using the proposed method, to compare them and choose the ISD. This design will be inherently safer if evaluated over the parameters studied in this work, but may not be so from other points of view.

6.3.2.4. Proposed designs

Three types of tanks are used in the proposed designs, above ground pressurized cylinders, mounded pressurized cylinders and pressurized spheres. The volumes of propane are restricted to a maximum of 3,000 m^3 for the spheres, to 3,200 m^3 for the mounded cylinders (Chodorowska, 2005) and to 300 m^3 for aboveground bullets. The designs used in the work are presented in Figure 6.10 (grey areas represent mounded tanks). Table 6.8 shows the number and types of tanks and their capacities.

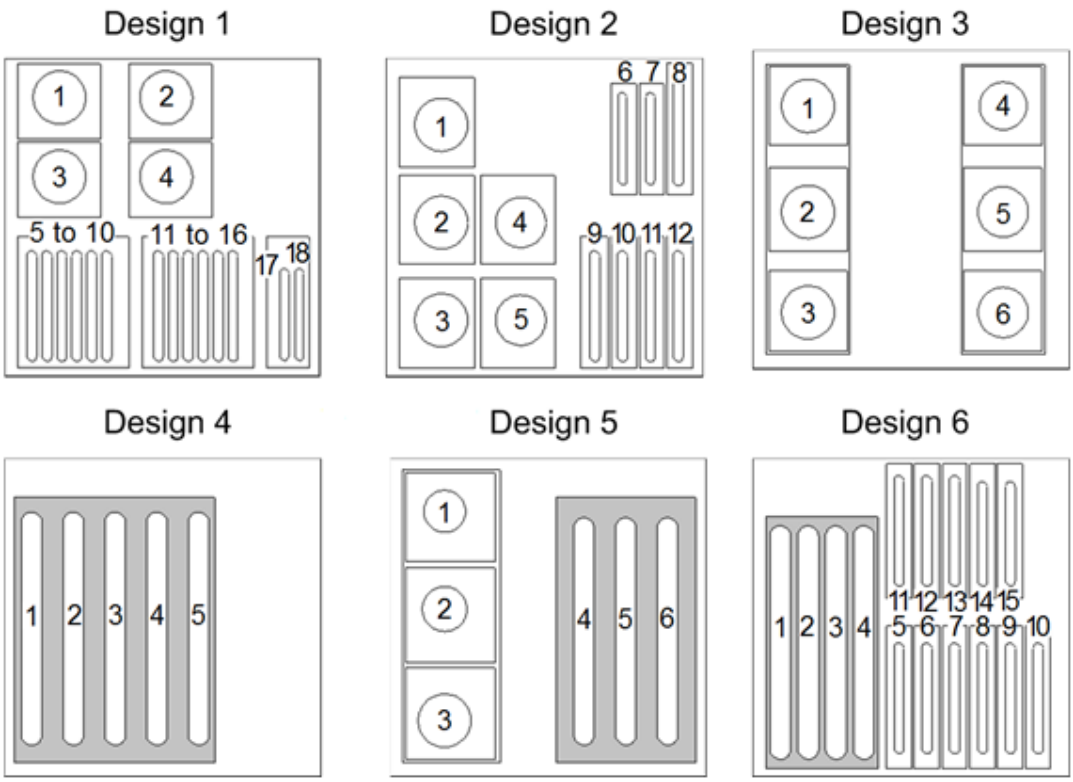


Figure 6.10. Designs proposed for the case study.

The proposed designs were intended as ways of applying the principles of ISD to the original plant. Design 1 is the most similar to the San Juanico terminal, although the number of tanks is reduced to less than half. The design includes pressurized spheres and bullets; the simplification principle is applied, as the layout is much less complicated than for the original facility, but the quantity of product stored in each tank is higher, which is against the minimization principle. It has to be said that due to the possibility of domino effect and its implications, the simplification of the layout may be more important than the minimization of the product in each tank.

Design 2 uses the same technology as the original and first designs, and the analysis made on Design 1 also applies to it, although more containment bunds are used and there are less storage units. Design 3 uses only pressurized spheres, with a much simpler layout

than previous designs, but with larger quantities of product stored in each tank. Designs 1 through 3 apply the simplification principle, while progressively going against minimization.

Table 6.8. Characteristics of the designs.

Design	Number of tanks	Tanks	Individual capacity (m^3)	Total capacity (m^3)
1	18	4 spheres	3,000	12,000
		12 above ground cylinders	300	3,600
		2 above ground cylinders	200	400
2	12	3 spheres	3,000	9,000
		2 spheres	2,500	5,000
		5 above ground cylinders	300	1,500
		2 above ground cylinders	250	500
3	6	3 spheres	3,000	9,000
		2 spheres	2,500	5,000
		1 sphere	2,000	2,000
4	5	5 mounded cylinders	3,200	16,000
5	6	1 sphere	3,000	3,000
		1 sphere	1,900	1,900
		1 sphere	1,500	1,500
		3 mounded cylinders	3,200	9,600
6	15	9 above ground cylinders	300	2,700
		2 above ground cylinders	250	500
		4 mounded cylinders	3,200	12,800

Design 4 introduces the substitution principle by using mounded bullets, which were not an available technology when the original installation was designed; the use of this type of tank also implies the moderation principle, as it reduces hazards due to the conditions at which the process is performed (the bullets being mounded will impede the possibility of domino effect); this design also presents a very simple layout, although the number of tanks is the lowest in any design (the quantity of product stored per tank is greater).

Designs 5 and 6 make use of all the principles applied in previous designs; the volume is stored in mounded bullets and above ground pressurized vessels, (spheres in Design 5 and cylinders in Design 6).

6.3.2.5. Method application and risk results

The first step to optimize the design is to define the initial LOCs (those presented in Section 3.1 will be used) and develop the resulting event trees for the different types of tanks; for this case study, above ground cylinders and spheres will share event trees, while the initial LOCs for mounded cylinders will develop in a different way (no possibility for BLEVE or pool fire occurrences). The trees used are those presented in Section 3.2.

After developing the event trees, and knowing the layout, the domino effect model can be applied over each design; for each branch produced the damage to equipment, loss of product, number of people affected, houses damaged and indirect costs can be estimated. The percentage of people that suffer lethal damage due to thermal radiation was estimated through probit analysis using Eq. (3.32). Damage to equipment and houses was estimated as shown in Section 3.5.2.2. The loss of product was estimated by setting a value of € 0.41 per kilogram of propane.

When multiplying the cost by the frequency of the branch, the risk for that unique event is obtained. After all the risks for every branch, tank and initial LOCs are added, the risk associated to the design is obtained.

Figure 6.11 shows a diagram that represents the risk calculation in the proposed method, taking as an example a G.1 release in Tank 10 for Design 1; continuous lines represent the possibilities that are explored in more detail in the diagram, while discontinuous lines stand for other possible accident sequences which are not presented.

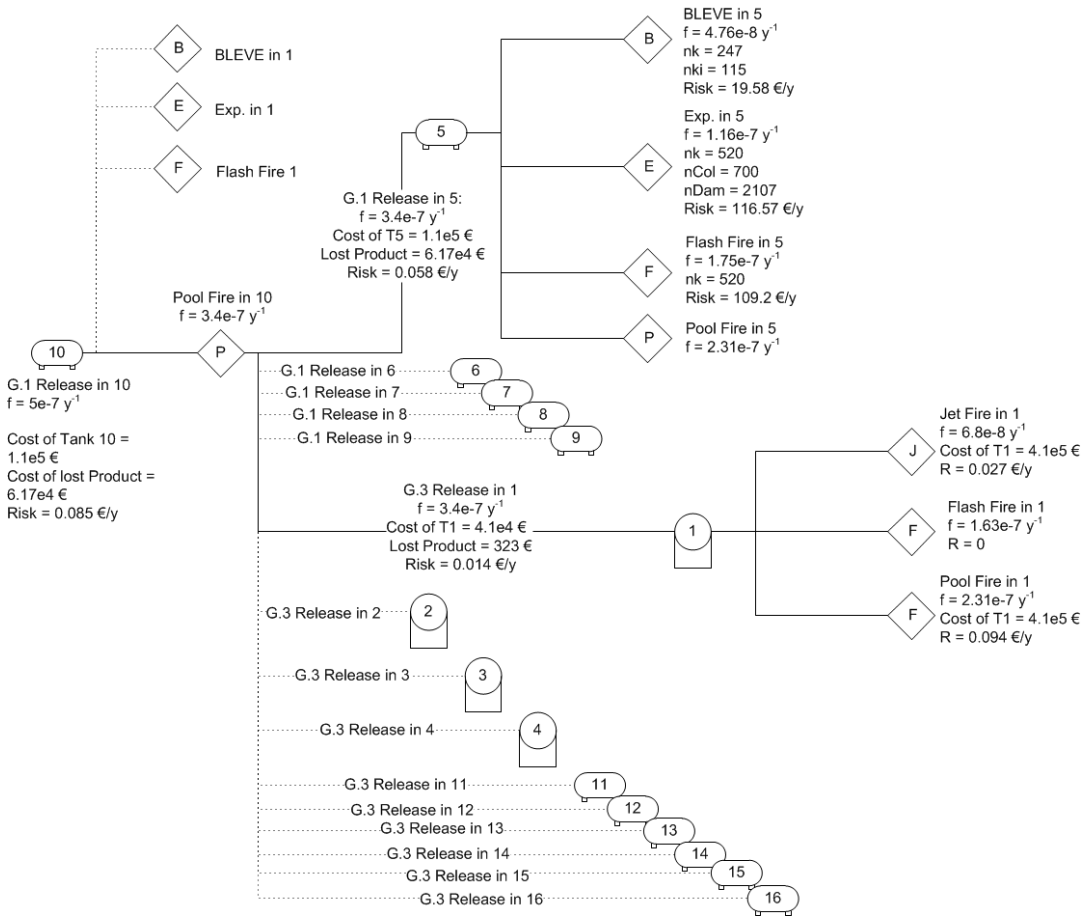


Figure 6.11. Accident sequences for G.1 release in Tank 10 of Design 1.

When a G.1 release occurs in tank 10, it is assumed that the equipment will be catastrophically damaged; therefore, G.1 releases entail the loss of the complete value of the equipment and of the spilled product. The risk for this stage is calculated these costs by the frequency of the G.1 event. After the release, it is possible that a BLEVE, an explosion, a flash fire or a pool fire happen (Figure 3.2); in this example, the possibility explored is the occurrence of the last accident.

If a pool fire occurs after the G.1 release in Tank 10, other equipment in the containment dike (Tanks 6 through 9) will be engulfed in flames, suffering G.1 LOCs,

while other equipment in the installation will suffer minor damages, represented as G.3 releases.

If Tank 5 suffers a catastrophic release, its cost, and the lost product will be equal to those of Tank 10 in the initial event; however, the risk decreases, due to the frequency of the secondary event. After this, Tank 5 may suffer one out of the set of accidents depicted in Figure 3.2. If a BLEVE occurs in Tank 5, people living near the installation will be affected greatly: 247 people will perish, while 115 will be injured; thus, previous events have risks that are orders of magnitude lower than this one. Similar analyses can be made for other possible accidents in Tank 5 after the release. The accident sequences continue to unfold after the accidents in Tank 5, but are not presented in Figure 6.11.

While a G.1 release in Tank 5 can escalate to grievous consequences, the G.3 release in Tank 1 only affects this unit, which is placed in an individual dike; at the moment of the release the tank will have suffered minor damages and a little quantity of product will be lost. A G.3 release in this type of equipment can lead to a jet fire, a flash fire or a pool fire; in this work, if the jet or pool fires occur, it is assumed that the tank will suffer severe damage, so the cost of these accidents will be related to the loss of the tank.

Once the sequences for the G.1 release in Tank 10 are studied, all the risks have to be added to obtain the value associated to the initial occurrence. After this, G.2 and G.3 releases in Tank 10 would have to be studied similarly. When all types of releases have been analyzed for all of the tanks, the risk associated to the particular design is found.

The values of risk obtained using the proposed method, for each of the designs (including the original) are presented in Table 6.9. Due to scaling issues the values were plotted in a logarithmic scale, as shown in Figure 6.12. DR represents the original design and D1 through D6, the proposed layouts.

Table 6.9. Risks associated to the original and proposed designs.

Design	Number of Tanks	Risk (€/y)			
		G.1	G.2	G.3	Total
DR	54	3.13×10^7	2.32×10^7	7.84×10^6	6.23×10^7
D1	18	4.11×10^6	4.10×10^6	1.50×10^6	9.72×10^6
D2	12	1.35×10^6	7.28×10^5	5.04×10^5	2.58×10^6
D3	6	2.47×10^5	1.41×10^5	1.18×10^2	3.89×10^5
D4	5	4.54×10^4	2.67×10^4	5.18×10^1	7.21×10^4
D5	6	2.24×10^5	2.88×10^4	1.05×10^2	2.53×10^5
D6	15	1.09×10^6	1.45×10^5	4.67×10^4	1.28×10^6

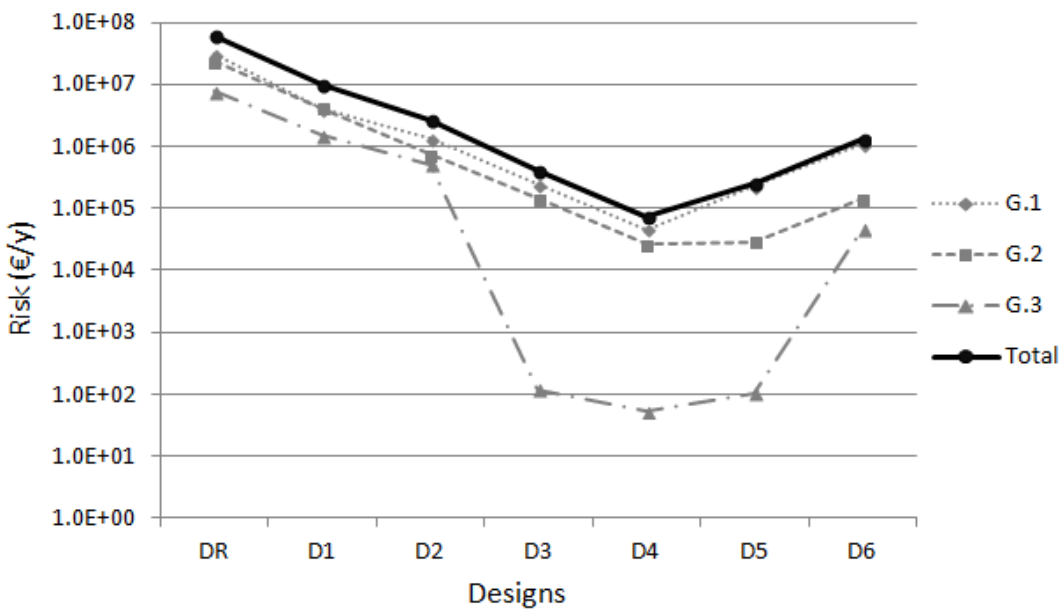


Figure 6.12. Risks associated to the designs.

The highest risk is associated to the original design, and the minimal to Design 4. Risk shows a tendency to increase as the layout becomes more complicated, which shows that, for storage installations, simplification may have a better risk reduction impact than minimization. This occurs because of the domino effect and the nature of risk as a

frequency – consequence binomial; as more tanks are built, the frequency of accidents increases, and, even though the consequences of initial accidents may be lesser, their escalation may lead to catastrophic results. It is clear that risk behavior is significantly affected by the closeness of population.

The other category of ISD that impacts greatly on risk in this case is substitution. Changing the types of tanks from above ground to mounded results in a risk decrease of more than one order of magnitude; this is because mounding prevents the occurrence of BLEVEs and impedes the propagation of accidents in a domino effect.

Figure 6.13 shows the proportion of risk derived from G.1, G.2 and G.3 releases for each design. G.1 and G.2 releases have a more significant impact on the overall risk, as the occurrence of these events entails higher initial (when the frequency is higher) costs, than the G.3 releases.

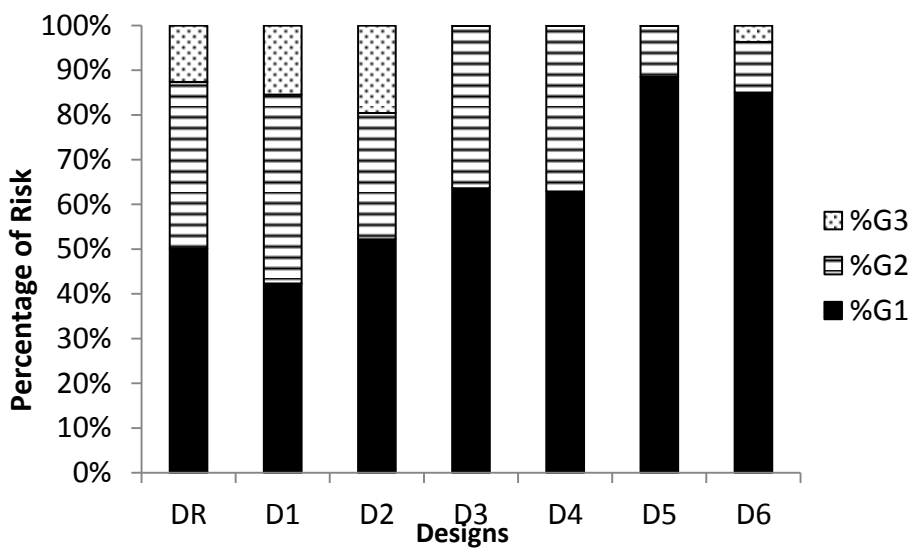


Figure 6.13. Risk proportion per type of release for each of the designs.

For the original design, G.1 releases share 50% of the risk, while G.2 have almost a 40% and G.3 contribute with little more than 10%; this is because due to the number of tanks sharing containment dikes and the distances between units, the continuous releases can be almost as hazardous as the instantaneous, as they may lead to BLEVEs, even though their initial consequences are less severe. G.3 releases tend to have a greater impact for designs that use above ground bullets than for those that use spheres, as these can store the same quantity as cylinders in less space, allowing the increase of distances between them. This trend reaches its maximum expression for Designs 3 and 5, for which there is almost no risk associated to G.3 releases, while for Design 6, risk associated to G.3 LOCs appears.

Risk for Design 4 is completely associated to G.1 and G.2 releases. These risks are related only to the possibility of a rupture in the tanks leading to the formation of a flammable cloud, as there is no possibility for BLEVE or pool fire occurring; however, a flammable cloud resulting from a release in a mounded tank will take longer time to form, or will have less mass, as the product would have to be released through the mounding. Another possibility would be that a pipe related to the tanks breaks, leading to a continuous release. The model is limited in this aspect, as it is not able to model the dispersion of substances through mounding, and it does not include piping. This leads to believing that risk associated to mounded tanks could be even lower. For this type of design the risk for G.3 releases will be more related to environmental issues, which are not evaluated in this work.

6.3.2.6. Multi-objective optimization. Investment vs. risk

The estimation of the cost of the installation for the possible designs will be based on the cost of the purchased equipment, adding additional costs for different requirements of the project like installation, piping, insulation, etc. as percentages of the cost of the equipment; the percentage ranges described in (Peters and Timmerhaus, 1991) will be used, varying them for each of the different equipment in each of the proposed designs.

The percentages used are presented in Table 6.10. The results for the costs of the different designs are presented in Table 6.11.

Table 6.10. Percentages of installation cost based on the cost of equipment for different types of tanks.

Operation	% of equipment cost	Type of Tank		
		Mounded	Above Ground	Sphere
Equipment Installation	30-60%	60%	30%	50%
Insulation Costs	8-9%	9%	8%	8%
Instrumentation and Control	6-30%	30%	25%	25%
Piping	60%	60%	60%	60%
Electrical Installation	10-15%	15%	15%	15%
Service Facilities	8-20%	20%	20%	20%
Land	4-8%	4%	8%	4%
Engineering and Supervision	30%	30%	20%	30%
Construction Expense	4-21%	21%	15%	21%
Contractor Fees	1.5-6%	6%	6%	6%
Contingencies	6%	6%	6%	6%
Start-up Expense	6%	6%	6%	6%

Table 6.11. Cost of the installations for each proposed design.

Design	Number of Tanks	Cost of Purchased Equipment (€)	Cost of the Installation (€)
D1	4 Spheres	1.65×10^6	1.05×10^7
	14 Above Ground	1.46×10^6	
D2	5 Spheres	1.96×10^6	9.25×10^6
	7 Above Ground	7.42×10^5	
D3	6 Spheres	2.21×10^5	7.76×10^6
D4	5 Mounded	3.08×10^6	1.13×10^7
D5	3 Spheres	5.79×10^5	8.82×10^6
	3 Mounded	1.85×10^6	
D6	4 Mounded	2.47×10^6	1.28×10^7
	11 Above Ground	1.18×10^6	

After the costs and risk associated to the different designs have been estimated, they can be plotted along the utopia point (where risk and investment are both at the minimum). Figure 6.14 shows this plot; on top, all the designs can be seen, while on the bottom, only the designs that are close to the utopia point are shown.

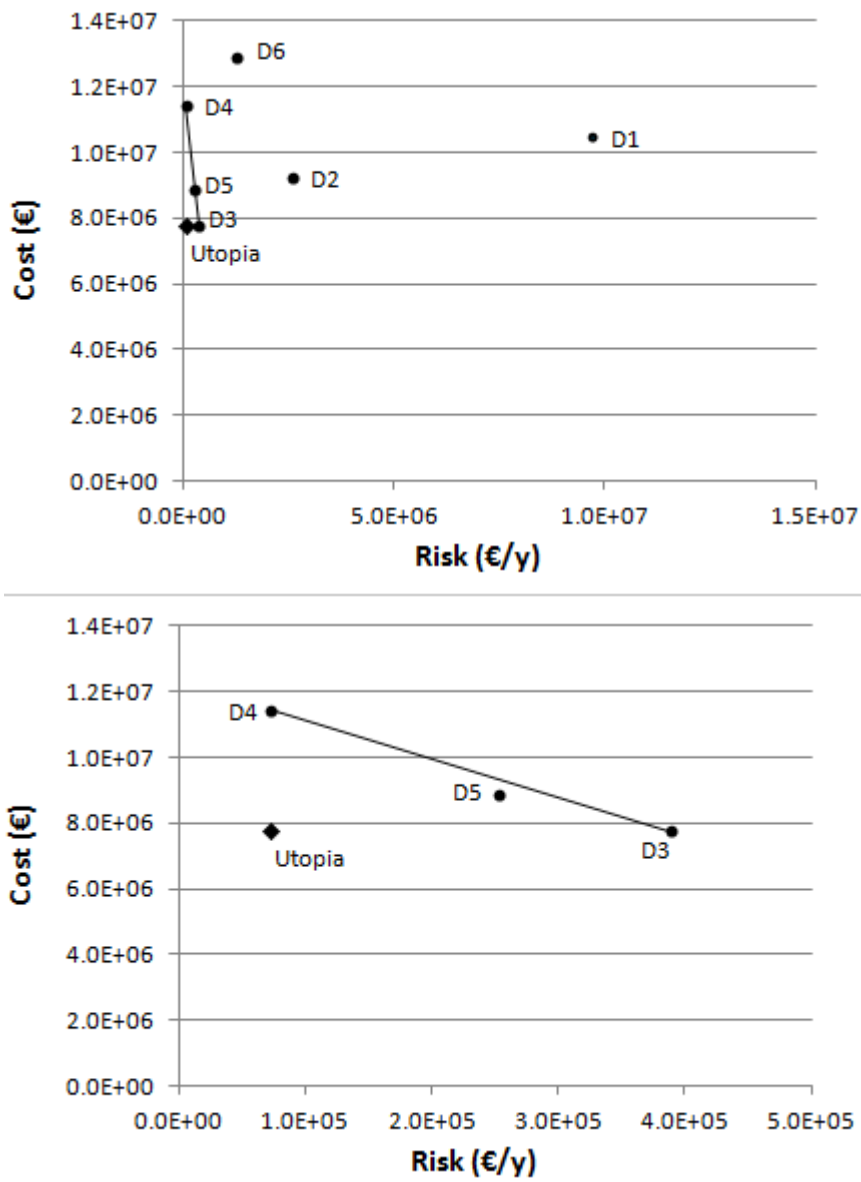


Figure 6.14. Investment cost vs. risk for the different proposed designs.

The options that fall under the line plotted from the design which has the lowest associated risk (Design 4) to that which represents the lowest investment (Design 3) are in the optimum region; therefore, only designs 3, 4 and 5 are within the area in which the relationship between risk and investment can be said to be optimal. The risks associated to designs 1 and 2 are too high for them to be considered, while Design 6 can also be discarded due to its large cost. The design closest to the utopia point is D5, meaning that this option is the best when approaching the problem from an investment vs. risk perspective (if both objectives are given the same importance); however, all 3, 4 and 5 designs are optimal solutions to the problem, and the final solution will depend on the emphasis that is put on each of the objectives during the design of the installation.

6.3.2.7. Constraints and validation of the model through the use of Riskcurves

Iso-risk curves geographically represent the individual risk associated to an industrial plant in nearby zones, connecting all the areas in which the individual risk is equal; in Europe, these curves are used for Land Use Planning (LUP), as required by the 96/82/EC or Seveso II Directive, which means that they must be calculated and presented in order for a project to be approved during its design phase. There are many criteria for LUP in Europe described in detail by Cozzani et al. (2006); in this case study, the criteria applied in Catalonia, which states that all vulnerable elements must be located outside the 10^{-6} curve, is applied as a constraint. Also, if a QRA is performed on each of the proposed designs, the curves obtained could be used to validate the risk estimation me that is proposed; the design for which the most significant curves are smaller will be the one that is inherently safer to the population surrounding the installation.

QRAs were performed on the original and on each of the proposed designs, using the commercial software developed by the TNO, Effects 8.1, to model releases and estimate effects of possible accidents, and Riskcurves 7.6 to produce the iso-risk curves from the Effects results. The LOCs, initial frequencies and event trees were the same that

were used for the proposed model; the QRAs were performed twice, first in a traditional manner and after this, taking domino effect into account by applying the methodology developed by the authors (CHAPTER 5). The results are shown in Figure 6.15 and Figure 6.16 (without and with domino effect).

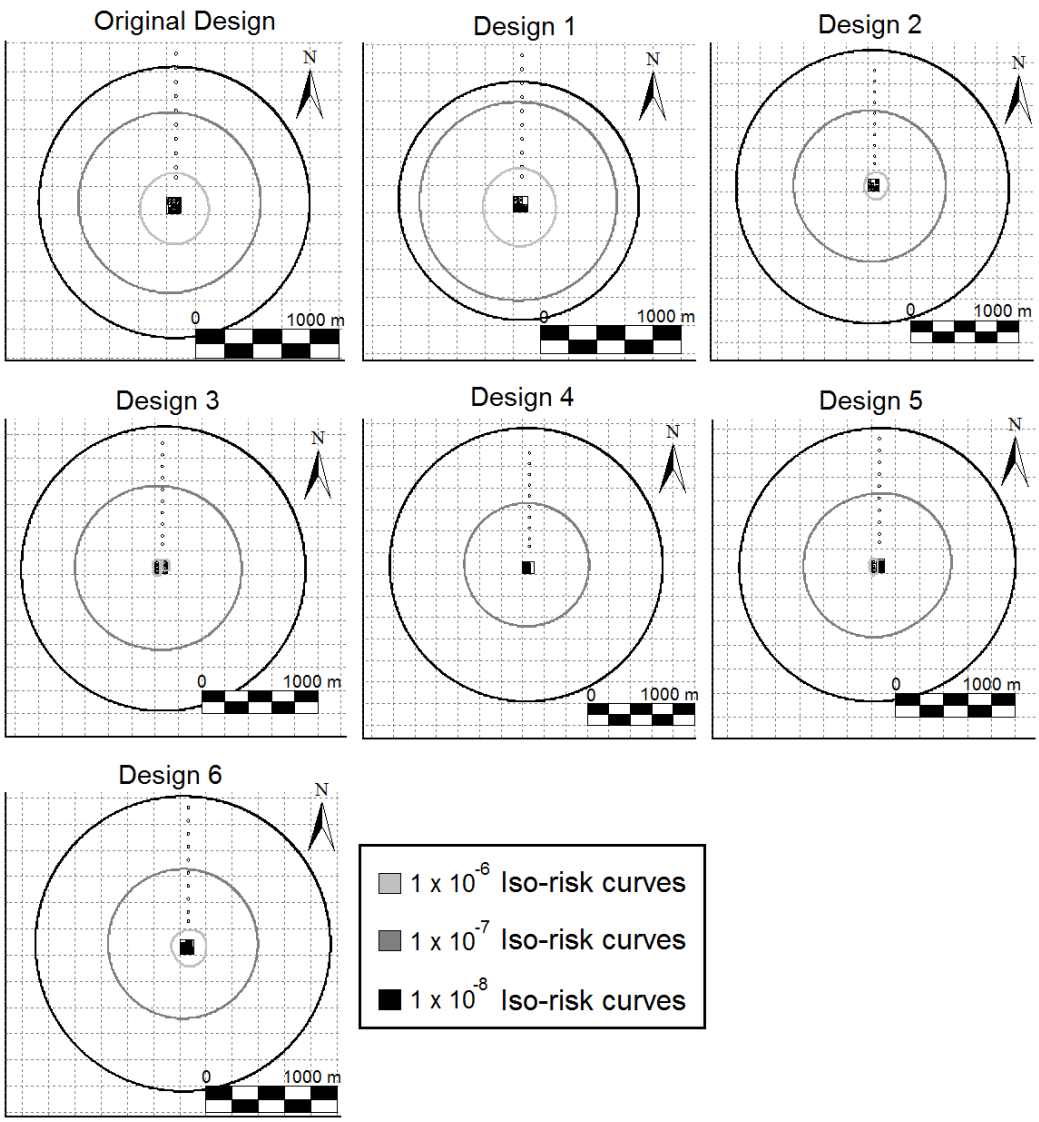


Figure 6.15. Iso-risk curves for each design without domino effect.

In Figure 6.15 the 10^{-6} curve for the Original Design and D1 are almost equal, and reach the first vulnerable elements 130 m north of the installation. For D2 and D6 the curve becomes smaller, no longer affecting vulnerable elements; for D3 and D5 the 10^{-6} curves are almost negligible and nearly contained within the site, whereas for D4 it is non-existent.

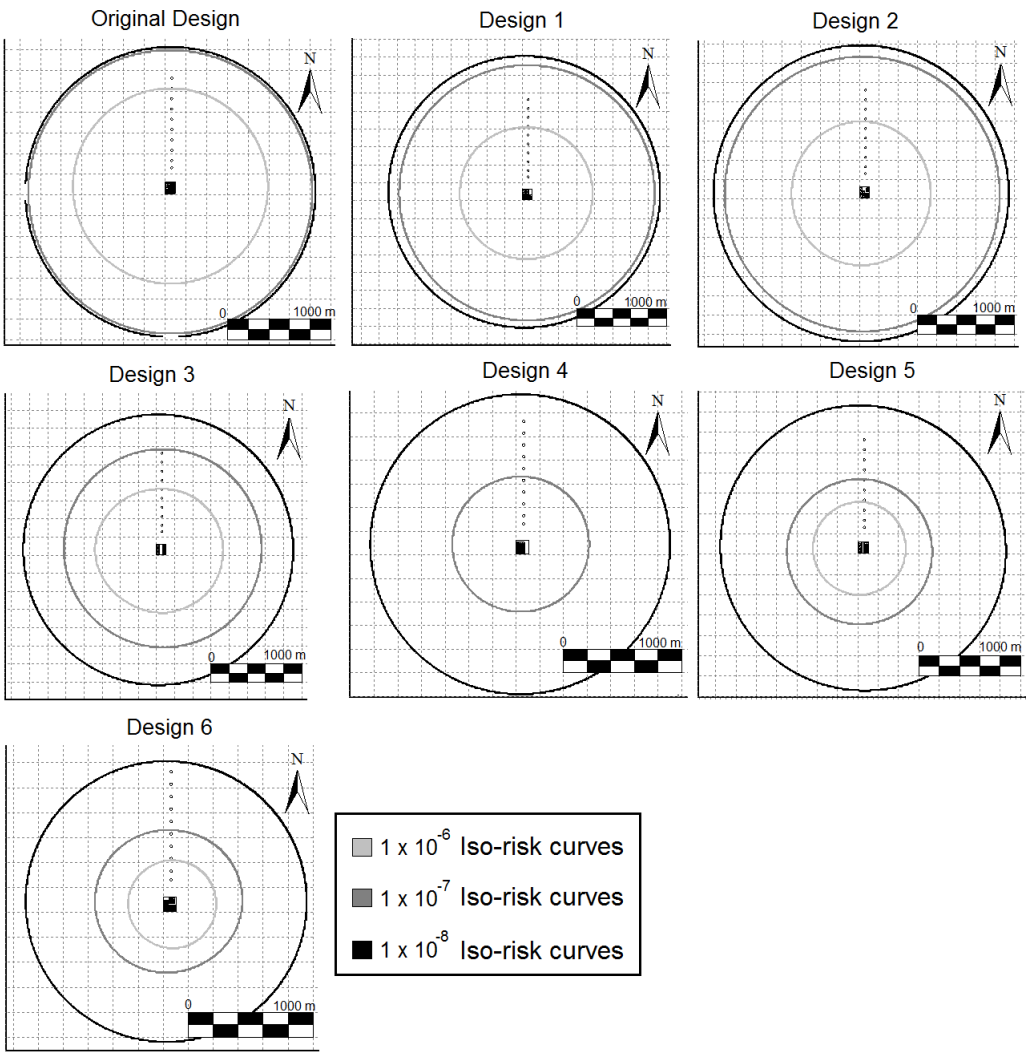


Figure 6.16. Iso-risk curves for each design taking domino effect into account.

It can be seen that the 10^{-7} and 10^{-8} curves also change significantly for each design, becoming larger as the 10^{-6} curves become smaller; however, this curves, although providing information about the risk associated to the installation are not used in the LUP criteria applied in Catalonia, and cannot constrain any of the designs. From Figure 6.15 it can be gathered that the safer design is D4; D3, which does not include mounded tanks, presents a lesser threat than D6, a consequence of the fact that domino effect was not taken into account for these results and the number of tanks in D6 is higher, which means that more scenarios are created and more frequencies are added to produce the iso-risk curves.

When domino effect is taken into account, the 10^{-6} risk curves increase significantly for all designs, except D4, which due to the type of storage involved does not suffer domino effect. In Figure 6.16, the Original Design has the biggest 10^{-6} curve, affecting 9 out of 10 vulnerable elements, and reaching a distance of almost a kilometer from the installation. For D1 and D2 the 10^{-6} curves are almost equal and reach 800 meters north of the installation, while for D3 the curve decreases slightly. The 10^{-6} curves become significantly smaller in the designs that store part of the hazardous product in mounded tanks, preventing some of the propane to be involved in domino accidents. From the three designs that apply this technology, D4 is the one that presents lower risk, followed by D6 and D5; this result is interesting, showing that it is possible that the design that uses more equipment is the one that represents lower risk to the population, as the mass stored in the different tanks is smaller.

In order to compare the results obtained with the proposed method and with those obtained using Riskcurves, the radius of the 10^{-6} curves, taking domino effect into account, and the values of risk obtained with the method have been presented in Figure 6.17. There are some differences in the tendencies of each of the curves, although they are generally similar; for both curves, the Original Design presents the highest values, decreasing until reaching the lowest value for D4, increasing for D5, and presenting divergent tendencies for D6.

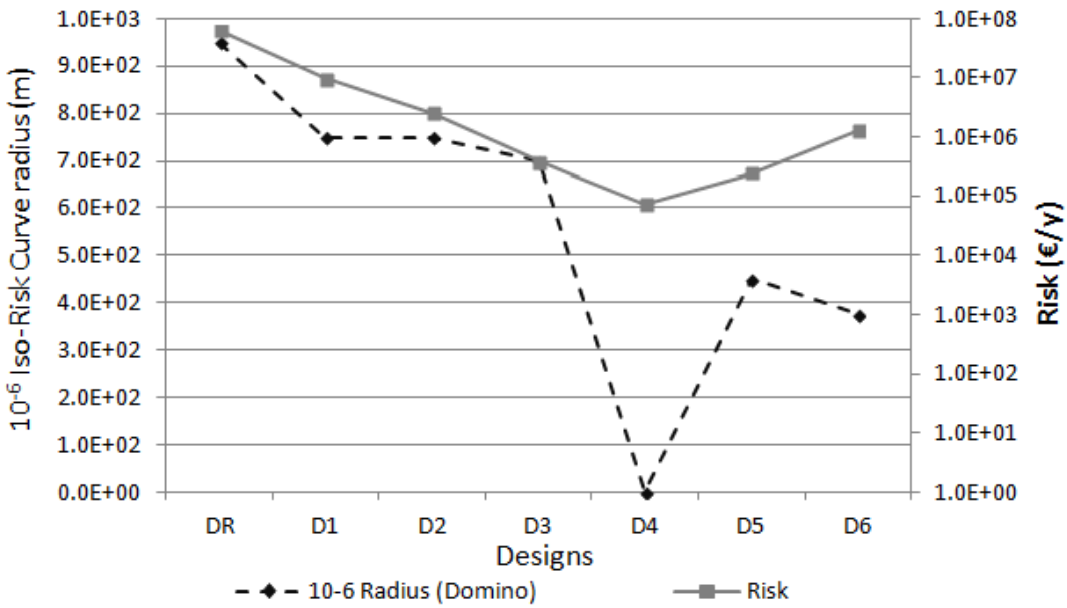


Figure 6.17. Risk vs. radius of 10^{-6} curves.

The differences between the results obtained with the proposed method and Riskcurves derives from the fact that the second does not take into account the risk associated to the loss of equipment or product, accounting only for the possible consequences on people. Because of this, the risk for D6 is higher for the proposed method than for D5, as more tanks mean that there are more possibilities for accident, and more possibilities for domino effects. This fact also explains the difference in slope for D1 and D2 between the results obtained using the different methods.

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possibilities for domino effects. This fact also explains the difference in slope for D1 and D2 between the results obtained using the different methods.

6.3.2.8. Selection of the optimal design and overall case study

It is clear that D4 is the safer design. If the curves that take domino effect into account are used to make the final decision, all other designs would be automatically discarded, as they do not comply with the LUP criterion that is applied as a constraint for the problem, which would render the multi-objective optimization performed useless. However, if the curves produced without taking domino effect into account are used (which would be the case in a real project performed nowadays), D2 through D6 would be possible solutions to the problem, and the optimal solution, taking into account all the information gathered, would be D5. The final solution will depend on the importance that is given to the different objectives of risk and investment when designing the installation and on the risk criteria that is applied on the project. However, it is necessary to stress that nowadays, it would be virtually impossible to build an installation so near to population as the PEMEX terminal was.

Certainly, the inherently safer design is D4, which eliminates risks associated to possible domino effects and greatly decreases affectation to the population, which ultimately, must be the most important goal when assessing project risk. As has been proven in recent years, accidentally affecting human lives or the environment can have major consequences that are very difficult to estimate, and that can have a crippling effect on the company involved; in this way, the best saving that can be made in any project is investing in risk minimization during the complete life cycle of the project, always striving to use an inherently safer design approach, which ensures the safety not only of the project, but also of the community and environment, so that accidents like the San Juanico disaster and many others, which have affected the lives of many people or greatly damaged the environment, do not occur again.

6.4. Chapter conclusions

The domino effect model has been successfully integrated into the initial optimization methodology, increasing its potential and usefulness in a significant way. The only decision variable available for the initial model was the number of tanks, always maintaining the mass in each of them equal. By introducing the domino effect model, many more variables can be used to optimize the design, including the layout, space available or type of tank; in this way, designs that are close to reality can be proposed and evaluated, in order to find an optimal solution that can actually be used during the basic design of the installation.

The final methodology proposed in this chapter is very adaptive; it allows for the proposal of different types of designs, which can use different technologies or have diverse layouts. A very important fact is that this final methodology permits the integration of ISD into the optimization procedure; a person can apply different designs based on different ISD strategies, and evaluate them using the methodology, in order to find the one that minimizes risk.

The introduction of ISD criteria into the earlier design stages of a project can help decrease the risk associated to it dramatically. It can be used to propose different designs that can be evaluated according to the risk they present, and compared from different points of view to select the better option.

The results obtained for the San Juanico case study are proof that new technologies developed since the days of the accident can have a highly positive impact on the reduction of the risk associated to an installation, and can be used to build safer plants. For example, mounding pressurized tanks for the storage of LPG avoid the possibility of BLEVE occurrence, and also decrease the probability of domino effect significantly, which reduces the risk to surrounding population and plant employees.

CHAPTER 7. CONCLUSIONS

The thesis can be considered to be a success, as it has produced a methodology that allows optimizing the design of storage terminals through the use of QRA, and introducing ISD strategies. This work presents the first time that QRA, ISD and a domino effect model are combined in order to produce a safety oriented optimization methodology. Some conclusions that can be gathered from this thesis are:

- The proposed methodology can be applied to storage installations of different characteristics, in which different types of substances are handled or that use different technologies.

- It can be used to optimize the design, not only finding an inherently safer solution, but also one which presents an optimal safety-investment proportion and complies with the LUP criteria followed in the country in which the installation is built. The fact that the methodology optimizes from a safety/investment ratio point of view is also one of the strengths of the work that makes it useful for application in real engineering.

- The method applies QRA to the design phase of installations in a satisfactory way, combining it with Inherently Safer Design strategies. This work demonstrates that widely applied risk analysis techniques, like QRA, can be modified in order to be used

at the basic engineering stage of a project, to help define the technology and layout to be used in an installation.

- Using this method during the basic engineering phase of a project, different possible designs can be evaluated in terms of safety and investment in order to find the optimal solution, always maintaining the possible effects of the project on the population as the most important objective.

- The method serves as a decision making tool in which different factors like possible accidents, their effects and consequences (not only on the population but also on the installation), the frequencies with which they can occur, the investment that has to be made in the project and the LUP criteria of the zone are unified in a cohesive way.

- Risk for industrial facilities has to be updated constantly, as more vulnerable elements can be placed near the facility. The proposed method can also be applied to an existing design, to evaluate the impact it could have over a changing landscape.

- It is very significant that the methodology has been tested using a real life case study involving a real layout, from which other designs (that could be found in actual installations today) are developed and evaluated. It is important that the proposed layouts are compared to a real one, so that a quantitative measure of the effectiveness of applying different ISD strategies is obtained.

It is the believe of the authors that this method can be a building block for other safety oriented optimization methods for the process industry, and that it can actually be used by process engineers as a decision making tool during the basic engineering stage of the design of a storage terminal. We believe that, although there is work to be made, the method presented in this work (and the vision it presents) has so much potential that it

could change the way in which safety and optimization are approached during the basic engineering of a project.

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PUBLISHED WORKS

A list of the works produced during the development of this thesisis presented next:

1. Bernechea, E., Arnaldos, J., 2011. Process optimization taking risk analysis into account. A domino effect study. Proceedings of the 10th Inter-American Congress of Computation Applied to the Process Industry (CAIP). Girona, Spain.
2. Bernechea, E., Arnaldos, J., 2011. Design optimization of a chlorine storage facility to achieve risk minimization. Proceedings of the 12th Mediterranean Congress of Chemical Engineering. Barcelona, Spain.
3. Bernechea, E., Arnaldos, J., 2012. Design optimization of storage facilities taking into account the domino effect. Proceedings of the 8th Global Congress on Process Safety (GCPS). Houston, USA.
4. Bernechea, E., Zamarripa, M., Arnaldos, J., 2012. Multi-objective optimization of hazardous substance storage facilities. The decision between risks and costs associated to the project. Proceedings of the 8th Global Congress on Process Safety (GCPS). Houston, USA.
5. Bernechea, E., Arnaldos, J., 2012. Taking domino effect into account in the Quantitative Risk Assessment of storage installations. Proceedings of the Mary Kay O'Connor Process Safety Center 15th Annual International Symposium. College Station, USA.

6. Bernechea, E., Vílchez, J., Arnaldos, J., Available online 2012. A model for estimating the impact of domino effect on accident frequencies in Quantitative Risk Assessments of storage facilities. Process Safety and Environmental Protection. http://dx.doi.org/10.1016/j.psep.2012.09.004
7. Bernechea, E., Arnaldos, J., 2013. Design optimization of hazardous substance storage facilities to minimize project risk. Safety Science, Vol. 51, 1, 46-62.
8. Bernechea, E., Seguí, X., Arnaldos, J., 2013. Domino effect model applied to the Hertfordshire oil storage terminal (Buncefield oil depot). Proceedings of the 9th Global Congress on Process Safety (GCPS). San Antonio, USA.
9. Bernechea, E., Massaguer, C., Arnaldos, J., 2013. Frequencies of accidents as functions of design variables. Proceedings of the 9th Global Congress on Process Safety (GCPS). San Antonio, USA.
10. Bernechea, E., Arnaldos, J., 2013. Applying ISD to the LPG terminal involved in the San Juanico disaster through the use of QRA. Proceedings of the 9th Global Congress on Process Safety (GCPS). San Antonio, USA.
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Optimización de Procesos Teniendo en Cuenta el Análisis de Riesgos. Estudio del Efecto Dominó

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RESUMEN

El efecto dominó es un fenómeno de gran importancia para el análisis de riesgo industrial, ya que su ocurrencia puede suponer la multiplicación de los efectos y consecuencias de un accidente; la probabilidad de que este fenómeno suceda depende directamente de las posiciones de los equipos en una instalación, por lo tanto, deben existir una o varias distribuciones óptimas para la localización de las unidades que minimicen la probabilidad de ocurrencia del efecto dominó. En este trabajo se ha desarrollado una metodología para encontrar una distribución óptima para tanques de almacenamiento de sustancias peligrosas, teniendo en cuenta la ocurrencia de dardos de fuego y el efecto dominó que estos pueden provocar; para lograr esto se han usado los principios de la optimización matemática y el análisis cuantitativo de riesgos. Los resultados obtenidos demuestran que las distribuciones utilizadas comúnmente no son siempre las más adecuadas para evitar la ocurrencia de efecto dominó para todos los escenarios de accidente posibles. La metodología desarrollada permite encontrar distribuciones óptimas para tanques de almacenamiento con el fin de evitar que el efecto dominó tenga lugar después de un accidente.

INTRODUCCIÓN

En el momento de realizar un análisis de riesgos para el diseño de una instalación, es necesario tener en cuenta la posibilidad de que ocurra efecto dominó al producirse un accidente en cualquier equipo de dicho establecimiento. El efecto dominó se puede definir como la concatenación de efectos que multiplica las consecuencias, debido a que los fenómenos peligrosos pueden afectar, además de los elementos vulnerables exteriores, otros recipientes, tuberías o equipos del mismo establecimiento o de otros establecimientos próximos, de tal manera que se produzca una nueva fuga, incendio, reventón, estallido en los mismos, que a su vez provoque nuevos fenómenos peligrosos. Debido a la importancia del efecto dominó para el análisis de riesgos, varios trabajos han sido publicados, desarrollando modelos con el fin de estimar la probabilidad de ocurrencia de este fenómeno a partir de un accidente inicial e integrando estos modelos al análisis cuantitativo de riesgos (Antonioni et al., 2009; Cozzani et al., 2005).

En el presente trabajo se ha desarrollado una metodología de diseño que tiene por función encontrar la disposición espacial óptima para tanques de almacenamiento, teniendo en cuenta las pérdidas económicas que las diferentes distribuciones pueden representar, si se incluye la posibilidad de ocurrencia de efecto dominó en el análisis cuantitativo de riesgos. Esto se logra a través del uso de la optimización matemática que, en los términos más generales, es una serie de métodos numéricos usados para encontrar e identificar las mejores opciones de una lista de alternativas, sin tener que enumerar y evaluar todas las posibilidades explícitamente. Aunque la optimización matemática ha sido aplicada ampliamente en muchos campos de la ingeniería, sólo

12th Mediterranean Congress of Chemical Engineering
2.Applied Chemical Engineering
2.1 Sustainable Development, Risk Analysis and Environ. Impact

DESIGN OPTIMIZATION OF A CHLORINE STORAGE FACILITY TO ACHIEVE RISK MINIMIZATION

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Scientific topic: Applied Chemical Engineering: Process Safety Management.

Risk and security have become of critical importance to the process industry in the design and development of new projects. It is an established fact that the risk associated to a project is inversely proportional to the investment made in safety; however, this investment is not always made in an optimal way, since it is not common to plan for the losses that could arise in the event of a major accident occurrence. A new methodology to optimize the design of a storage plant in order to minimize the risk, and improve the way in which money is invested in safety has been developed. This is achieved by redefining the way in which risk is usually estimated, and applying the principles of mathematical optimization to quantitative risk analysis.

The design variable for the optimization methodology developed will be the number of tanks used to store the chlorine, as it will allow manipulating (to a point) the mass involved in a possible release. To calculate the risk in this work, equation (1) will be used; it is an expansion of the traditional definition of risk.

$$r_{(n)} = \sum_{n_f=1}^{n} \left[C_n^{n_f} \cdot C_{T\,(n_f)} \cdot f \cdot P_{(n_f)} \right] \qquad (1)$$

The risk for n number of units is $r_{(n)}$ and n_f is the number of units that fail at the same time; $C_n^{n_f}$ is the combinatory of accidents that can occur when n_f units out of n that are built, suffer failure; C_T is the total cost of the accident, which can be estimated by calculating the effects and consequences of the event, like the toxic concentration of the cloud in case of a loss of containment, and the number of people that can be affected negatively by it; f is the accident frequency and $P_{(n_f)}$ is the probability of failure per storage unit.

The objective function of the optimization is the risk associated to the installation, which will decrease as the number of equipment increases, as the probability of the totality of the toxic mass being released becomes smaller. The only constraint used is the individual risk, which has to be lower than 10^{-6}, an accepted limit of risk used in various countries, as Netherlands or Catalunya, and will be calculated as the regular risk, but only taking into account the number of fatalities. The solution will be the number of tanks for which the risk of accident reaches a minimum, or is lower than the curve obtained by multiplying the frequency of accident by the cost of investment, which is, the moment where the costs originated by the accident are lower than the investment costs.

Figure 1 shows an example of the results obtained for a case study in which 19000 kg of chlorine have to be stored, and there are houses inhabited by 18 people at 300 m of distance; a release of the totality of the contents over 10 minutes is evaluated. The optimal quantity of storage units to build in this case would be of seven. It is demonstrated that using this methodology it is possible to express risk as a function that depends on a design variable that can be manipulated in order to find the optimum risk associated to a project.

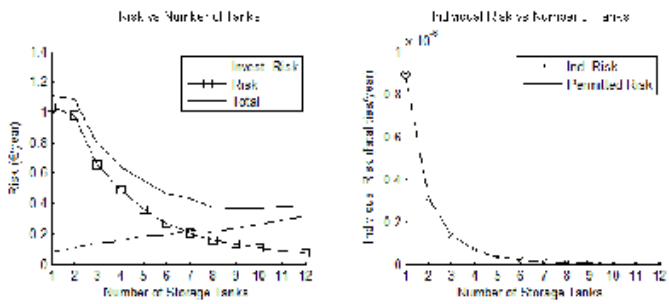

Figure 1. Optimization results.

Design Optimization of Storage Facilities Taking Into Account the Domino Effect

Paper ID# 244749

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Keywords: Quantitative Risk Analysis, Domino Effect, Optimization, Storage Facilities, Hazardous Substances.

Abstract

Storing hazardous substances is a process that entrails high risk, and in which many resources are spent in the planning of safety measures; however, safety could be included at the initial stages of the design of this type of installations, by optimizing the number of tanks that are used to store the substance. The effects and consequences of major accidents are directly proportional to the mass of materials involved in them; therefore, if the mass was divided in more containing units, the consequences at the moment of an accident occurrence would be lesser. However, as more units are used to store a dangerous substance in an installation, the risk of domino effect occurrence at the moment of an accident also increases. The objective of this paper is to develop a methodology that allows finding the optimum number of units that have to be used to store dangerous materials, taking the possibility of domino effect occurrence into account. The proposed methodology is described and applied to a case study as a decision making tool, obtaining results that demonstrate that the design of storage installations can be improved from a risk point of view, by combining quantitative risk analysis and optimization techniques.

1. Introduction

Storing hazardous materials is a necessary but risky process. Historical analysis [1] reveals that 17% of the major accidents in the chemical industry happen during the storage process, and the National Fire Protection Association (NFPA) reported [2] that in 2009, 13% of the major fire accidents that occurred in the USA happened in storage facilities, causing losses of $69,980,000. These numbers demonstrate that it is necessary to continue working on the improvement of safety in dangerous substance storage facilities.

When a process unit suffers an accident, the effects (mechanical or thermal) this event can have on the surrounding equipment can trigger subsequent waves of accidents, which can increase the consequences of the initial event significantly; this phenomenon is referred to as the domino effect, and it has been formally defined as a cascade of events

Multi-Objective Optimization of Hazardous Substance Storage Facilities. The Decision Between Risks and Costs Associated to the Project

Paper ID# 244753

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Keywords: Quantitative Risk Analysis, Multi Objective Optimization, Storage Facilities, Hazardous Substances.

Abstract

The design storage installations for dangerous substances can be optimized from a safety and risk point of view by combining quantitative risk analysis and mathematical optimization techniques; the consequences of accidents are directly proportional to the mass involved in them, which means that in a storage installation, if the totality of the stored substance is divided into more tanks, the consequences when an accident occurs in any of the units will be less significant than if all the mass was stored in one tank (in installations where there is low possibility of domino effect occurrence). However, as more tanks are used to store the mass, the economical investment will also increase; then, a situation arises between two conflicting objectives, that can be solved through the use of multi objective optimization.

In this paper, a method to solve the multi objective optimization problem between risk and investment for storage facilities that have low domino effect probability of occurrence is proposed and applied to a case study involving a facility that stores chlorine. The final result is the design that represents the best compromise solution between risk and investment for the installation.

1. Introduction

Different types of risk analyses are generally performed on the chemical industry in order to determine if a plant or installation complies with the safety standards set by the regulatory organisms, these techniques are commonly applied to finished designs, and are rarely used to apply a modification on the layout or structure of the plant or process. It is a well known fact that safety can be incorporated at any stage of the design, but better results are obtained if it is applied at its earliest stages, however, when designing a

Taking Domino Effect into Account in the Quantitative Risk Assessment of Storage Installations

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Abstract

Domino effect is a phenomenon that can have a profound impact on the risk associated to a plant, but that is very difficult to model, and usually not taken into account when performing quantitative risk assessment (QRA); when domino effect is taken into account in QRA, it is through the use of methods that are very complicated and time consuming, or that rely on rules of thumb or criteria that has no real mathematical basis.

A method for developing sequences of accidents associated to a domino effect phenomenon that occurs after a generic loss of containment event, and calculating their frequencies, has been developed using and approach based on event tree analysis and threshold values for equipment failure. The domino effect sequences will be developed for all the tanks in a storage installation and the frequencies will be summed for every type of accident and each tank. These frequencies can then be introduced in risk analysis software (Riskcurves 8.1) in order to produce iso-risk curves, and have a measure of the impact that domino effect can have on risk by comparing the curves to those obtained when common frequencies are used.

The method will be applied to a propylene and ethylene storage facility; the first substance is stored in a pressurized sphere, while the second is kept in an atmospheric tank. The domino sequences will be generated, and the iso-risk curves obtained when applying the methodology will be compared against those obtained when performing a traditional QRA.

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A model for estimating the impact of the domino effect on accident frequencies in quantitative risk assessments of storage facilities

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ABSTRACT

It is well known that the domino effect can have a major impact on accidents in storage facilities, as it can increase the consequences of an initial event considerably. However, quantitative risk assessments (QRAs) do not usually take the domino effect into account in a detailed, systematic way, mostly because of its complexity and the difficulties involved in its incorporation. We have developed a simple method to include the domino effect in QRAs of storage facilities, by estimating the frequency with which new accidents will occur due to this phenomenon. The method has been programmed and implemented in two case studies. The results show that it can indeed be used to include the possibility of domino effect occurrence in a QRA. Furthermore, depending on the design of a facility, the domino effect can have a significant effect on the associated risk.

Keywords: Domino effect; Quantitative risk assessment; Storage facilities

1. Introduction

Quantitative risk assessment (QRA) is a method that defines the risk associated with a storage facility by estimating the consequences and frequencies of a set of possible accidents. This information can be used to draw graphs and curves that show the effect of the aforementioned risk on the region. QRA is widely used and has a special impact on the risk planning and land use planning (LUP) criteria in different countries. In Europe, individual risk curves obtained from QRA determine the safest plant location, considering the surrounding population. In the case of an existing facility, the results of a QRA may determine that it is safe, that it needs to be modified to lower the risk it presents to the population or that it should cease operation. For a new project, the QRA may determine that the chosen location is suitable, that the design should be adjusted, or that the project cannot be built in the selected zone. QRA is an important analysis that can have a profound impact on the design or operation of a plant.

The domino effect is defined as a cascade of events in which the consequences of previous accidents are increased spatially and temporally by following ones, thus leading to a major accident (Delvosalle, 1996). Many QRAs do not account for the domino effect in their common scenarios, as it is very difficult to model. A tool that facilitates the inclusion of the domino effect in QRA scenarios would be very useful for the risk analysis industry. Some authors have successfully modeled and integrated the domino effect into QRA calculations (Khan and Abassi, 1998; Cozzani et al., 2005; Antonioni et al., 2009; Abdolhamidzadeh et al., 2010). However, none of these models apply specifically to storage facilities or approach the problem from the same perspective as this study. We propose an easy method that uses event trees to systematically generate domino effect sequences in storage facilities, starting from the initial loss of containment events (LOCs) described in the CPR18E (purple book) (CPR18E, 2005), and ending with the major accidents that could occur depending on the substance and type of equipment involved. Once the sequences are

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Design optimization of hazardous substance storage facilities to minimize project risk

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ABSTRACT

The storage of dangerous substances is a high risk procedure: a historical analysis revealed that 17% of the major accidents associated with the chemical industry are related to this process. When a storage facility is designed, the investment in safety is not always optimal. The safety measures that are applied are sometimes redundant or ill-maintained. One way to improve safety in a storage facility would be to take advantage of the fact that dividing the mass of dangerous substance results in less catastrophic accidents. In this paper, we present a new method for optimizing the design of storage plants and minimizing the risk by calculating the ideal number of tanks and improving the way in which money is invested in safety. This is achieved by redefining how to estimate risk and by applying the principles of mathematical optimization to quantitative risk analysis. The method is explained step by step. We also present two case studies and a validation of the method using risk analysis software and iso-risk curves.

1. Introduction

The storage of dangerous substances is a process that comprises significant risks. A historical analysis (Casal and Vilchez, 2010) revealed that 17% of the major accidents in the chemical industry happen during the storage process. The National Fire Protection Association (NFPA) reported (Badger, 2010) that in 2009, 13% of the major fire accidents that occurred in the USA happened in storage facilities, causing $69,980,000 in losses. These papers demonstrate that there are still improvements to be made in the storage of dangerous substances, as accidents in this process continue to occur and the losses caused by such events are substantial.

During the design of a project that includes a storage facility, a vast amount of resources are invested in security measures that are meant to prevent a major accident from occurring in the storage units. These measures can make the project significantly more expensive. They include different types of fire protection, pressure relief valves and insulation. Sometimes these protective measures are not applied correctly, and they are occasionally redundant or ineffective. This problem of obtaining the optimum set of protective measures for a plant has been studied by Caputo et al. (2011). At other times, safety equipment, such as fire protection systems, are not maintained properly and therefore cannot prevent accidents. At the time of a major accident, the wrong design, application or maintenance of safety measures results in double loss of money, as the investment in the devices is worthless if they are ineffective. Even when money is spent on the design, purchase and installation of security devices, they may not work as expected, and are often damaged or destroyed during an accident. This adds to the losses caused by the event.

One aspect of the process of storing dangerous substances is usually not taken into account during a project's design phase: the consequences of a major accident are inversely proportional to the mass of substance involved. Therefore, an accident will have less impact if the mass is divided into more containment units. This aspect can be addressed before the previously mentioned security measures are developed and implemented. In fact, we should be able to determine the optimal number of containment units when a storage facility is designed. This optimal way of dividing the mass means that if an accident happens, the cost of the consequences of the event will be lower than the cost of the investment in designing and building the facility, including the security measures that are deemed necessary to ensure the safety of the project.

In this paper, we develop and describe a new way of quantifying the risk associated with a storage facility for dangerous substances. This measure of risk allows us to combine the cost of consequences and the probabilities of different accidents occurring. It can be formulated as a function that depends on the number of tanks used to store the dangerous material. This function can be evaluated for different cases, in which one, two or n units are used to store the mass. As more units are built, the consequences of the most likely accidents will diminish, but there will be more possible accidents, and the overall frequency of occurrences will increase. In addition, the financial investment in the project will increase as more units are used. Thus, a theoretical optimal can be reached, at which the

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Domino Effect Model Applied to the Hertfordshire Oil Storage Terminal (Buncefield Oil Depot)

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1. Introduction

On December 11, 2005, a series of explosions occurred at the Buncefield Oil Storage Terminal, located in Hemel Hempstead, Hertfordshire, England. The explosions resulted in large fires which spread throughout the installation, causing more than 40 injuries, the destruction of most of the installation and the emission of large clouds of black smoke to the atmosphere; the accident also caused significant damage to residential and commercial properties in the vicinity of the terminal, the evacuation of population centers near the terminal, and an overall economic loss estimated at close to £ 1 billion [1].

The Buncefield disaster is a perfect example of domino effect in the oil industry; the initial explosion, caused due to the overflow of one of the tanks, caused fires that engulfed more than 20 storage tanks, and resulted in the destruction of a significant part of the terminal. The domino effect is defined as a cascade of events in which the consequences of previous accidents are increased both spatially and temporally by following ones, thus leading to a major accident [2]. This definition describes perfectly the situation that occurred in the Buncefield terminal.

One of the characteristics that made this accident the object of many researches was that the overpressure wave ensuing from the first explosion was much higher than would be expected from a Vapor Cloud Explosion (VCE). However, the aim of this manuscript is not to model the exact explosion, or to determine the reasons that caused the overpressure resulting from it to be higher than expected; much works have been dedicated to this endeavor, producing satisfactory

Frequencies of Accidents as Functions of Design Variables

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1. Introduction

The mainstream definition of Risk is that it is a measure of the damage caused on humans, the environment or material property, in terms of the probability of occurrence of an accident and the magnitude of the damage it causes. This can be expressed mathematically as follows:

$$Risk = Frequency \cdot Consequences \quad \text{[Eq. 1]}$$

Risk is then, a function of the frequency of occurrence and consequences of a possible accident.

Often, a Quantitative Risk Assessment (QRA) of a specific equipment or installation has to be performed; in Europe the Seveso Directive makes it compulsory for installations that work with a certain amount of dangerous materials. In order to perform a QRA it is necessary to define initial Loss of Containment Events (LOCs) in the studied equipment, to later estimate the frequencies of the accidents that may result from these releases, and the consequences of said events. These values can finally be combined in order to obtain a measure of the risk that the installation poses over individuals or communities.

There is a wide variety of techniques that can be applied to estimate the frequency of an accident, like historical analysis, failure trees or event trees, subjective estimation, Bayesian analysis or Monte Carlo simulations. In Catalonia and Spain it is common to use the values of frequency provided by "The Purple Book" (CPR18E) [1] for the possible LOCs that can occur in different equipment. Later, event trees which depend on the probabilities of occurrence of certain events

Applying ISD to the LPG Terminal Involved in the San Juanico Disaster through the use of QRA

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1. Introduction

The San Juanico Disaster (Mexico, 1984) has been one of the most devastating accidents in the history of the process industry. The San Juanico installation was a Liquefied Petroleum Gas (LPG) terminal, in which important quantities of flammable materials (a mixture of propane and butane) were handled, and the area involved in the incident consisted of 6 spheres and 48 pressurized cylinders, with a capacity of around 16,000 m^3 of LPG. On November 19, 1984, a LPG leak in some part of the installation resulted in the formation of a flammable cloud, which ignited and caused a series of explosions, some of them BLEVEs (Boiling Liquid Expanding Vapor Explosions), and fires, which resulted in the destruction of a great part of the installation and on severe consequences on the surrounding population.

Over the years, a great population had grown very close to the facility, which was a major safety issue, and proved to be disastrous when the accident occurred. Nowadays, in many countries, it is not permitted for people to build residential structures near industrial installations, but this does not mean that this situation has stopped occurring everywhere in the world. The San Juanico installation had been designed and constructed according to API (American Petroleum Institute) standards and codes of the time, and many lessons have been learned from this incident; however, it is important that we ask ourselves how long have we come in terms of design and safety since the days of the disaster, and that we apply techniques that have become widely used in the field of process safety in order to answer this question.

The objective of this work is to demonstrate that a design which applies Inherently Safer Design (ISD) principles could be proposed for the San Juanico terminal, resulting in a significant risk reduction. To achieve this, the risk associated to the original San Juanico layout and to 6 proposed designs, which include ISD principles, will be estimated through the use of QRA and a domino effect model; in this way, it will be illustrated that different applications of conventional